Ambient-temperature high damping capacity in TiPd-based martensitic alloys

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Abstract

Shape memory alloys (SMAs) have attracted considerable attention for their high damping capacities. Here we investigate the damping behavior of Ti50(Pd50−x Dx) SMAs (D = Fe, Co, Mn, V) by dynamic mechanical analysis. We find that these alloys show remarkably similar damping behavior. There exists a sharp damping peak associated with the B2–B19 martensitic transformation and a high damping plateau (Q−1 ~ 0.02–0.05) over a wide ambient-temperature range (220–420 K) due to the hysteretic twin boundary motion. After doping hydrogen into the above alloys, a new relaxation-type damping peak appears in the martensite phase over 270–360 K. Such a peak is considered to originate from the interaction of hydrogen atoms with twin boundaries and the corresponding damping capacity (Q−1 ~ 0.05–0.09) is enhanced by roughly twice that of the damping plateau for each alloy. Moreover, the relaxation peaks are at higher temperatures for the TiPd-based alloys (270–370 K) than for the TiNi-based alloys (190–260 K). We discuss the influence of hydrogen diffusion, mobility of twin boundaries and hydrogen–twin boundary interaction on the temperature range of the relaxation peak. Our results suggest that a martensite, with appropriate values for twinning shear and hydrogen doping level, provides a route towards developing high damping SMAs for applications in desired temperature ranges.

Keywords:
Shape memory alloys
Internal friction
Hydrogen
Twin boundary
Twinning shear

1. Introduction

The damping capacity (Q−1), is usually considered a measure of internal friction (IF) and represents the capacity of a material to convert mechanical energy of vibration into heat dissipated in the material [1,2]. Materials with high damping capacity are attracting much attention today owing to their wide potential applications, ranging from noise/vibration reduction, shock absorption to energy conversion [1–6]. Damping mechanisms in these materials are either associated with the stress-induced movement of crystalline defects (point defects, dislocations, etc.) or linked to the stress-driven motion of certain interfaces (domain boundaries or phase front), which is thermodynamically irreversible [6–8].

Shape memory alloys (SMAs) are promising candidates for high damping alloys as they exhibit both high damping capacity and good mechanical properties [9–12]. They undergo a reversible martensitic transformation (MT) between a symmetric high-temperature parent phase and a lower symmetry, close-packed martensite phase in response to changes in temperature or applied stress [13]. The high damping capacity of SMAs is related to the hysteretic motion of interfaces and the following two damping sources are always present in such transforming alloys [8,14]. One of these is associated with the martensitic transformation during which the phase front between coexisting parent phase and martensite regions is generally mobile but strongly dissipative [8]. This type of dissipation depends sensitively on thermal gradients and the internal friction peak drops considerably at a fixed temperature. Thus, it is usually called a “transient peak” and is undesirable in practical applications [9,15]. The other damping source appears as a “broad relaxation peak” in the martensite phase, the microstructure of which is composed of martensite variants with different crystallographic orientations [13]. The twin boundaries between the variants hysteretically move via the movement of wall kinks [16], and hence dissipate a large fraction of the available mechanical energy during their stress driven motion [11]. This dissipation is insensitive to cooling/heating rate but sensitive to crystalline point defects [8], crystalllographic orientation [17,18], and grain size [19–21].

Of these two sources, the high damping capacity in the martensite phase has recently attracted much attention from the viewpoint of practical applications as the damping capacity is independent of...
cooling/heating rate and is nearly thermal-hysteresis free [10,22,23]. After a relaxation-type internal friction peak was first reported in 1968 in the B19’ martensite phase of a Ti-Ni alloy [24], the high damping capacity in martensite phase has been observed in a series of SMAs with high density of twin boundaries, such as Ti-Ni [25], Ti-Ni-Fe [26], Mn-Cu [27], Au–Cd [28], and Cu-Zn-Al-Ni [29]. In addition, a number of efforts have been made to clarify the origin of the energy dissipation and several explanations have been proposed, including dislocation relaxation and dislocation–point defect interaction [30,31]. Yoshida et al. have also proposed that it originates solely from twin boundary motion and considered the high damping capacity in Ti50(Ni50–xCu)x alloys to be due to the highly mobile nature of twin boundaries in martensite phase [32]. Very recently Mazzolai et al. first reported the connection between martensite damping peaks and hydrogen [10,12,33,34]. Fan et al. also conducted critical experiments on Ti-Ni-Cu and found that hydrogen and twin boundaries are two necessary ingredients to obtain the high relaxation peak in the martensite phase of Ti-Ni based alloys [9,25,35]. Recent simulations by Ding et al. suggest that the low frequency internal friction includes an extrinsic defect component and an intrinsic microstructure component [16]. The former is due to the extrinsic defects pin and de-pin some mobile interfaces, and the later is dominated by jamming and avalanches (–jersks) of the intrinsic microstructure, like the twin junctions [16]. The comparison of damping behavior between hydrogen-free and hydrogen-doped TiNi-based alloys by Mazzolai et al. and Fan et al. supports the view that high damping capacity in martensite phase involves both intrinsic (twin boundaries) and extrinsic (hydrogen) contributions [9,33–36].

Through extensive studies on the damping behavior of several hydrogen-free and hydrogen-doped SMAs, Fan et al. have demonstrated that the hydrogen–twin boundary interaction could be a rather general damping source in SMAs [37]. However, one of the shortcomings in these studies is that the most useful damping peak (relaxation-type in most cases) in the martensite phase is usually within a too low temperature region (200–300 K) which greatly restricts possible applications [9,10,12,22,25,35]. Our previous results have shown that it is possible to shift the relaxation damping peak to the ambient-temperature range in a TiPd-based martensitic alloy [23]. In particular, we showed that the Ti50(Pd42Cr8) alloy with M, of 520 K, which is much higher than that for TiNi-based SMAs (M, 290–350 K), possesses a broad relaxation-type damping peak with Q−1 from 305–370 K for hydrogen-doped alloy and a damping plateau with Q−1 from 250–450 K for hydrogen-free alloy [23]. However, such an ambient-temperature damping peak has been reported only in this alloy so far, and it is unclear how general the above finding is, in particular, whether M, is the only factor in determining the temperature of the damping peak or not.

The aim of this work is to explore the generality of the ambient-temperature relaxation-type damping peak in TiPd-based SMAs and to determine the key factors affecting the temperature at which the peak is observed. We systematically study the damping behavior of four TiPd-based alloys: Ti50(Pd42Fe8), Ti50(Pd38Co12), Ti50(Pd40Mn10) and Ti50(Pd42V8) by employing low frequency dynamic mechanical analysis (DMA). Our paper is organized as follows. In Section 2 we describe the experimental details. Section 3 shows in detail the damping behavior of these four TiPd-based alloys and their dependence on the existence of hydrogen, cooling rate, displacement amplitude and frequency of the ac stress field during the DMA measurement. In Section 4, we discuss the possible origin of both the high damping plateau and broad relaxation peak in the martensite phase of TiPd-based SMAs and clarify the key factors determining the temperature at which the relaxation peak is observed in TiNi-based and TiPd-based alloys. Finally, we suggest guiding principles for the development of high damping SMAs for applications in a desired temperature range.

2. Experimental method

In the present study, four kinds of TiPd-based SMAs, including Ti50(Pd42Fe8), Ti50(Pd38Co12), Ti50(Pd40Mn10) and Ti50(Pd42V8), were employed. Base ingots were made by induction melting of 99.9% pure Ti, 99.9% pure Pd, and 99.9% pure Fe, Co, Mn and V in an argon atmosphere. The specimens were spark-cut into proper sizes, 1 × 2 × 2 mm3 for differential scanning calorimetry (DSC) measurements and 1 × 2 × 10 mm3 for dynamical mechanical analysis (DMA) measurements. They were solution-treated at 1373 K for 1 h in an evacuated quartz tube, followed by water quenching into ice-water. To study the effect of hydrogen, we dehydrogenated the solution-treated specimens by annealing in a vacuum furnace at 1173 K for 4 h. The hydrogen atoms can be removed from the specimen due to its low solubility at high temperature. The hydrogen-doped specimens were obtained by annealing the solution-treated specimens at 873 K for 4 h in a hydrogen atmosphere. The hydrogen content in these hydrogen-doped specimens is almost the same and around 0.35 at%, which was measured by quantitative chemical analysis of the insert gas fusion method (IG).

DSC was performed to characterize the M, of these alloys with a cooling and heating rate of 10 K/min. The storage modulus and internal friction (tan δ) were measured by DMA measurements in a single cantilever mode. In order to investigate how the damping behavior of these alloys depended on the parameters during DMA measurement, the storage modulus and internal friction (tan δ) as a function of temperature were measured at different displacement amplitudes (5/15/30/45/60 μm), the corresponding strain amplitudes are 0.57/1.70/3.5/7.0 × 10−3), different frequencies (0.2/0.4/1/10/20 Hz) and different cooling/heating rates (1 K/min, 4 K/min, step-cooling). In step-cooling the specimens were kept iso-thermally for 5 min at every testing temperature to reach an equilibrium state (see details in Ref. [35]).

3. Experimental results

3.1. Martensitic transformation behavior of TiPd-based martensitic alloys

As clearly seen from the DSC results shown in Fig. 1, the transformation between parent phase and martensite phase in Ti50(Pd42Fe8), Ti50(Pd38Co12), Ti50(Pd40Mn10) and Ti50(Pd42V8) alloys is characterized by the sharp exothermic and endothermic peaks during cooling and heating, respectively. As for the binary Ti–Pd alloys, [38] the parent phase has a cubic B2 structure and the martensitic phase has an orthorhombic B19 structure in these four systems. There is no other structural transformation below the B2–B19 transformation temperature. From DSC results, the M, on cooling for Ti50(Pd42Fe8), Ti50(Pd38Co12), Ti50(Pd40Mn10) and Ti50(Pd42V8) alloy is identified to be 479 K, 442 K, 391 K and 430 K, respectively.

3.2. Damping behavior of hydrogen-free TiPd-based martensitic alloys

In this section we will show the damping behavior of these four hydrogen-free TiPd-based alloys and its dependence on the parameters during DMA measurement. The internal friction and storage modulus as a function of temperature for each alloy is shown in Fig. 2. Clearly, the damping behavior is strikingly similar in these alloys, i.e., one sharp internal friction peak located at the high temperature side and a broad damping plateau that lies immediately below the sharp internal friction peak.

The internal friction peak at the high temperature side located in the range 390–480 K is accompanied by a dip in storage modulus. This internal friction peak and storage modulus dip corresponds to
the B2–B19 martensitic transformation and the transformation temperature is in agreement with DSC results (Fig. 1). We note that the peak position does not change, but the peak height decreases with increasing frequency. This is a characteristic of a martensitic transformation in SMAs. In the low-temperature martensite phase, a broad damping "plateau" covers the ambient-temperature range (220–420 K). The damping capacity of Ti50(Pd42Fe8), Ti50(Pd38Co12), Ti50(Pd40Mn10) and Ti50(Pd42V8) alloys is around 0.046, 0.055, 0.04 and 0.023, respectively (room temperature values), which is about 2–5 times higher than that in its corresponding parent phase state. Such high damping capacity over a wide ambient-temperature range is rare for known high-damping alloys, except the similar high damping plateau in Ti50(Pd45Cr5) martensitic alloy.

We note that despite the above similarities, there still exists certain differences in the damping plateau of these four alloys. For example, the damping plateau in Ti50(Pd42Fe8) alloy is rather flat over a wide temperature range, i.e., the damping capacity does not change with decreasing temperature. On the contrary, the damping plateau in Ti50(Pd40Mn10) alloy is not flat and the damping capacity almost linearly decreases on cooling. For Ti50(Pd38Co12) and Ti50(Pd42V8) alloys, the damping plateau is also quite flat, but there exists a small hump around 280 K and 320 K (indicated by dotted arrows in Fig. 2(b) and (d)), respectively. A possible reason for this phenomenon is that we did not remove hydrogen completely during dehydrogenation treatment and there could still exist a very small amount of hydrogen. But we cannot get the exact hydrogen concentration, as the amount of hydrogen is too trivial to be detected by our method after dehydrogenation. The interaction between hydrogen atoms and twin boundaries is likely to lead to such a small hump, as will be shown in a later section.

3.2.1. Displacement amplitude dependence of the damping behavior in hydrogen-free TiPd-based martensitic alloys

Here we show only the results for the Ti50(Pd42Fe8) alloy, since the displacement amplitude dependence of the damping behavior in the four alloys is very similar. The internal friction at 0.2 Hz as a function of temperature for different displacement amplitudes (5 μm, 15 μm, 30 μm, 45 μm and 60 μm) is shown in Fig. 3(a). We can see that the sharp internal friction peak associated with the B2–B19 transformation is independent of the displacement amplitude, i.e. both the peak temperature and peak height do not change with displacement amplitude.

The damping plateau, however, in the martensite phase shows strong dependence on displacement. With increasing displacement amplitude from 5 μm to 60 μm, the damping capacity increases dramatically from 0.02 to 0.11. As will be discussed later, such damping plateau is a result of the hysteretic motion of twin boundaries. Larger displacement amplitudes drive more dramatically the twin boundary
motion. Thus the energy dissipation (internal friction) increases with increasing displacement amplitude. Meanwhile, the damping plateau becomes less flat. The hump at around 250 K (indicated by the arrow in Fig. 3(a)) becomes more obvious with increasing displacement amplitude. A detailed comparison of the sharp transformation peak and the damping plateau at 250 K as a function of displacement amplitude is shown in Fig. 3(b). From this viewpoint, the damping capacity associated with the martensitic transformation is more stable than the damping plateau if the SMAs are subjected to different displacement amplitudes.

3.2.2. Cooling rate dependence of damping capacity in hydrogen-free TiPd-based martensitic alloys

Here we show only the results for Ti50(Pd42Fe8) in Fig. 4 because the cooling rate dependence of the damping behavior is quite similar in the other three alloys. The internal friction peak corresponding to the B2–B19 transformation strongly depends on the cooling rate. The peak height dramatically diminishes when the cooling rate decreases from 4 K/min, through 1 K/min to step-cooling and the peak position slightly shifts to high temperature. By contrast, the damping behavior of the plateau in the martensite phase is much more stable irrespective of the cooling rate and only the damping capacity shows a slight decrease. This demonstrates that the damping plateau is far superior to the sharp internal friction peak when the SMAs serve under large temperature vibrations.

3.3. Damping behavior of hydrogen-doped TiPd-based martensitic alloys

We doped about 0.35 at% hydrogen into the four TiPd-based alloys, and the corresponding internal friction and storage modulus as a function of temperature is shown in Fig. 5. The damping behavior of these alloys is also quite similar and two internal friction peaks can be observed in our measurement window. At high temperatures the sharp damping peak, which is accompanied by a storage modulus dip, corresponds to the B2–B19 transformation. It is the same as the one in hydrogen-free TiPd-based alloys shown in Fig. 2. The peak position does not change with frequency but the damping capacity (peak height) decreases with increasing frequency.

At low temperatures in the martensite phase, there is a broad internal friction peak covering the ambient-temperature range (270–360 K), with damping capacity (peak height) around 0.08, 0.07, 0.07 and 0.046 for the four alloys. The fact that the storage modulus shows no dip within this temperature range indicates that there is no structure change[40,41]. However, it is clear that the broad peak and corresponding storage modulus show strong
frequency dispersion and the peak temperature shifts to higher temperature with increasing frequency. The peak temperature versus frequency behavior follows the Arrhenius relation (as shown in Fig. 6) for these four alloys, suggesting some characteristic relaxation associated with the damping peak. These results are similar to the broad relaxation-type damping peak in the martensite phase of TiNi-based alloys and Ti₅₀(Pd₃₅Cr₅) [9,23]. The Arrhenius plots give activation energies of 0.84 eV, 0.72 eV, 0.72 eV and 0.9 eV, and relaxation times of the order of $10^{-14}$ s, $10^{-13}$ s, $10^{-12}$ s and $10^{-14}$ s for Ti₅₀(Pd₄₂Fe₈), Ti₅₀(Pd₃₈Co₁₂), Ti₅₀(Pd₄₀Mn₁₀) and Ti₅₀(Pd₄₂V₈) alloys, respectively, as listed in Table 1.

Here we also report another damping peak at even lower temperature which appears between 200 K and 270 K just below the above mentioned relaxation peak. From Fig. 5, the presence of the low temperature peak (200–270 K) is quite clear in hydrogen-doped Ti₅₀(Pd₄₂Fe₈) and Ti₅₀(Pd₄₂V₈) alloys, but almost invisible in hydrogen-doped Ti₅₀(Pd₃₈Co₁₂) and Ti₅₀(Pd₄₀Mn₁₀) alloys. The peak temperature is also frequency dependent and typically shows relaxation properties. Since this peak disappears in H-free TiPd-based alloys (as shown in Fig. 2), it should be closely related to the presence of hydrogen. However, further work is required to clarify the origin of this low temperature relaxation peak, which is not central to the present study. Below the relaxation peaks, at the lowest temperatures of the measurement (150 K) for example, the damping value is systematically smaller in the hydrogen-doped alloys than in the hydrogen-free ones. Such a difference between them is in agreement with earlier observations in TiNi-based alloys [33]. These observations indicate that the twin boundaries are pinned by hydrogen atoms below the relaxation peaks.

3.3.1. Displacement amplitude dependence of damping capacity in hydrogen-doped TiPd-based martensitic alloys

For brevity, we show only the results for the Ti₅₀(Pd₄₂V₈) alloy. The damping capacity versus temperature curves at 0.2 Hz for different displacement amplitudes are compared in Fig. 7(a). On one hand for the sharp peak associated with the B₂–B₁₉ transformation, there is little dependence on the displacement amplitude, but there still exists some difference from H-free alloys, i.e., with increasing displacement amplitude, the peak temperature slightly shifts to lower temperature and the peak height also shows a slight increase. This could be due to the pinning effect of hydrogen on the movement of the phase front between martensite and parent phase. The pinning effect will hinder the B₂–B₁₉ transformation and result in greater energy dissipation during the transformation under a larger displacement amplitude. On the other hand, the relaxation peak in the martensite phase shows strong dependence on the displacement amplitude. The peak position does not change but the peak height increases almost linearly with increasing displacement amplitude, as shown in Fig. 7(b). Similar to the damping capacity of the plateau in H-free alloys, the energy dissipation during twin boundary-hydrogen interaction naturally increases with increasing displacement amplitude. The low temperature peak also shows similar dependence on the displacement amplitude.

3.3.2. Cooling rate dependence of damping capacity in hydrogen-doped TiPd-based martensitic alloys

We show results for hydrogen-doped Ti₅₀(Pd₄₂V₈) as the behavior is quite similar for the other three alloys. The internal friction versus temperature at cooling rates of 4 K/min, 1 K/min with step cooling is shown in Fig. 8. We can see that the cooling rate dependence of the damping behavior is similar to hydrogen-free alloys. For the sharp transformation peak, with decreasing cooling rate its peak position slightly shifts to higher temperature whereas the peak height shows an obvious drop which typically characterizes the martensitic transformation in SMAs. For the relaxation peak in the martensite phase, the peak position also shifts to higher temperature, but the peak height only decreases...
slightly compared to that of the transformation peak. This is also the main feature of relaxation peaks in the martensitic phase of SMAs. Such contrasting behavior again demonstrates that the relaxation peak is more stable than the transformation peak when SMAs are subjected to large temperature variations.

4. Discussion

4.1. The promise of TiPd-based martensitic alloys for high damping ambient-temperature applications

We have seen that besides the sharp internal friction peak associated with the B2–B19 transformation, there exists a broad damping plateau or relaxation-type damping peak covering the ambient-temperature range in the four TiPd-based alloys studied. The reported damping behavior in TiNi-based alloys is quite similar to our TiPd-based SMAs despite their different product phases. Therefore, a detailed comparison of the transformation and damping behavior between TiNi-based and TiPd-based SMAs is given in Table 1.

Fig. 6. In(f) versus 1/T plot of the broad damping peak well fits the Arrhenius relationship (where T is the peak position corresponding to each frequency), indicating that they are all relaxation-type damping peaks.
aspect lies in the different temperatures at which the relaxation peaks are observed. For hydrogen-free alloys, the temperature range of the plateau is just below $M_s$. Thus, the plateau of TiNi-based alloys covers the temperature range 140–320 K, whereas that for TiPd-based alloys is over a much broader range (220–450 K) on the higher temperature side. For hydrogen-doped alloys, the relaxation peak in TiPd-based alloys is also at higher temperatures (270–370 K) compared to TiNi-based alloys (190–260 K). This suggests that both the plateau and relaxation peaks shift to higher temperature while maintaining high damping capacity in the five TiPd-based alloys. Thus, the presence of ambient-temperature high damping capacities might be a general property in TiPd-based alloys.

Many high damping metallic alloys, besides SMAs, exhibit both high damping capacity and good mechanical properties, although the underlying mechanism for their damping can vary. Thus, the damping capacity and its temperature location of several well-known high damping alloys are compared with our TiPd-based alloys (abbreviated as Ti$_{50}$(Pd$_{42}$V$_8$)) in Fig. 9. There is a Snoek-type relaxation peak with $Q / C_0 \approx 0.08$ in TiNb$_{25}$-(3O) alloy [2], a Zener-type relaxation peak with $Q / C_0 \approx 0.04$ in CuNi$_{0.5}$ alloy [42] and $Q / C_0 \approx 0.03$ in pure Mg [43,44], but all these peaks are located above the ambient-temperature range. Mn–Cu based alloys are well-known for their high damping capacity ($Q / C_0 \approx 0.04$), but the peak is located around 200 K below the ambient temperature range [27]. Although the damping behavior is at ambient-temperature in both Ni$_2$MnGa [45] and Mg–Ni alloys [46,47], the damping capacity of $Q / C_0 \approx 0.03$ is fairly low, compared with the TiPd-based alloys. Therefore, the TiPd-based martensitic alloys,

<table>
<thead>
<tr>
<th>Alloy (at%)</th>
<th>$M_s$ (K)</th>
<th>Structure (martensite)</th>
<th>Damping plateau in H-free alloys</th>
<th>Relaxation-type damping peak in H-doped alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Damping capacity</td>
<td>Temperature range (K)</td>
</tr>
<tr>
<td>Ti$<em>{50}$(Ni$</em>{48}$Fe$_2$)</td>
<td>290</td>
<td>R (trigonal)</td>
<td>0.05</td>
<td>230–260</td>
</tr>
<tr>
<td>Ti$<em>{50}$Ni$</em>{50}$</td>
<td>330</td>
<td>B19 (monoclinic)</td>
<td>0.02</td>
<td>140–320</td>
</tr>
<tr>
<td>Ti$<em>{50}$(Ni$</em>{30}$Cu$_{20}$)</td>
<td>348</td>
<td>B19 (orthorhombic)</td>
<td>0.05</td>
<td>170–300</td>
</tr>
<tr>
<td>Ti$<em>{50}$(Pd$</em>{40}$Mn$_{10}$)</td>
<td>391</td>
<td>B19 (orthorhombic)</td>
<td>0.04</td>
<td>220–340</td>
</tr>
<tr>
<td>Ti$<em>{50}$(Pd$</em>{42}$V$_8$)</td>
<td>430</td>
<td>B19 (orthorhombic)</td>
<td>0.023</td>
<td>250–400</td>
</tr>
<tr>
<td>Ti$<em>{50}$(Pd$</em>{38}$Co$_{12}$)</td>
<td>442</td>
<td>B19 (orthorhombic)</td>
<td>0.055</td>
<td>220–390</td>
</tr>
<tr>
<td>Ti$<em>{50}$(Pd$</em>{45}$Cr$_5$)</td>
<td>479</td>
<td>B19 (orthorhombic)</td>
<td>0.046</td>
<td>220–420</td>
</tr>
<tr>
<td>Ti$<em>{50}$(Pd$</em>{42}$Cl$_3$)</td>
<td>520</td>
<td>B19 (orthorhombic)</td>
<td>0.05</td>
<td>250–450</td>
</tr>
</tbody>
</table>

Fig. 7. The displacement amplitude dependence of damping behavior in the hydrogen-doped Ti$_{50}$(Pd$_{42}$V$_8$) alloy at 0.2 Hz. (a) Internal friction versus temperature curves for different displacement amplitudes. (b) The damping capacity associated with B$_2$–B19 transformation (MT peak) and that of the broad peak at 300 K (indicated by the arrow in (a)) as a function of displacement amplitude.

Fig. 8. The cooling rate dependence of damping behaviors in hydrogen-doped Ti$_{50}$(Pd$_{42}$V$_8$) alloy at 0.2 Hz.
especially the hydrogen-containing ones, can possess both high damping capacity and broad ambient-temperature range. Fig. 9 shows that they appear superior to other damping materials in this regard.

### 4.2. Possible origin of the high damping capacity in TiPd-based martensitic alloys

This lies in aspects of the high damping plateau and the relaxation peak. We have seen that the damping capacity in the parent phase is quite low compared to the martensite phase. Because there exists mobile twin boundaries in the martensite phase we focus on the damping plateau results from the hysteretic motion of twin boundaries under external stress. As schematically shown in Fig. 10(a), the martensite phase is composed of various martensite variants, which are related by twin boundaries. When the ac stress field is applied, domain wall kinks form and move with the help of stress [16]. These processes are highly dissipative and the energy of vibration is converted into heat within the materials, i.e., the internal friction in the martensite phase. However, why the damping plateau remains stable over such a broad temperature range still remains unclear and needs further investigation. In addition, as the twin patterns relax at very high temperatures (270–1010 Hz), the internal friction originating in twin boundaries is always observed in Resonance Ultrasonic Spectroscopy [16]. Thus, in our low frequency window (0.2–20 Hz), the hydrogen-free samples did not show any frequency dependence. The similar damping plateau in H-free TiNi-based alloys can be similarly understood and their different damping capacities can be attributed to the different motilities of their twin boundaries.

Regarding the relaxation peak in the martensite phase (270–360 K) of hydrogen-doped TiPd-based alloys, the different damping behavior of hydrogen-free and hydrogen-doped TiPd-based alloys strongly suggests that hydrogen is necessary for the appearance of relaxation peaks and supports the twin boundary–hydrogen interaction mechanism [37]. However, the detailed mechanism remains unclear. Hydrogen is supposed to be at or near twin boundaries due to the elastic interaction and decelerates the twin boundary motion under stress, as schematically shown in Fig. 10(b) [22]. At high temperatures, the diffusion of hydrogen atoms is quite fast due to high thermal energy and it can always follow the twin boundary motion, which results in small internal friction. At low temperatures, twin boundaries are essentially pinned by hydrogen atoms due to the slow diffusion of hydrogen. As a result, the internal friction is also low. At intermediate temperatures between the two extremes, twin boundaries can move together with hydrogen under viscous damping with maximum time lag (loss). Thus, the relaxation peak can only appear in finite temperatures as observed in many SMAs.

### 4.3. Key factors determining the temperature of the high damping capacity in martensite phase of SMAs

This provides effective guidelines for shifting the high damping capacities to desired temperature ranges for applications.

#### 4.3.1. Key factor determining the temperature of the high damping plateau

For hydrogen-free alloys, there exists a high damping plateau in the martensite phase sweeping a wide temperature range. Since the damping plateau appears just after the martensitic transformation, the upper temperature limit is the martensitic transformation temperature $M_s$. Therefore, the key factor determining the temperature location of the high damping plateau in hydrogen-free alloys is the corresponding martensitic transformation temperature $M_s$ of SMAs.

For hydrogen-doped alloys shown in Table 1, corresponding to the high $M_s$ of TiPd-based alloys, the relaxation peak is located within a high temperature range (270–370 K); for low $M_s$ of TiNi-based alloys, the relaxation peak is located at much lower temperatures (190–260 K). This indicates that the relaxation peak will shift to higher temperatures with increasing $M_s$. It is noted that $T_{Ms}$(Pd$_{40}$Co$_{12}$) has higher $M_s$ than $T_{Ms}$(Pd$_{40}$Mn$_{10}$), but the relaxation peak temperature for the former is lower. Therefore, the $M_s$ is not the only factor determining the temperature of relaxation peak in SMAs. In the following Section 4.3.2, we show other possible factors.

#### 4.3.2. Key factors determining the temperature of the relaxation peak

Application of a small ac external stress field will result in the motion of twin boundaries together with their hydrogen atoms to move back and forth so as to follow the external field viscously.
There will be an energy barrier for the system to overcome in order to respond to the small ac stress field. The required thermal activation energy to overcome such an energy barrier determines the temperature of the relaxation peak. The higher energy barrier requires larger thermal activation energy and hence the relaxation peak occurs at higher temperature. As the peak originates from the hydrogen–twin boundary interaction, the activation energy for the peak may arise from several contributions, including hydrogen diffusion, twin boundary mobility and the hydrogen and twin boundary interaction.

4.3.2.1. Hydrogen diffusion. Mazziolai et al. have shown that the activation energy for hydrogen–twin boundary relaxation peak (about 0.51 eV) in TiNi alloy approximately coincides with that for hydrogen diffusion (0.5 eV) in TiNi alloy [36]. This suggests that hydrogen diffusion dominates the hydrogen–twin boundary relaxation peak in TiNi alloy [36]. Following the same protocol, it is worthwhile to compare the activation energy of our relaxation peak with that of hydrogen diffusion in TiPd-based alloy. However, the activation energy for hydrogen diffusion in TiPd-based alloy is not available in the literature. Fortunately, TiNi and TiPd are both Ti-based intermetallics and possess a B2 structure in their parent phase. We thus assume that the activation energy for hydrogen diffusion in TiPd-based alloy is similar to the value in TiNi-based alloy. The assumed activation energy for hydrogen diffusion is about 70% of the activation energy we obtained for hydrogen–twin boundary relaxation peak (0.7–0.9 eV). This suggests that the hydrogen diffusion plays an important role in hydrogen–twin boundary relaxation peaks in TiPd-based alloys, as the presence of hydrogen provides a viscous matrix for the movement of twin boundaries. On the other hand, the activation energy (0.7–0.9 eV) for hydrogen–twin boundary relaxation peak in TiPd-based alloys is about 0.2–0.4 eV higher than the assumed activation energy for hydrogen diffusion (0.5 eV). Such extra activation energy can be attributed either to the hysteretic twin–boundary motion or the hydrogen–twin boundary interaction.

4.3.2.2. Size of twinning shear of martensite phase. The hysteretic twin–boundary motion contributes to the hydrogen–twin boundary relaxation peak by providing a fairly high background, as seen from the high damping plateau (0.02–0.04) in hydrogen-free TiPd alloys (shown in Fig. 2). Such energy dissipation from twin boundary motion is related to its mobility under stress field. One can consider that the lower mobility leads to difficulty in the motion of twin boundaries and consequently provides a larger contribution to the activation energy of the hydrogen–twin boundary relaxation peak. It has been known that one of the most important factors that affect the mobility of twin boundaries is the size of twinning shear of the martensite phase [9,32,35,37]. As pointed by Fan et al., the small twinning shear of R-phase in Ti–Ni–Fe alloy results in high mobility of twin boundaries and extremely high damping capacity [35]. Thus, the size of twinning shear affects the mobility of the twin boundary and consequently influences the activation energy of the relaxation peak.

In the following we will show how the size of twinning shear influences the activation energy of the hydrogen–twin boundary relaxation peak and consequently the temperature location of the relaxation peak. Table 2 compares the size of twinning shear for three martensites (R, B19 and B19’) in TiNi-based alloys and B19 martensite in TiPd-based alloys. The magnitude of the twinning shear for B19 martensite structure in TiPd-based alloys is much larger than that for the other martensite structures in TiNi-based alloys. When applying a small ac external stress field, the twin boundaries together with hydrogen atoms will move back and forth to follow the external field viscously. For TiNi-based SMAs, the small twinning shear leads to the high mobility of the corresponding twin boundaries. Thus, the energy barrier that the twin boundary needs to overcome is small and the required thermal activation energy is small. To observe the relaxation peak at a certain temperature within our frequency range, the thermal activation energy should be comparable to the thermal energy k_{B}T, according to the Arrhenius relation [50]. Consequently, the relaxation peak appears at lower temperatures. By contrast, for TiPd-based SMAs the large twinning shear results in low mobility of the corresponding twin boundaries under ac external field. The corresponding energy barrier is thus large and the required thermal activation energy is also large. As a result, the relaxation peak appears at higher temperature [50]. The above preliminary consideration suggests that the size of twinning shear may play a role on determining the temperature of the hydrogen–twin boundary interaction peaks in TiNi-based and TiPd-based SMAs.

4.3.2.3. The interaction between hydrogen and twin boundaries. Besides the contributions from hydrogen diffusion and the twin-boundary motion, one also needs to consider the interaction between hydrogen and twin boundary, as the case in defect-dislocation relaxation (Snoek-Koster peak). For the Snoek-Koster peak, besides the activation energy for point defect diffusion, there exists an additional activation contribution. This was thought to originate from either the binding energy of the point defect to the dislocation or the dragging of point defect by dislocations, in addition to the formation enthalpy of kink pairs [51,52]. In our hydrogen–twin boundary relaxation peak, we speculate that the hydrogen atom and twin boundary interact in a similar way, despite the fact that we have planar defects instead of line defects. That is, the dragging of hydrogen atoms by twin boundaries gives rise to the extra activation energy. Due to the lack of the activation energy of hydrogen diffusion and twin boundary relaxation in TiPd-based alloys, it is hard to estimate the contribution to the total activation energy of the hydrogen–twin boundary interaction peaks.

Finally, we note that the Ti–Ni–Cu alloy appears an exception to the general rule. For example, as shown in Table 1 the M_{s} of Ti_{50}(Ni_{30}Cu_{20}) and Ti_{50}(Pd_{40}Mn_{10}) do not differ much, but their relaxation peak temperature still shows a large difference. Although M_{s} is higher and the twinning shear is larger for Ti_{50}(Ni_{30}Cu_{20}) alloy than that for Ti_{50}(Ni_{40}Fe_{20}), the relaxation peak temperature in Ti_{50}(Ni_{40}Cu_{20}) is similar to that in Ti_{50}(Ni_{40}Fe_{20}).
lower than that of TiSn(Ni4AlFe3) (which should be higher from our discussion above.). The damping behavior of Ti–Ni–Cu alloy may due to the fact that it has the same B19 martensite phase with the same orthorhombic structure as the TiPd-based alloys, but its twinning modes and magnitude of twinning shear shows a large difference from TiPd-based alloys. These interesting aspects of Ti–Ni–Cu alloy need further study.

5. Conclusions

The damping behavior of four hydrogen-free and hydrogen-doped TiPd-based martensitic alloys has been studied and compared to TiNi-based alloys. The main results and conclusions are as follows:

(1) The hydrogen-free TiPd-based alloys exhibit a high damping plateau over a broad temperature range of 220–450 K after the B2–B19 martensitic transformation. The damping plateau is considered to originate from energy dissipation during the hysteretic movement of twin boundaries under ac external stress field.

(2) The hydrogen-doped TiPd-based alloys exhibit a relaxation high damping peak over a broad ambient-temperature range of 270–370 K after the B2–B19 martensitic transformation. The different damping behaviors between hydrogen-free and hydrogen-doped alloys strongly support the idea that the relaxation is due to twin boundary–hydrogen interaction and the latter could be a general damping source in SMAs.

(3) The high damping plateau and relaxation damping peak over a broad ambient-temperature range could be generally present in TiPd-based alloys and this makes them promising for ambient-temperature applications. In particular, the temperature and frequency-insensitive high-damping plateau over the entire ambient-temperature range in hydrogen-free TiPd-based alloys may find important applications in environments with large temperature differences.

(4) The martensitic transformation temperature (M_s), the hydrogen–twin boundary interaction, diffusion of hydrogen and the size of twinning shear of the martensite phase can be key factors affecting the temperature location of the high damping capacity in the martensite phase of SMAs.

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