

Twofold role of dislocations in the relaxation behavior of Ti–Ni martensite

Genlian Fan^{a,b}, Kazuhiro Otsuka^{a,b}, Xiaobing Ren^{a,b,*}, Fuxing Yin^c

^a Multi-disciplinary Materials Research Center and State Key Laboratory for Mechanical Behaviour of Materials, Xi'an Jiaotong University, Xi'an 710049, China

^b Ferrous Physics Group, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047, Japan

^c Innovative Materials Engineering Laboratory, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047, Japan

Received 7 August 2007; received in revised form 28 September 2007; accepted 13 October 2007

Abstract

The relaxation peak in Ti–Ni-based shape memory alloys is attracting much attention as a high damping source, and its origin was recently revealed to be the interaction between twin boundaries and hydrogen. However, reports on the thermal cycling effect, which is characterized by the peak height decrease with cycling, seem to suggest that dislocations may also affect the relaxation behavior. To understand the role of dislocations in the twin boundary–hydrogen interaction peak, changes in the relaxation behavior with thermal cycling were systematically studied by dynamical mechanical analysis for both H-containing and dehydrogenated Ti₅₀Ni₅₀ samples. Our results show that although the origin of the relaxation peak is not related with dislocations, dislocations can affect the twin boundary–hydrogen interaction process in two opposite ways. First, tangled dislocations (created by thermal cycling) make twin boundary motion difficult. On the other hand, dislocations can also absorb hydrogen from twin boundaries and make twin boundary motion easier. All the thermal cycling effects in dynamic tests and dc tensile tests can be explained by the above dual role of dislocations in the twin boundary–hydrogen interaction process.

© 2007 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Internal friction; Thermal cycling; Hydrogen; Twin boundary; Relaxation

1. Introduction

A high and broad relaxation-type internal friction (IF) peak, usually called the “200 K peak” (because it appeared at around 200 K when measured at low frequency), was first found in the martensitic states of Ti–Ni-based shape memory alloys several decades ago [1,2]. Similar peaks have also been found in many other shape memory alloys, such as Mn–Cu [3], Cu–Zn–Al–Ni [4] and Ti–Ni-based ternary alloys [5]. Unlike the IF peak associated with the martensitic transformation, the high relaxation peak does not exhibit cooling/heating rate dependence [5]. This important

feature makes this peak an attractive damping source for developing high damping materials with high strength, and has been widely explored over the past decades [2–14]. Several speculations have been made to interpret the relaxation behavior. Dislocation relaxation [2] and dislocation–point defect (vacancies) interaction [6–8] are the most popular proposals, since dislocations and vacancies unavoidably exist in these alloys. Twin boundaries relaxation under external stress is another prevailing hypothesis, since the relaxation peak was always observed in the martensitic state, in which twin boundaries are abundantly present [5]. Mazzolai et al. first reported the linkage of martensite peaks with hydrogen and made extensive studies [9–13]. Over the past years the role of hydrogen has been an interesting but controversial issue, and several possibilities have been suggested: the hydrogen Snoek/Zener effect [9,12,13], the hydrogen–dislocation interaction effect [14]

* Corresponding author. Address: Ferrous Physics Group, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047, Japan. Tel.: +81 29 859 2731; fax: +81 29 859 2701.

E-mail address: Ren.Xiaobing@nims.go.jp (X. Ren).

and the hydrogen–twin boundary complex effect [10,13]. Despite these efforts, the origin of the “200 K peak” still remains controversial. Very recently, our study in a Ti–Ni–Cu alloy proved the origin of the effect to be the twin boundary–H interaction by two critical experiments [15]. First, the relaxation peak was shown to disappear in a nearly single variant martensitic state (achieved by applying pre-strain in the martensitic state) of an H-containing $\text{Ti}_{50}\text{Ni}_{30}\text{Cu}_{20}$ single crystal sample, while the relaxation peak reappeared after being cooled down from the parent phase, through which the sample was again brought into a multivariant state. Secondly, the relaxation peak was observed to disappear even in the multivariant state when the hydrogen in the sample was removed (dehydrogenated) in a dynamic vacuum, while it reappeared when it was re-annealed in hydrogen atmosphere. The above experimental results clearly indicate that the relaxation peak originated from the interaction between twin boundaries and hydrogen. We also showed that hydrogen can be inadvertently introduced into Ti–Ni-based alloys during heat treatment and chemical etching; this confirmed an earlier speculation [12]. A recent study [16] has also shown the significant effect of hydrogen on internal friction peaks of an Ni-rich Ti–Ni alloy.

Although most of the experimental results related with the relaxation peak can be explained by the twin boundary–H interaction, there is one phenomenon that cannot be explained by this mechanism alone: the thermal cycling effect reported by Zhu et al. in the near-equiatomic Ti–Ni alloys [6,8]. The height of the relaxation peak was found to decrease after thermal cycling between the martensite and the parent phase, while it recovered if the sample was annealed above 823 K [6]. It is well-known that dislocations can be easily introduced during the thermal cycling between the parent phase and the martensite in near-equiatomic Ti–Ni alloys, due to the large transformation strain associated with B2–B19' transformation [17,18]. Thus it is most likely that the thermal cycling effect is closely related to the dislocations produced during thermal cycling. Earlier studies [6,8] speculated that the relaxation peak might be a result of the interaction between dislocations and point defects (presumably vacancies). The thermal cycling effect was attributed either to the decrease in dislocation mobility with increasing dislocation density [6] or to the elimination of the quenched-in vacancies [8]. However, our previous results (mentioned above) strongly suggest that the relaxation peak stems from the interaction between twin boundaries and hydrogen atoms, and dislocation–point defect interaction is not responsible for the relaxation peak. This poses a puzzling question: how can a twin boundary–H interaction peak be significantly affected by dislocations (created by thermal cycling)? Furthermore, it is important to keep the damping capacity stable if this damping peak is being used for real applications. Thus finding out the underlying mechanism for the thermal cycling effect on the relaxation behavior is not only of fundamental interest but also important for applications.

Aiming to clarify the effect of dislocations on the relaxation behavior, we compared the thermal cycling effect in an H-containing $\text{Ti}_{50}\text{Ni}_{50}$ sample with that in a dehydrogenated one by dynamical mechanical analysis (DMA) and dc tensile testing. As a result, we found that dislocations are not involved with the origin of the relaxation peak, since the dislocation–H interaction itself cannot produce the “200 K peak”. However, dislocations do have a dual role in the twin boundary–H interaction process. On one hand, tangled dislocations increase the barrier for twin boundary motion and make it difficult to move; on the other hand, dislocations can also absorb hydrogen from twin boundaries and make the twin boundary motion easier. As will be discussed in the following, all the thermal cycling effects in dynamical (ac) test and dc test can be explained consistently by considering the dislocations' dual effects on the twin boundary–H interaction process. Based on the above results, we also suggest an important guideline for developing stable high damping materials.

2. Experimental

In the present study we used $\text{Ti}_{50}\text{Ni}_{50}$ alloy, which exhibits one step B2–B19' martensitic transformation ($M_s = 341$ K, $A_f = 383$ K). The samples were solution-treated at 1173 K in vacuum-sealed quartz tubes, followed by water quenching and chemical etching. Our previous work [15] has proved that hydrogen is introduced into the sample during such a process, and the hydrogen incorporated is about 0.06 at.% by chemical analysis. Therefore the samples so treated are called “H-containing samples” hereafter. To obtain hydrogen-free samples for making a comparison with the above H-containing samples, some samples were dehydrogenated at 1173 K in a dynamic vacuum. We name such samples as “DeH samples” hereafter (for more details, see Ref. [15]). Internal friction ($\tan\delta$) and storage modulus were measured by DMA Q800 from TA Instruments. Samples with a size of $30 \times 2.5 \times 1.0$ mm³ were measured in single cantilever mode at a constant amplitude of 30 μm . Six frequencies (20, 10, 4, 1, 0.4, 0.2 Hz) were swept when samples were cooled/heated with a temperature rate of 2 K min⁻¹. The thermal cycling was performed in the following way: samples were first equilibrated at 140 K and heated up to 433 K as the first thermal cycle. They were then cooled back down to 140 K before being reheated as the second thermal cycle – and thus with the later cycles. $\tan\delta$ and storage modulus data during heating procedures were recorded to show the thermal cycling effect.

To further verify the dislocation effect on the twin boundary–H interaction, we also compared the thermal cycling effect on the critical stress for twinning in an H-containing $\text{Ti}_{50}\text{Ni}_{50}$ sample with that in a dehydrogenated one by dc tensile testing. The $\text{Ti}_{50}\text{Ni}_{50}$ samples for such a purpose had a size of $50 \times 2.5 \times 0.8$ mm³ and were tested with a SHIMADZU AG-20I tensile machine. The samples were loaded at 145 K in pentane cooled with liquid nitrogen;

the strain rate was $5 \times 10^{-6} \text{ s}^{-1}$. After each loading, the samples were heated to 433 K to recover to the parent phase and cooled down again to 145 K for the next loading.

To check whether dislocation–H interaction can also produce the relaxation peak, a $\text{Ti}_{48}\text{Ni}_{52}$ sample (which does not transform into martensite) prepared in the following way was tested by DMA. It was first solution-treated at 1273 K then water quenched and chemically etched. It contained hydrogen after the above treatment. Then the sample was further subject to cold working to introduce dislocations (10% thickness reduction by cold rolling). $\text{Tan } \delta$ and storage modulus measurements for the sample before and after cold working were taken in the same way as for $\text{Ti}_{50}\text{Ni}_{50}$ samples.

3. Results

3.1. Internal friction and storage modulus in H-containing and DeH $\text{Ti}_{50}\text{Ni}_{50}$ samples

In this section, we report the damping behavior of H-containing and DeH $\text{Ti}_{50}\text{Ni}_{50}$ samples before subjecting to thermal cycling. Fig. 1 shows (a) $\text{tan } \delta$ and (b) storage modulus curves for H-containing and DeH $\text{Ti}_{50}\text{Ni}_{50}$ samples during the heating process. First, we can see that the reverse martensitic transformation from B19' to B2 occurs

at about 370 K for both H-containing and DeH samples, accompanied by a sharp IF peak whose peak height greatly depends on frequency, and a steep increase of storage modulus due to the disappearance of high-density mobile twin boundaries. These are the well-known features for the IF associated with a martensitic transformation [19].

Now, let us see the interesting damping behavior in the B19' martensitic state, which contains high-density of twin boundaries. For the H-containing sample, a high IF peak appears at about 200 K (empty symbols in Fig. 1a). It is a relaxation-type peak, whose peak position shows strong frequency dependence and shifts to higher temperature with increasing frequency. This relaxation peak was usually called the “200 K peak” in the previous studies [2–15]. The activation energy and frequency factor for this relaxation peak was determined by Arrhenius plot to be about 0.51 eV and 10^{12} , respectively, which are close to the data reported in the literature [6,9,10]. The storage modulus corresponding to the relaxation peak (empty symbols in Fig. 1b) also shows a typical relaxation feature, exhibiting a step-like decrease with increasing temperature, with the “step temperature” depending on frequency. Compared with the H-doped sample, the DeH $\text{Ti}_{50}\text{Ni}_{50}$ sample (solid symbols in Fig. 1) shows only a low plateau in the $\text{tan } \delta$ curve with little frequency dependence, which can be attributed to the twin boundary motion under ac stress [19,20]. Correspondingly, the storage modulus decreases linearly

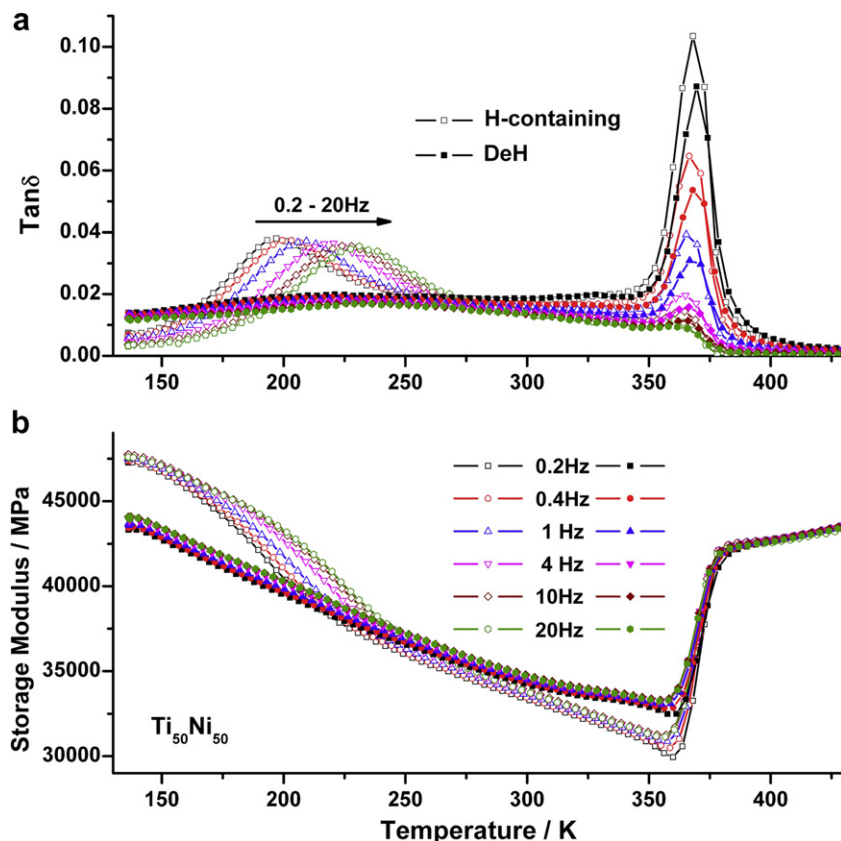


Fig. 1. (a) $\text{Tan } \delta$ and (b) storage modulus for the H-containing (empty symbols) and DeH (solid symbols) $\text{Ti}_{50}\text{Ni}_{50}$ samples during heating.

with increasing temperature with negligible frequency dependence.

In addition, we can see that the storage modulus for the H-containing sample is much higher than that of the DeH sample at the lowest temperature (140 K) in our temperature window. The significant differences between the H-containing sample and the DeH sample indicate the important role of hydrogen in producing this relaxation peak. According to our previous study on Ti–Ni–Cu alloy [15], the nature of this relaxation peak is attributed to the interaction between mobile twin boundaries and hydrogen, because no peak was found either without twin boundaries or without hydrogen, and the peak appears only when both twin boundaries and hydrogen are present.

3.2. Internal friction and storage modulus in a twin-free, $Ti_{48}Ni_{52}$ sample – possibility of the 200 K peak arising from the interaction between dislocations and hydrogen

Despite the 200 K peak being proved to be due to the interaction between twin boundaries and hydrogen, there is a possibility that such an interaction can be equally well interpreted by an interaction between dislocations and

hydrogen. This is because certain twin boundaries have been viewed geometrically as piles of dislocations [21], so the interaction between twin boundaries and hydrogen may be viewed as the interaction between the constituent dislocations and hydrogen. Although this geometrical view about the twin boundary has yet to be proved a reflection of its physical nature, we need to take this view seriously, because if such a view is valid then the 200 K peak could still originate from a dislocation–H interaction.

Here we designed an experiment to prove that dislocation–H interaction cannot generate an IF peak in the whole temperature range we studied. We studied a $Ti_{48}Ni_{52}$ alloy which does not undergo martensitic transformation [22] and thus has no twin boundaries. We first tested whether hydrogen alone (without introducing dislocations) could generate a relaxation peak. The internal friction and storage modulus for the solution-treated (i.e. H-containing) $Ti_{48}Ni_{52}$ sample are shown in the left column of Fig. 2. The shallow storage modulus dip and the corresponding $\tan \delta$ peak at about 150 K are due to a recently discovered strain glass transition [23,24]. Clearly, no relaxation peak was detected in the temperature range from 180 to 270 K, where the relaxation peak of our interest is expected to appear. This

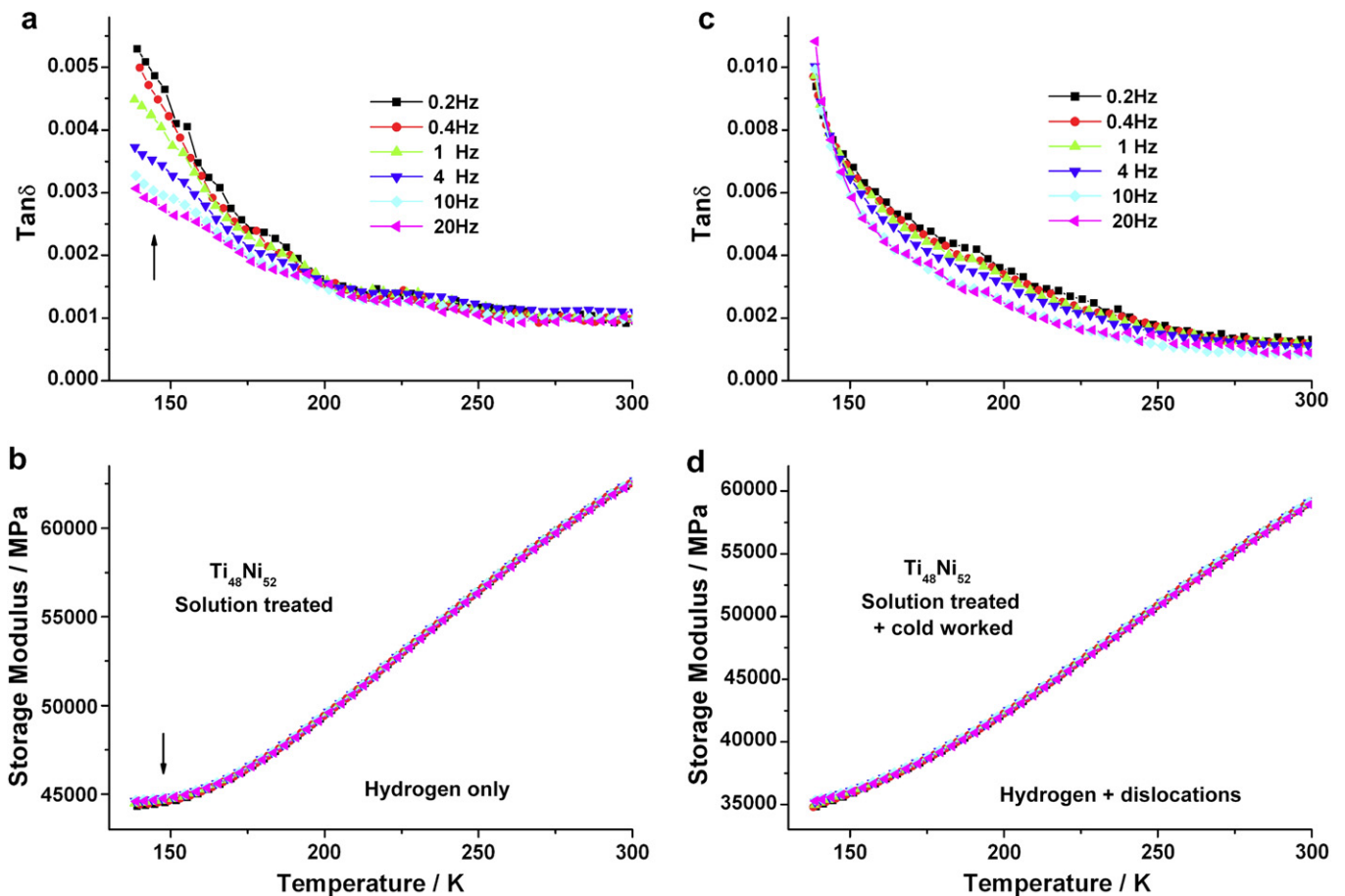


Fig. 2. $\tan \delta$ and storage modulus for $Ti_{48}Ni_{52}$ sample: (a and b) the solution-treated sample (i.e. H-containing); (c and d) the same sample after further cold working (10% thickness reduction) and chemical etching (i.e. H + dislocations). The arrows in (a) and (b) indicate the strain glass transition temperature.

experiment indicates that hydrogen alone does not create a relaxation peak in the temperature range we studied. We further examined whether there exists a relaxation peak when both hydrogen and dislocations are present. We introduced dislocations by cold working the above H-containing samples, so that the sample contained both dislocations and hydrogen. The result for this H-containing, dislocation-containing $\text{Ti}_{48}\text{Ni}_{52}$ sample is shown in the right column of Fig. 2. Apparently, still no sign of relaxation peak can be seen in the temperature range where the twin boundary–H interaction peak usually appears. From the above results we can conclude that dislocation–H interaction cannot produce the “200 K peak”, i.e. dislocations are not directly involved in the origin of the relaxation peak.

3.3. The thermal cycling effect on relaxation behavior

After determining that dislocation is not related with the origin of the relaxation peak, we now proceed to our main interest, the thermal cycling effect on the relaxation behavior of H-containing and DeH $\text{Ti}_{50}\text{Ni}_{50}$ samples. Fig. 3 shows the $\tan \delta$ (a) and storage modulus (b) curves on heating during three thermal cycles for the H-containing sample. To clearly show the changes of relaxation peak height with thermal cycling, the data of one frequency (0.4 Hz) are shown for

each thermal cycle. For the first cycle (open squares), a well-developed relaxation peak can be seen at about 200 K. In the later cycles the peak height decreases greatly, and has almost vanished after three thermal cycles. Therefore, the change in the peak height with thermal cycling in this H-containing sample is very similar to that reported in earlier literature [6,8]. In addition, we notice that the corresponding storage modulus (Fig. 3b) in the low temperature range decreases after thermal cycling as the solid arrow indicates; but in the high temperature range it increases after thermal cycling, as indicated by the dashed arrow. The storage modulus curve for the third heating looks very similar to that of the DeH sample in Fig. 1, decreasing linearly with increasing temperature. We also notice that the reverse transformation temperature of the B19'–B2 transformation shifts to a lower temperature after thermal cycling. This decrease in transformation temperature is not surprising, because the tangled dislocations introduced during the thermal cycles increase the barrier for martensitic transformation [17,18,22,26].

The $\tan \delta$ (a) and storage modulus (b) changes with thermal cycling for the DeH $\text{Ti}_{50}\text{Ni}_{50}$ sample are shown in Fig. 4 for comparison. The internal friction plateau in the martensite decreases slightly after each thermal cycle, while the storage modulus increases after thermal cycling, as indicated by the arrow. This change is contrary to that in

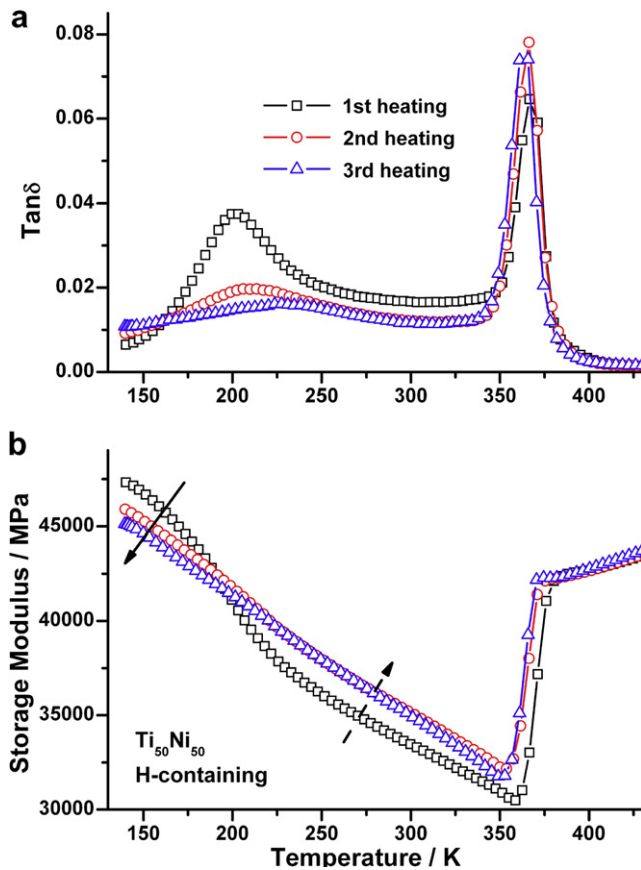


Fig. 3. (a) $\tan \delta$ and (b) storage modulus changes with thermal cycling for the solution-treated $\text{Ti}_{50}\text{Ni}_{50}$ sample (H-containing, with 0.06 at.% H).

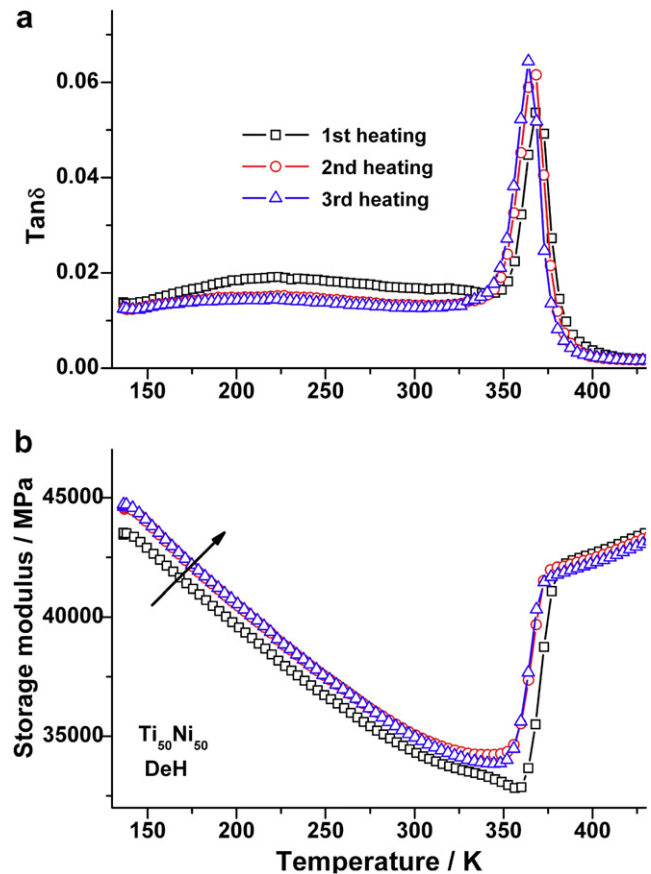


Fig. 4. $\tan \delta$ and storage modulus changes with thermal cycling for the dehydrogenated $\text{Ti}_{50}\text{Ni}_{50}$ sample (DeH).

the H-containing sample. It would be interesting to know why introducing dislocations can reduce the IF in both the H-containing sample and the DeH sample but causes opposite changes in storage modulus. We will cover this in the discussion section later.

4. Discussion

4.1. Twofold role of dislocations in the relaxation behavior

Our results in the preceding sections demonstrate two key points, which are the basis for understanding the “200 K peak” and the thermal cycling effect on the relaxation behavior.

First, the H-containing $\text{Ti}_{50}\text{Ni}_{50}$ sample exhibits a well-developed relaxation peak at about 200 K, whereas the cold-worked, H-containing $\text{Ti}_{48}\text{Ni}_{52}$ alloy, which contains both dislocations and hydrogen (but no twin boundary), does not exhibit a similar relaxation peak (Fig. 2). The above results directly exclude the possibility of the dislocation–H interaction being the origin for the relaxation peak. Together with the twin boundary effect and the hydrogen effect that we already explored in a Ti–Ni–Cu alloy [15], we have checked all the possible mechanisms for the relaxation peak in martensite. Now it is safe to reach a conclusion concerning the origin of this relaxation peak: it is the interaction between twin boundaries and hydrogen that produces the relaxation peak. This is the basis for the following discussion on the thermal cycling effect.

Secondly, we have demonstrated that thermal cycling effects exist both in the H-containing sample and the DeH one. Although both the relaxation peak in H-containing sample and the IF plateau in the DeH sample decrease after thermal cycles, the storage modulus in the low temperature range exhibits opposite changes. It decreases in the H-containing sample while increasing in the DeH sample after thermal cycles. Thus, the central questions here are the following: why can thermal cycling-induced dislocations reduce the relaxation peak or even eliminate it? Why do the dislocations have different effects on the storage modulus in the relaxation peak temperature range between the H-containing case and the DeH case?

In the following, we shall show that the contrasting results between the H-containing sample and the DeH one are actually due to the dual role of dislocations in the relaxation behavior. Before we discuss the dislocation effect on the relaxation peak, let us first consider the thermal cycling effect in the DeH sample, which is simpler due to the absence of hydrogen. From the finding that the storage modulus increases with thermal cycling, we can deduce that twin boundary motion is actually hindered by the induced dislocations. As a consequence, the IF plateau due to twin boundary motion also decreases with thermal cycling. Thus the thermal cycling effect in the DeH sample can be explained simply by considering hindrance effect of dislocations on twin boundary motion. Such a hindrance effect also exists in the H-containing sample, result-

ing in the increase of the storage modulus in the high temperature range, as indicated by the dashed arrow in Fig. 3. But the storage modulus in the low temperature range decreased rather than increased after the introduction of dislocations, indicating that the twin boundary mobility increases with the introduction of dislocations. So there must be another effect caused by dislocations, which can increase the mobility of twin boundaries.

How can the tangled dislocations increase the mobility of twin boundaries in H-containing samples? The answer to this question requires not only an understanding of the dislocation role in the relaxation behavior, but also a deeper understanding of the mechanism of this relaxation peak. The relaxation peak originates from the interaction between twin boundaries and hydrogen, as we discussed above. Accompanying the appearance of the relaxation peak, the storage modulus exhibited step-like changes with temperature, while in the DeH sample the storage modulus only showed linear changes with temperature. This comparison tells us that the presence of hydrogen greatly hinders the twin boundary motion under ac stress and makes the material appear harder. So the role of hydrogen in the relaxation peak should be a pinning effect to the twin boundaries motion in a broad sense.

Fig. 5 schematically illustrates the interaction between twin boundaries and hydrogen. Hydrogen is supposed to locate at or near twin boundaries due to an elastic interaction. When applying a small ac stress, twin boundaries must drag hydrogen atoms in order to move themselves. At very low temperature, the diffusion of hydrogen is quite slow due to the low thermal energy, so twin boundaries are

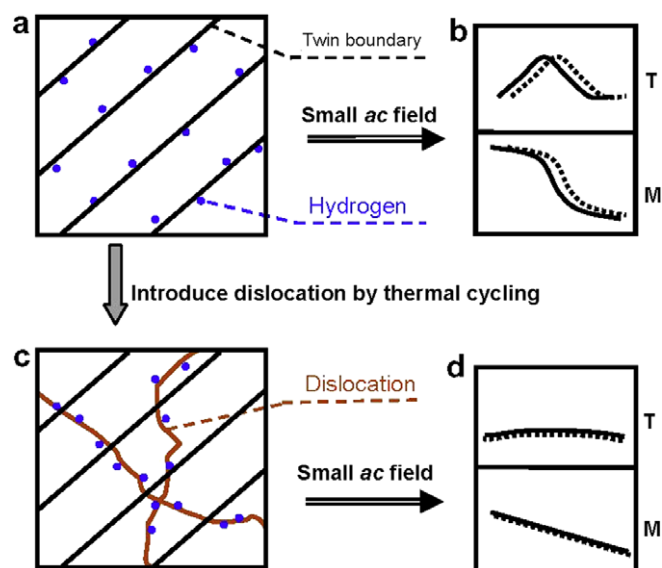


Fig. 5. Schematic illustration of the interaction between twin boundaries and hydrogen before (a) and after (c) segregation of hydrogen to dislocations. (b and d) The corresponding response of materials as a function of temperature before and after introducing dislocations, respectively. T and M represent $\tan \delta$ and storage modulus, respectively. The solid line and dotted line in (c) and (d) present two different frequencies.

essentially pinned by hydrogen, which makes the material appear hard and exhibit high storage modulus and low loss, as shown in Fig. 5b. At high temperature, the diffusion of hydrogen can always follow the motion of twin boundaries, thus the material exhibits very low storage modulus and low loss. At the peak temperature (between the two extremes), hydrogen has intermediate mobility, and thus the twin boundaries exhibit a viscous motion with the maximum time lag (loss), but the modulus is intermediate. Clearly the loss and the modulus are frequency-dependent. Therefore, the above explains why there is a peak in IF around 200 K and why it is frequency-dependent. A quantitative modeling of the twin boundary–H interaction and the associated internal friction will be given elsewhere.

From the above twin boundary–H interaction picture, we know that it is the hydrogen that greatly decreases the mobility of twin boundaries in the low temperature range. So a very likely way for dislocations to make the twin boundary motion easier is to remove hydrogen from the twin boundaries, namely, by absorbing hydrogen from them. Intuitively, hydrogen would prefer dislocation sites to twin boundaries, because dislocations have “infinite” strain at the core (i.e. strain is divergent at the continuum limit) and thus can interact more strongly with hydrogen than is the case for twin boundaries (where strain is not divergent). Now we show that this idea can fully explain the observed increase in twin boundary mobility for H-containing samples after thermal cycling. After thermal cycling, hydrogen atoms that were originally located at twin boundaries partially diffuse to the newly created dislocations sites, as illustrated in Fig. 5c. So the amount of hydrogen that is involved in the twin boundary–H interaction decreases, and consequently much lower $\tan\delta$ and storage modulus are obtained (Fig. 5d). This agrees with the report that the relaxation peak height also depends on hydrogen concentration [13,14]. If all hydrogen atoms were removed from twin boundaries by dislocations, no relaxation peak would be observed, since twin boundary–H interaction does not exist in the absence of hydrogen (as observed experimentally). After three thermal cycles, the IF and storage modulus curves (open triangles in Fig. 3) for the H-containing sample were almost the same as those for the DeH sample. Thus the idea that dislocations absorb H from twin boundaries fits very well with the experimental results.

Therefore, dislocations do have a dual role in the relaxation behavior: one is the hindrance of twin boundary motion and the other is the absorption of hydrogen from twin boundaries, thereby making twin boundary motion easier. In the H-containing sample, these two effects compete with each other and produce an opposite effect on the storage modulus at low temperature compared with at high temperature. At low temperature, the original high storage modulus due to the hydrogen pinning effect is greatly reduced after hydrogen is absorbed by the cycling-created dislocations. So the second effect dominates and results in a lower storage modulus after thermal cycling. At high temperature, the pinning effect of hydrogen to twin boundaries is very weak; as a

consequence, the first effect dominates and results in an increase in the storage modulus after thermal cycling. For the DeH sample, which has an absence of hydrogen, dislocations have only one effect, i.e. the hindrance of the twin boundary motion, so the storage modulus increases monotonously after thermal cycling. Thus all the experimental results for the H-containing samples and DeH samples can be understood by considering dislocations’ dual role in the relaxation behavior.

We can also explain the annealing effect by the above scenario. The transformation-induced dislocations will be annealed out at temperature higher than the recrystallization temperature. Therefore, the hydrogen, which had segregated to dislocations after thermal cycling, now becomes free and migrates to the twin boundaries again after cooling from high temperature. So the relaxation peak caused by twin boundary–H interaction reappears after annealing at high temperature.

It should be noted that the explanation for the thermal cycling effect for H-containing samples is based on the fundamental assumption that hydrogen has a stronger binding force with dislocations than with twin boundaries, so that the introduced dislocations during thermal cycling will “grab” hydrogen atoms from the twin boundaries. Here we provide indirect proof for this important assumption. If hydrogen has stronger binding with dislocations than with twin boundaries, we should observe that, for a sample with higher hydrogen concentration, more dislocations are needed to completely remove the hydrogen from twin boundaries, i.e. more thermal cycles must be performed to fully eliminate the relaxation peak. Therefore, we annealed our sample in a quartz tube containing H_2 gas at 873 K to dope more hydrogen into the sample. We call this sample the “H-doped” sample to distinguish it from the naturally H-containing samples. The hydrogen concentration for this H-doped sample is about 0.2 at.%, as determined by chemical analysis (this hydrogen concentration is three times higher than that in the “H-containing sample”). Fig. 6 shows the changes of $\tan\delta$ and storage modulus with thermal cycling for this sample. Both the relaxation peak and the storage modulus in the H-doped sample were greatly decreased after thermal cycles. But compared with the results of the H-containing sample in Fig. 3, more thermal cycles are needed to fully eliminate the peak, as we expected. The low IF peak can still be seen after 20 thermal cycles. Therefore, the above result supports our idea that hydrogen has a stronger binding force with dislocations than with twin boundaries, and thus tends to segregate to the dislocations during thermal cycling.

4.2. The thermal cycling effect on the critical stress for twinning

To further verify our scenario for the thermal cycling effect, we will discuss the thermal cycling effect shown in dc tensile tests. In dc tensile testing, the physical quantity reflecting twin boundary mobility (in the ac measurement,

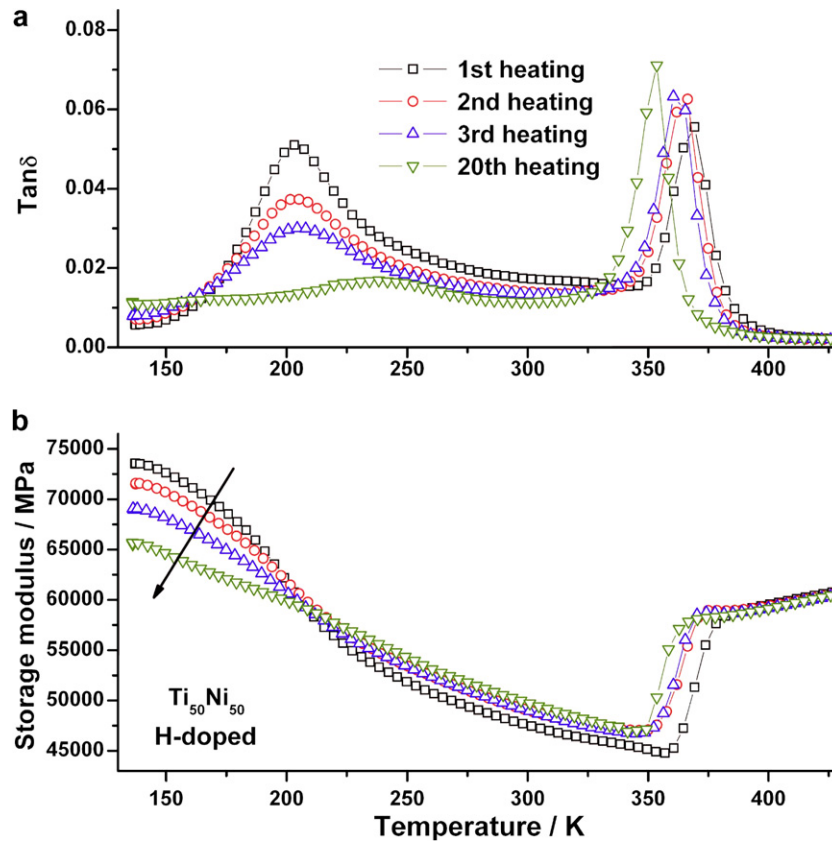


Fig. 6. (a) $Tan\delta$ and (b) storage modulus changes with thermal cycling for the H-doped $Ti_{50}Ni_{50}$ sample, in which hydrogen concentration is three times higher (0.2 at.%) than the sample used for Fig. 3.

it is the storage modulus) is the critical stress for twinning. Since the transformation-induced dislocations should also affect the large-scale twinning process, we expect to reach the same conclusion from the dc tensile tests as from the ac measurement.

The changes of critical stress for twinning with thermal cycling for DeH and H-containing $Ti_{50}Ni_{50}$ samples are shown in Fig. 7a and c, respectively. All the tensile experiments were carried out at 145 K, which corresponds to the lowest temperature in our DMA tests. As the yielding is not very sharp in most cases, we define the critical stress for twinning by a double tangent method shown in the inset of Fig. 7b. With this definition, Fig. 7b and d shows the changes of critical stress with the number of thermal cycles for the DeH and H-containing samples, respectively. From Fig. 7a and b, we can see clearly that the critical stress for twinning increases with thermal cycling for the DeH sample, while it decreases with thermal cycling for the H-containing sample (Fig. 7c and d). The cycling effect is most significant at first cycle and tends to saturation at later cycles. All these features found in the dc tensile test are the same as those measured by the ac mechanical test (DMA) shown in Fig. 3. In addition, we can also see a typical yielding in the first-loading curve for the H-containing sample (indicated by the arrow in Fig. 7c). Such yielding has been found in many body-centered cubic metals and

is generally viewed as evidence for the pinning of point defects to dislocations [25]. Here in our sample, the yielding is due to the pinning effect of hydrogen to twin boundaries. Similar yielding was not found in the DeH sample.

Here we will show that the above changes of the critical stress with thermal cycling in H-containing and DeH samples can also be explained by the dual dislocation effect on the twinning process. The twinning process during tensile testing will be hindered by the high-density, tangled dislocations introduced during thermal cycling. So the critical stress for the DeH sample increases after thermal cycling. But for the H-containing sample, twin boundaries are originally pinned by hydrogen. The initial critical stress for twinning is much higher than that for the DeH sample because of the hydrogen pinning, which is evidenced by the presence of the yielding in the first-loading stress–strain curve (Fig. 7c). After thermal cycling, dislocations are introduced and they absorb hydrogen from the twin boundaries, and thus twin boundary motion becomes easier. This leads to a decrease in the critical stress for the second loading and the concomitant disappearance of the yielding effect (stress drop) due to hydrogen pinning. With a further increase of the number of thermal cycling (thus more dislocations), there is little further decrease in the critical stress because most of the hydrogen has already segregated to the dislocations.

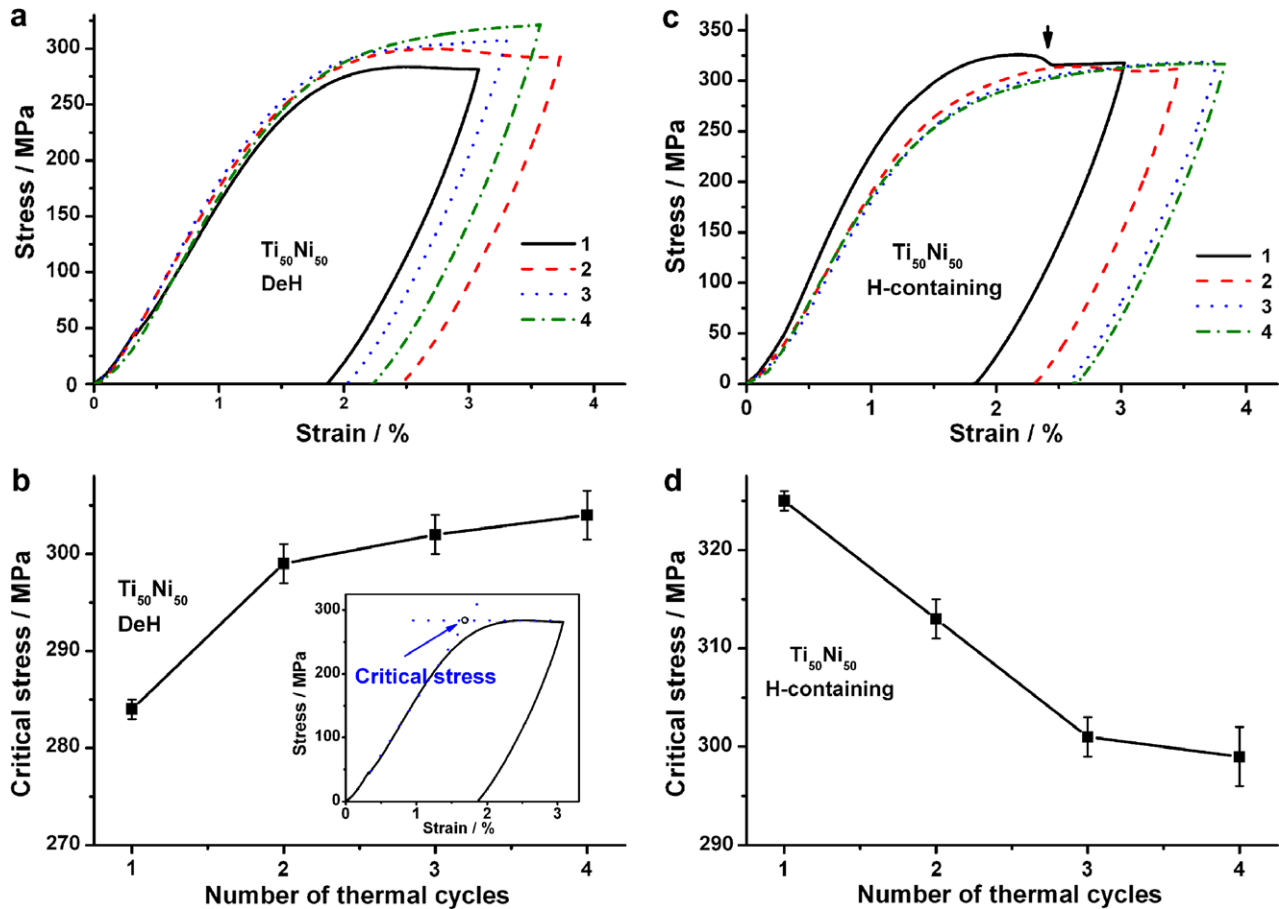


Fig. 7. Stress–strain curves as a function of the number of thermal cycles for the DeH sample (a) and H-containing sample (c), respectively. The change in critical stress with the number of thermal cycles for the DeH and H-containing samples are shown in (b) and (d), respectively. Each tensile testing was carried out at 145 K after heated up to parent phase at 433 K. The inset in (b) shows the definition of critical twinning stress by a double tangent method.

Therefore, the thermal cycling effects in both the dc tensile tests and the DMA tests support a unified scenario that dislocations have a dual role in the twin boundary–H interaction process.

4.3. Guideline for obtaining high and stable damping peaks

From the above discussion, we know that dislocations introduced during thermal cycling between parent phase and martensite greatly reduce the peak height of the relaxation peak by absorbing hydrogen. But for practical applications of the high damping materials, it is very important to keep the damping capacity stable. Thus to utilize the high relaxation peaks produced by the twin boundary–H interaction, it is vitally important to avoid introducing dislocations. Since dislocations are introduced due to the large transformation strain of martensitic transformation [17,18,26], choosing an alloy with a small transformation strain is an easy way to keep the relaxation peak stable. Recently, we observed an ultrahigh relaxation peak in the R-phase state of an H-containing Ti₅₀Ni₄₈Fe₂ alloy, whose peak height is shown not to be sensitive to the thermal cycles between B2–R transformation (Fig. 4 in Ref. [27]).

This is because the transformation strain for B2–R transformation is only one-tenth of that for the B2–B19' transformation and few dislocations are introduced during the thermal cycling [17,22,26]. Another way to avoid introducing dislocations is to choose an alloy with high critical stress for slip. The quite high relaxation peak in the B19 martensite in Ti–Ni–Cu alloys corresponds to this case [5,15] for which the critical stress for slip is much higher than those in Ti–Ni binary alloys, and thus nearly no thermal cycling effect is observed in these alloys. Thus we can conclude that a high and stable relaxation peak can be obtained in an H-containing martensitic alloy with a small transformation strain and/or with a high critical stress for slip.

5. Conclusions

To clarify the basic mechanism of the relaxation peak in the martensitic state of Ti–Ni alloys and to understand the role of dislocations in the thermal cycling effect, we investigated the damping behavior of Ti₅₀Ni₅₀ and Ti₄₈Ni₅₂ samples by DMA and tensile tests and obtained the following conclusions.

- (1) The relaxation peak (200 K peak) appears in the H-containing Ti₅₀Ni₅₀ sample, but disappears in the DeH sample. No relaxation peak is observed for the H-containing and cold-worked Ti₄₈Ni₅₂ alloy, which does not exhibit martensitic transformation in our temperature range. These results further support the twin boundary–H interaction model and directly exclude the dislocation–H interaction model as the origin of the relaxation peak.
- (2) The storage modulus and $\tan \delta$ in the H-containing Ti₅₀Ni₅₀ sample decrease after thermal cycling, while the storage modulus increases in the DeH sample after thermal cycling.
- (3) The critical stress for twinning in dc tensile tests also decreases after thermal cycling for the H-containing Ti₅₀Ni₅₀ sample, but it increases in the DeH sample after thermal cycling.
- (4) The opposite changes of ac storage modulus and dc critical stress with thermal cycling in H-containing samples in comparison with the DeH samples are due to the dual role of transformation-induced dislocations. On one hand, the tangled dislocations will decrease the mobility of twin boundaries and make the material appear harder. On the other hand, dislocations absorb the pinning centers (hydrogen) from twin boundaries and make twin boundary motion easier. All thermal cycling effects in the H-containing sample and the DeH sample can be explained by the above mechanism.
- (5) For utilizing the high relaxation peak produced by twin boundary–H interaction, we suggest choosing a martensitic alloy with a small transformation strain and/or a high critical stress for slip in order to avoid introducing dislocations.

Acknowledgements

The present work was supported by a Grant-in-Aid for Scientific Research (B) from JSPS, National Natural Science Foundation of China under Grant No. 50720145101 and National Basic Research Program of China under Grant No. 2004CB619303, as well as the 111 project of China. We thank S. Ito for the chemical analysis of our

samples. We also thank T. Suzuki, Y. M. Zhou, Y. Wang, J. Zhang, X.D. Ding, S. Yang and W. F. Liu for helpful discussions.

References

- [1] Hasiguti R, Iwasaki K. *J Appl Phys* 1968;39:2182.
- [2] Iwasaki K, Hasiguti R. *Trans JIM* 1987;28:363.
- [3] Yin F, Nagai K, Watanabe K, Kawahara K. *Mater Trans* 2003;44:1671.
- [4] Shen HM, Huang YN, Zhang ZF, Yang Z, Wang XM, Wang YN, Tan SS. *Mat Res Soc Symp Proc* 1996;398:513.
- [5] Yoshida I, Monma D, Iino K, Otsuka K, Asai M, Tsuzuki H. *J Alloys Compd* 2003;355:79.
- [6] Zhu JS, Schaller R, Benoit W. *Phys Lett A* 1989;141:177.
- [7] Lin HC, Wu SK, Chou TS. *J Alloy Compd* 2003;355:90.
- [8] Wu SK, Lin HC, Chou TC. *Mater Trans* 2006;47:711.
- [9] Biscarini A, Campanella R, Coluzzi B, Mazzolai G, Mazzolai FM. *Acta Mater* 1999;47:4525.
- [10] Mazzolai FM, Biscarini A, Campanella R, Coluzzi B, Mazzolai G, Rotini A, et al. *Acta Mater* 2003;51:573.
- [11] Biscarini A, Coluzzi B, Mazzolai G, Mazzolai FM, Tuissi A. *J Alloy Compd* 2003;356–357:669.
- [12] Mazzolai FM, Coluzzi B, Mazzolai G, Biscarini A. *Appl Phys Lett* 2004;85:2756.
- [13] Coluzzi B, Biscarini A, Mazzolai G, Mazzolai FM, Tuissi A, Villa E. *Key Eng Mater* 2006;319:1–8.
- [14] Sakaguchi T, Uehara T, Kogo Y, Takeuchi S, Igata N. *Mater Trans* 2005;46:1306.
- [15] Fan G, Zhou Y, Otsuka K, Ren X, Nakamura K, Ohba T, et al. *Acta Mater* 2006;54:5221.
- [16] Mazzolai FM, Biscarini A, Coluzzi B, Mazzolai G, Villa E, Tuissi A. *Acta Mater* 2007;55:4243.
- [17] Miyazaki S, Igo Y, Otsuka K. *Acta Metall* 1986;34:2405.
- [18] Tadaki T, Nakata Y, Shimizu K. *Trans JIM* 1987;28:883.
- [19] Van Humbeeck J. In: Schaller R, Fantozzi G, Gremaud G, editors. *Mechanical Spectroscopy Q^{-1}* 2001. Trans Tech Publications; 2001. p. 396.
- [20] San Juan J, NÓ ML. *J Alloy Compd* 2003;355:65.
- [21] Christian JW, Mahajan S. *Prog Mater Sci* 1995;39(1/2):1–158.
- [22] Otsuka K, Ren X. *Prog Mater Sci* 2005;50:511.
- [23] Shampa S, Ren X, Otsuka K. *Phys Rev Lett* 2005;95:205702.
- [24] Wang Y, Ren XB, Otsuka K. *Phys Rev Lett* 2006;97:225703.
- [25] Debatist R. *Internal friction of structural defects in crystalline solids*. Amsterdam: North-Holland Publishing Company; 1972. p. 28–31, 322–90.
- [26] Ren X, Miura N, Zhang J, Otsuka K, Tanaka K, Koiwa M, et al. *Mater Sci Eng A* 2001;312:196.
- [27] Fan G, Zhou Y, Otsuka K, Ren X. *Appl Phys Lett* 2006;89:161902.