Inherent Internal Friction of Ti$_{51}$Ni$_{39}$Cu$_{10}$ Shape Memory Alloy

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Ti$_{51}$Ni$_{39}$Cu$_{10}$ SMA is more suitable than Ti$_{50}$Ni$_{50}$ SMA for use as a high damping alloy at room temperature because it has higher inherent internal friction and wider martensitic transformation temperature range. Experimental results show that $\tan \delta $ values of both IF$_{Tr}$ and IF$_{B19^\prime}$ of Ti$_{51}$Ni$_{39}$Cu$_{10}$ SMA are linearly proportional to $\sigma_0/v^{1/2}$ when the applied $v$ and $\sigma_0$ are within 10 Hz and 15 $\mu$m, respectively. Since defects and dislocations pin the martensite twin boundaries and obstruct their mobility, it is important to prevent the introduction of defects or dislocations into the solution-treated Ti$_{51}$Ni$_{39}$Cu$_{10}$ SMA to maintain its high inherent internal friction.

Keywords: shape memory alloys (SMA), martensitic transformation, internal friction, dynamic mechanical analysis

1. Introduction

TiNi-based alloys are known as the most important shape memory alloys (SMAs) because of their excellent properties in shape memory effect, superelasticity and high damping characteristics.\(^{1-18}\) When heating and cooling TiNi-based SMAs, there is an internal friction ($\tan \delta $) peak with a storage modulus ($E_0$) minimum corresponding to the martensitic transformation.\(^{5}\) In addition, it has been reported that the formation of martensitic R-phase in TiNi-based SMAs can strongly soften the storage modulus and thus augment the internal friction during transformation.\(^{13}\) The damping characteristics of TiNi-based alloys are closely related to experimental features such as temperature rate (heating or cooling rate) $T$, frequency $v$ and amplitude $\sigma_0$. Moreover, it has been proposed that the internal friction of a first-order phase transformation is comprised of IF$_{Tr}$, IF$_{PT}$, and IF$_{I}$.\(^{19-22}\) The first term IF$_{Tr}$, which appears at low $v$ and nonzero $T$ is the transitory internal friction. Furthermore, according to Delorme’s theory,\(^{19}\) the $\tan \delta $ value of IF$_{Tr}$ is proportional to the volume transformed per unit time. Therefore, IF$_{Tr}$ should diminish gradually when the specimen is kept isothermally at a constant temperature. The second term IF$_{PT}$ is the internal friction because of the phase transformation and is independent of $T$. The third term IF$_{I}$ is the intrinsic internal friction contributed from the single phase such as the austenitic or martensitic phase. In the low frequency range, the internal friction peak observed during martensitic transformation is mainly ascribed to the first term IF$_{Tr}$, instead of IF$_{PT}$ and IF$_{I}$. Therefore, most of the internal friction studies of TiNi-based SMAs focus on the damping characteristics of IF$_{Tr}$.\(^{2-18}\) However, for high damping materials, it is more important to consider the damping characteristics of IF$_{PT}$ and IF$_{I}$ since most engineering applications for these materials are used at a constant temperature (especially at room temperature) instead of a constant temperature rate. Here, the term (IF$_{PT}$+IF$_{I}$) is referred to as the inherent internal friction. Therefore, the inherent internal friction (IF$_{PT}$+IF$_{I}$) during martensitic transformation and the intrinsic internal friction IF$_{I}$ of each single phase in Ti$_{50}$Ni$_{50}$ SMA have been systematically studied by a dynamic mechanical analyzer (DMA) under isothermal conditions.\(^{23-25}\) Nevertheless, the main failing of Ti$_{50}$Ni$_{50}$ TiNi SMA is that the peak temperature and peak height of the inherent internal friction associated with martensitic transformation is not high enough for practical high damping applications. To overcome the intrinsic limitations of Ti$_{50}$Ni$_{50}$ SMA, substituting Cu for Ni in TiNi binary SMAs has been known to soften the storage modulus at martensite start temperature ($M_s$) and to promote the damping capacity of the SMA.\(^{5}\) In addition, it is well known that Ti-rich TiNi binary SMAs display a higher $M_s$ temperature than Ti$_{50}$Ni$_{50}$ SMA.\(^{26}\) Thus, in this study, Ti-rich Ti$_{51}$Ni$_{39}$Cu$_{10}$ (in atomic %) SMA with two-stage B2$\leftrightarrow$B19$\leftrightarrow$B19' martensitic transformation is used to examine its inherent internal friction (IF$_{PT}$+IF$_{I}$) by DMA under isothermal conditions. Since it shows a low $E_0$ value through a wide temperature range of martensitic transformation from 253 K to 333 K, it is expected that Ti$_{51}$Ni$_{39}$Cu$_{10}$ SMA has a higher inherent internal friction around room temperature.

2. Experimental Procedures

Ti$_{51}$Ni$_{39}$Cu$_{10}$ SMA was prepared by conventional vacuum arc remelter. The as-melted ingot was hot-rolled at 1123 K into a 2 mm thick plate and then the plate was solution-treated at 1173 K for 1 h followed by quenching in water. The as solution-treated plate was cut into test specimens with 40 x 4.7 x 1.3 mm$^3$ for DMA testing and of about 30 mg weight for differential scanning calorimetry (DSC). Transformation temperature and latent heat of the martensitic transformation were determined by DSC test using TA Q10 DSC equipment with a constant cooling rate of 10 K/min. $\tan \delta $ and $E_0$ of the specimen were measured by TA 2980 DMA equipment with a single cantilever at $T = 3$ K/min and $\sigma_0 = 5$ $\mu$m (strain amplitude = 5.7 $\times$ 10$^{-5}$). The isothermal damping characteristics of Ti$_{51}$Ni$_{39}$Cu$_{10}$ SMA were also studied by TA 2980 DMA but tested under isothermal conditions. The detailed procedure for the isothermal DMA test was as follows. The specimen was initially cooled from...
423 K at a constant cooling rate of 3 K/min and was kept isothermally at the set temperature for 30 min. After 30 min isothermal treatment, the specimen was heated to 423 K, which is well above the austenite finish temperature ($A_f$) to ensure that all of the specimen had returned to the B2 parent phase. Then the specimen was cooled to another isothermal temperature at a constant cooling rate of 3 K/min and held isothermally at that temperature for another 30 min, and this process was repeated. The set temperatures were chosen successively from 348 K to 203 K with 25 different set temperatures.

3. Experimental Results

Figure 1(a) shows DSC, DMA and storage modulus cooling curves for as-solution-treated Ti$_5$S$_3$Ni$_{39}$Cu$_{10}$ SMA. As shown in Fig. 1(a), there are two transformation peaks, that is, the B$\text{2}$$\rightarrow$$\text{B19}$ and B$\text{19}$$\rightarrow$$\text{B19'}$ peaks obtained in DSC and DMA $\tan \delta$ cooling curves. Also from Fig. 1(a), the storage modulus curve declines gently in the B2 parent phase while cooling and then drops drastically, showing two minimums during the B$\text{2}$$\rightarrow$$\text{B19}$ and B$\text{19}$$\rightarrow$$\text{B19'}$ transformations. Figure 1(b) plots the curves of $\tan \delta$ value vs. isothermal interval when the specimen is held isothermally at B$\text{2}$$\rightarrow$$\text{B19}$ and B$\text{19}$$\rightarrow$$\text{B19'}$ peak temperatures for 0 ~ 30 min. In Fig. 1(b), $\tan \delta$ values of both B$\text{2}$$\rightarrow$$\text{B19}$ and B$\text{19}$$\rightarrow$$\text{B19'}$ transformation peaks decrease with increasing isothermal interval and reach a steady value after 30 min. As shown in Fig. 1(b), the decayed $\tan \delta$ value of isotherm represents the transitory internal friction IF$_{Tr}$, while the steady $\tan \delta$ value after 30-min isotherm is the inherent internal friction (IFPT+IFI).

Figure 2(a) plots the $\tan \delta$ value of the inherent internal friction (IFPT+IFI) of Ti$_5$S$_3$Ni$_{39}$Cu$_{10}$ SMA measured under 30-min isothermal at different temperatures. The $\tan \delta$ curve of Fig. 1(a) (measured at $T = 3 \text{ K/min}$) is also plotted in Fig. 2(a) for comparison. As shown in Fig. 2(a), there is an inherent $\tan \delta$ peak corresponding to the B$\text{2}$$\rightarrow$$\text{B19}$ transformation, say (IFPT+IFI)$_{B\text{2}$$\rightarrow$$\text{B19}}$, appearing with a $\tan \delta$ value of 0.024 when the isothermal temperature is set at 333 K. When the isothermal temperature is set at 283 K, another inherent internal friction peak corresponding to B$\text{19}$$\rightarrow$$\text{B19'}$ transformation, say (IFPT+IFI)$_{B\text{19}$$\rightarrow$$\text{B19'}}$, appears with a $\tan \delta$ value of 0.035. To examine the thermal cycling effect on the $\tan \delta$ value of inherent internal friction (IF$_{Tr}$+IF$_I$), the same specimen is subjected to 5 rounds of 30-min isothermal treatment, and the results of 1st (Fig. 2(a)), 3rd and 5th rounds are presented in Fig. 2(b). As shown in Fig. 2(b), the $\tan \delta$ value of (IFPT+IFI)$_{B\text{2}$$\rightarrow$$\text{B19}}$ remains almost constant, that of (IFPT+IFI)$_{B\text{19}$$\rightarrow$$\text{B19'}}$ decreases and eventually approaches 0.023 at the 5th round. Furthermore, the measured $\tan \delta$ values of (IFPT+IFI)$_{B\text{2}$$\rightarrow$$\text{B19}}$
Therefore, it is suggested that both (IF PT+IFI)B2\textsuperscript{2→B19} and (IF PT+IFI)B19\textsuperscript{R} and (IF PT+IFI)B19\textsuperscript{0} transformation under isothermal condition collapses much faster than that of B19→B19' transformation. A similar phenomenon is also noted in cold-rolled and annealed Ti\textsubscript{50}Ni\textsubscript{50} SMA since the tanδ value of IF\textsubscript{Tr} of B2→R transformation decreases much faster than that of R→B19' transformation\textsuperscript{23} under isothermal conditions. It is well known that the phase interfaces of B2/B19 and B19/B19' developed during B2→B19 and B19→B19' transformations, respectively, can have good damping capacity. Furthermore, the plentiful twin boundaries inherent in B19' martensite but not seen in B19 martensite\textsuperscript{27,29} can waste more energy. The variation between B19 and B19' martensites accounts for the tanδ value of IF\textsubscript{Tr} of B2→B19 transformation collapsing much faster than that of B19→B19' under isothermal conditions.

Meanwhile, as shown in Fig. 2(b), transformation temperature and tanδ value of (IF PT+IFI)B2→B19 remain almost constant, while those of (IF PT+IFI)B19→B19' decrease after 3 rounds of 30-min isothermal treatment. This is because there are many defects or dislocations induced by thermal cycling that can depress the B19→B19' transformation temperature. Although the accumulation of dislocations after multiple loading cycles can generate an internal stress to assist the martensitic transformation, these introduced defects and dislocations also impede the twin boundaries’ mobility of B19’ martensite and decrease its damping capacity. On the other hand, the thermal cycling effect on tanδ value of (IF PT+IFI)B2→B19 is inconspicuous because the transformed B19 martensite is twin-free during B2→B19 transformation.\textsuperscript{29} Since the tanδ value and the transformation temperature range of (IF PT+IFI)B19→B19' are larger and wider than those of (IF PT+IFI)B2→B19, this means that (IF PT+IFI)B19→B19' is more significant than (IF PT+IFI)B2→B19 in the damping applications. Therefore, it is necessary to prevent the introduction of defects or dislocations in the solution-treated Ti\textsubscript{50}Ni\textsubscript{50}Cu\textsubscript{10} SMA to ensure that (IF PT+IFI)B19→B19' was high inherent internal friction.

### 4.2 Comparing damping characteristics of Ti\textsubscript{50}Ni\textsubscript{50} SMA and Ti\textsubscript{51}Ni\textsubscript{39}Cu\textsubscript{10} SMA

Figures 4(a) and 4(b) plot the tanδ and \( E_0 \) values of (IF PT+IFI), respectively, of Ti\textsubscript{51}Ni\textsubscript{39}Cu\textsubscript{10} SMA and those of equiatomic TiNi SMA cold-rolled and annealed at 923 K for 2 min\textsuperscript{23} and 30 min.\textsuperscript{25} The experimental parameters used for all specimens in Fig. 4 are \( \nu = 1 \text{ Hz} \) and \( \sigma_0 = 5 \mu \text{m} \) (strain amplitude \( = 5.7 \times 10^{-3} \)). Of these, Ti\textsubscript{51}Ni\textsubscript{39}Cu\textsubscript{10} alloy shows the lowest storage modulus and thus the highest tanδ value of (IF PT+IFI) during the 1st round of 30-min isothermal treatment. However, as shown in Fig. 4, the measured \( E_0 \) minimum increases and thus the tanδ value of (IF PT+IFI) decreases during the 3rd round. This feature is associated with the increasing defects or dislocations introduced by thermal cycling which impede the martensitic transformation and twin boundaries’ mobility in the martensite, as discussed in Section 4.1.

In Fig. 4(a), the cold-rolled Ti\textsubscript{50}Ni\textsubscript{50} alloy annealed at 923 K for 2 min displays B2→R and R→B19' inherent internal friction peaks, while the same cold-rolled alloy annealed at 923 K for 30 min shows only a single B2→B19' peak in cooling. As shown in Figs. 4(a) and 4(b), the tanδ

### 4 Discussion

#### 4.1 Inherent internal friction of B2→B19 and B19→B19' transformation

As shown in Fig. 1(b), the tanδ value of IF\textsubscript{Tr} of B2→B19 and (IF PT+IFI)B2→B19' of the 5th round are almost the same as those of the 3rd round. This shows the effect of thermal cycling is negligible after 3 rounds of 30-min isothermal treatment.

Figures 3(a) and 3(b) plot the tanδ values of (IF PT+IFI)B2→B19 and (IF PT+IFI)B19→B19' measured at different values of \( \nu \) and \( \sigma_0 \), respectively, of the specimen after 5 rounds of 30-min isothermal treatment. As shown in Fig. 3, both tanδ values of (IF PT+IFI)B2→B19 and (IF PT+IFI)B19→B19' are linearly proportional to \( \sigma_0/\nu^{1/2} \) when the applied \( \nu \) and \( \sigma_0 \) are within 10 Hz and 15 \( \mu \text{m} \) (strain amplitude \( \leq 1.71 \times 10^{-3} \)), respectively. This feature is similar to the damping characteristics of (IF PT+IFI)B2→R and (IF PT+IFI)R→B19' in equiatomic TiNi SMA, which shows two-stage B2→R→B19' martensitic transformation.\textsuperscript{23} Therefore, it is suggested that both (IF PT+IFI)B2→B19' and (IF PT+IFI)B19→B19' are associated with the stress-assisted martensitic transformation and stress-assisted motions of the twin boundaries.

**Fig. 3** Tanδ values of (IF PT+IFI)B2→B19 and (IF PT+IFI)B19→B19' obtained as a function of (a) \( \sigma_0 \) and (b) 1/\( \sqrt{\nu} \).

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values of B2→R and R→B19\textsuperscript{0} inherent internal friction peaks are higher than those of the B2→B19 peak because the R-phase which corresponds to the strong softening of storage modulus is not formed in the latter.\textsuperscript{25} This means the forming of R-phase can increase the tan\(\delta\) values of inherent internal friction in Ti50Ni50 SMA. Nevertheless, for TiNi-based binary SMAs, the introduction of R-phase during martensitic transformation is usually associated with TiNi SMAs’ cold-rolling or thermal cycling, or forming Ti3Ni4 precipitates by aging Ni-rich TiNi SMAs. In other words, forming the R-phase can soften the\(E_0\) value, but at the same time it can also make the inherent internal friction of Ti50Ni50 SMA worse. This is because the twin boundaries’ mobility in R-phase can be anchored by the introduced defects or dislocations or Ti3Ni4 precipitates. Therefore, as shown in Fig. 4(a), Ti50Ni50 SMA shows a good inherent internal friction (tan\(\delta\) > 0.02) only in a narrow temperature range of R→B19\textsuperscript{0} martensitic transformation (from 275.5 K to 283 K). The results of Fig. 4 show that adding Cu into TiNi SMAs can improve its inherent internal friction since the transformation sequence can be adjusted by Cu content without introducing extra defects or dislocations or forming Ti3Ni4 precipitates.\textsuperscript{30} As shown in Fig. 4, the solution-treated Ti51Ni39Cu10 alloy displays the lowest storage modulus and the highest tan\(\delta\) value (0.03 at 298 K) in a wide transformation temperature range (253 K to 333 K). Obviously, from the viewpoint of damping applications, Ti51Ni39Cu10 SMA is more suitable than Ti50Ni50 SMA for use as a high-damping material at room temperature.

5. Conclusions

Experimental results reveal that tan\(\delta\) values of inherent internal friction for both (IF\textsubscript{PT}+IF\textsubscript{IF})B2→B19 and (IF\textsubscript{PT}+IF\textsubscript{IF})B19→B19 of Ti51Ni39Cu10 SMA are linearly proportional to \(\sigma_0/\sqrt{\nu}\) when the applied \(\nu\) and \(\sigma_0\) are within 10 Hz and 15 \(\mu\)m, respectively. The fact that the tan\(\delta\) value of IF\textsubscript{PT} of B2→B19 transformation under isothermal condition collapses much faster than that of B19→B19 is related to the many twin boundaries inherent in B19\textsuperscript{0} martensite but not seen in B19 martensite. After 3 rounds of 30-min isothermal treatment, the tan\(\delta\) value of (IF\textsubscript{PT}+IF\textsubscript{IF})B19→B19 decreases more significantly than that of (IF\textsubscript{PT}+IF\textsubscript{IF})B2→B19 because the increasing defects or dislocations introduced by thermal cycling impede the twin boundaries’ mobility of B19\textsuperscript{0} martensite. Therefore, it is essential to avoid introducing extra defects or dislocations into solution-treated Ti51Ni39Cu10 SMA to keep its high inherent internal friction. The solution-treated Ti51Ni39Cu10 alloy displays a higher tan\(\delta\) value and a wider transformation temperature range than cold-rolled and annealed Ti50Ni50 SMA because there are no cold-rolled defects or dislocations, as well as no Ti3Ni4 precipitates in the former. Thus, from the viewpoint of damping applications, solution-treated Ti51Ni39Cu10 SMA is more suitable than Ti50Ni50 SMA for use as a high-damping alloy at room temperature.

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Fig. 4 (a) Tan\(\delta\) and (b) storage modulus values of Ti51Ni39Cu10 SMA and 30% cold-rolled equiatomic TiNi SMA annealed at 923 K for 2 min\textsuperscript{23} and 30 min\textsuperscript{25} measured after 30-min isotherm at different temperatures.