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ORIGINAL RESEARCH

Martensitic transformation involved mechanical behaviors and wide hysteresis of NiTiNb shape memory alloys

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Abstract On the basis of thermoelastic martensitic transformation involved, the mechanical behaviors of NiTiNb shape memory alloys were experimentally studied and their wide hysteresis effect was theoretically discussed. It was found that even at the same temperature NiTiNb shape memory alloys perform different mechanical behaviors when under different states. In addition, the yielding behavior for the reorientation of martensite is dependent on the martensitic transformation temperature of NiTiNb alloys. The alloy with lower M_s temperature exhibits lower yield stress for the reorientation of martensite. According to kinetic and thermodynamic analysis of thermoelastic martensitic transformations, a relationship between the relaxation of elastic energy and the hysteresis expansion was established. It is suggested that the mechanism for wide hysteresis of NiTiNb shape memory alloys is predominantly attributed to the Nb element dissolved in the matrix of NiTi(Nb) phase, rather than the precipitated β -Nb phase. This mechanism gains support from the present experimental study that the NiTiNb alloys with low Nb content exhibit wide transformation hysteresis upon a proper pre-deformation.

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1. Introduction

Phase transformation and mechanical properties have been key issues of Shape Memory Alloys (SMAs) because their mechanical behavior and transformation characteristics are of importance with regard to their application in various situations [1–4]. As a matter of fact, the mechanical properties and phase transformation are closely interrelated aspects, due to their nature of thermoelastic martensitic transformation in SMAs [1]. It has been well recognized that the mechanical properties of SMAs are closely dependent on the temperature at which the mechanical test was carried out [2]. For example,

SMA exhibits the lowest yield strength at their martensitic starting (M_S) temperature, and then the yield strength increases with increasing or the decreasing temperature. Thus, the mechanical behavior of SMA is closely dependent on the stability of martensite, especially in a temperature range where the martensitic transformation and the reorientation of martensite variants can be induced by external stress or strain.

Recently, martensite stabilization in SMA has attracted attention due to its academic significance and technical importance [1]. The phenomenon of martensite stabilization was firstly observed in Cu based SMA. In order to explain the stabilization of martensite, some possible mechanisms were proposed, for example, martensite boundary pinning by vacancies or vacancy clusters [5,6], martensite ordering induced lowering of free energy [7,8], and the suppression of transformation by fault structure in martensite, and so on [9]. Although aging does not influence the stabilization of martensite in NiTi SMA, it has been observed that pre-deformation of NiTi and Cu-based SMA remarkably stabilize the martensite phase, leading to a significant hysteresis expansion [10–13]. Actually, transformation hysteresis is a very important aspect for the design and application of SMA in various functional purposes. It is of theoretical and technical significance for scientific research and development of advanced SMA materials by understanding the origin of transformation hysteresis and hysteresis expansion.

In order to elucidate the mechanism of pre-deformation induced martensite stabilization, a lot of studies have been carried out on binary NiTi, ternary NiTi based and CuAlNi SMA [10–15]. However, regarding the mechanism for the stabilization of martensite, the explanations proposed so far are controversial. For example, Lin et al. [10] considered that the martensite stabilization could be ascribed to an inhibition of reverse martensitic transformation by dislocations and other defects produced in plastic deformation. On the contrary, Liu and Galvin [16] assumed that the dislocations produced by plastic deformation have no effective contribution to the martensite stabilization.

In particular, with respect to the transformation hysteresis expansion induced by deformation of $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$, a typical SMA with wide hysteresis, two different interpretations have been proposed, i.e. the difficulty in shape recovery due to the irreversible deformation of Nb-rich particles [17], and co-contribution from the relaxation of elastic energy and the deformation of β -Nb phase [11]. Based on extensive examination of the dependence of hysteresis expansion on the deformation of NiTi, NiTiNb and single crystal CuAlNi SMA, Piao and co-workers [11] assumed that the pre-deformation induced wide hysteresis might be a general criterion for thermoelastic martensitic transformations, and they concluded that the relaxation of elastic strain energy might be applicable to qualitatively explain this phenomenon.

In the present study, martensitic transformation involved in mechanical behaviors of NiTiNb SMA was taken into consideration. Based on kinetic and thermodynamic analysis of thermoelastic martensitic transformations, the mechanical behaviors and the wide hysteresis effect of NiTiNb SMA were discussed.

2. Experimental

Series NiTi and NiTiNb alloys with different Nb contents were prepared by induction melting of pure Ti (99.8 mass%),

Ni (99.96 mass%) and Nb (99.9 mass%) in a water-cooled copper hearth. The ingots were melted for four times repeatedly and annealed at 1123 K for 24 h for homogenization. All the samples used for tests and examinations were cut from 1.2 mm plates prepared by hot rolling at 1123 K, followed by annealing at 1123 K for 1 h and then quenching in ice water.

The characteristic transformation temperatures were determined by recording the variation of electric resistance with temperature and by Differential Scanning Calorimetry. In the present paper, M_S and M_f are used to represent the temperatures at which martensite transformation starts and finishes, and A_S and A_f represent the temperatures at which the reverse transformation to austenite starts and finishes. Microstructure observation of the alloys was performed with a JSM 5600 scanning electron microscope.

Tensile tests of NiTi and NiTiNb specimens were carried out using a MTS-800 mechanical tester. Stress–strain curves were recorded at a strain rate of 1.1×10^{-3} /s and at different temperatures. The temperature below room temperature can be achieved through cooling alcohol by liquid nitrogen.

3. Results and discussion

3.1. Microstructure and transformation temperature

It has been established that the microstructure of NiTiNb SMA is dependent on both the Nb content and the ratio of Ni to Ti. Accordingly, NiTiNb SMA with different Nb contents and Ni/Ti ratios were prepared in the present study to investigate their transformation characteristics and mechanical behavior.

Fig. 1 shows the SEM micrographs of some typical NiTiNb alloys with different compositions, $\text{Ni}_{50}\text{Ti}_{49}\text{Nb}_1$, $\text{Ni}_{50}\text{Ti}_{47}\text{Nb}_3$, $\text{Ni}_{49.6}\text{Ti}_{45.9}\text{Nb}_{4.5}$ and $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$. It is clearly seen that the microstructure are closely related to the addition content of Nb element and to the ratio of Ni to Ti. Experimental results indicated that for $\text{Ni}_{50}\text{Ti}_{50-x}\text{Nb}_x$ series alloys, only when the Nb content is greater than 2 at%, $\text{Ni}_{50}\text{Ti}_{47}\text{Nb}_3$ for example, a few of the isolated β -Nb particles can precipitate in NiTi(Nb) matrix (NiTi(Nb) represents the NiTi metallic compound with dissolution of Nb atoms). Higher Ni/Ti ratio favors the suppression of precipitation of β -Nb phase. For example, $\text{Ni}_{49.6}\text{Ti}_{45.9}\text{Nb}_{4.5}$ alloy is characterized by a single NiTi phase, even though the percentage of Nb reaches 4.5 at%. Nevertheless, β -Nb phase could precipitate from a NiTiNb alloy with very high Nb content. As the most classical SMA with wide hysteresis, $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ features in a composite microstructure, consisting primary NiTi(Nb) phase and eutectics of NiTi(Nb) and β Nb, as shown in Fig. 1(d).

Table 1 lists the characteristic martensitic transformation temperatures by measurement of electric resistance vs. temperature or by differential scanning calorimetry. The data of Table 1 indicate that the transformation temperatures decrease substantially with the increasing Ni/Ti ratio in NiTiNb alloys. In addition to Ni/Ti ratio, the content of Nb also has influence on the M_S temperature to some extent [18]. Note that the $\text{Ni}_{49.6}\text{Ti}_{45.9}\text{Nb}_{4.5}$ alloy with single NiTi(Nb) phase possesses a similar M_S temperature with the $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ alloy featuring in composite structure. This is useful to investigate the effect of structural aspects on the transformation involved mechanical behavior and transformation hysteresis. By comparison,

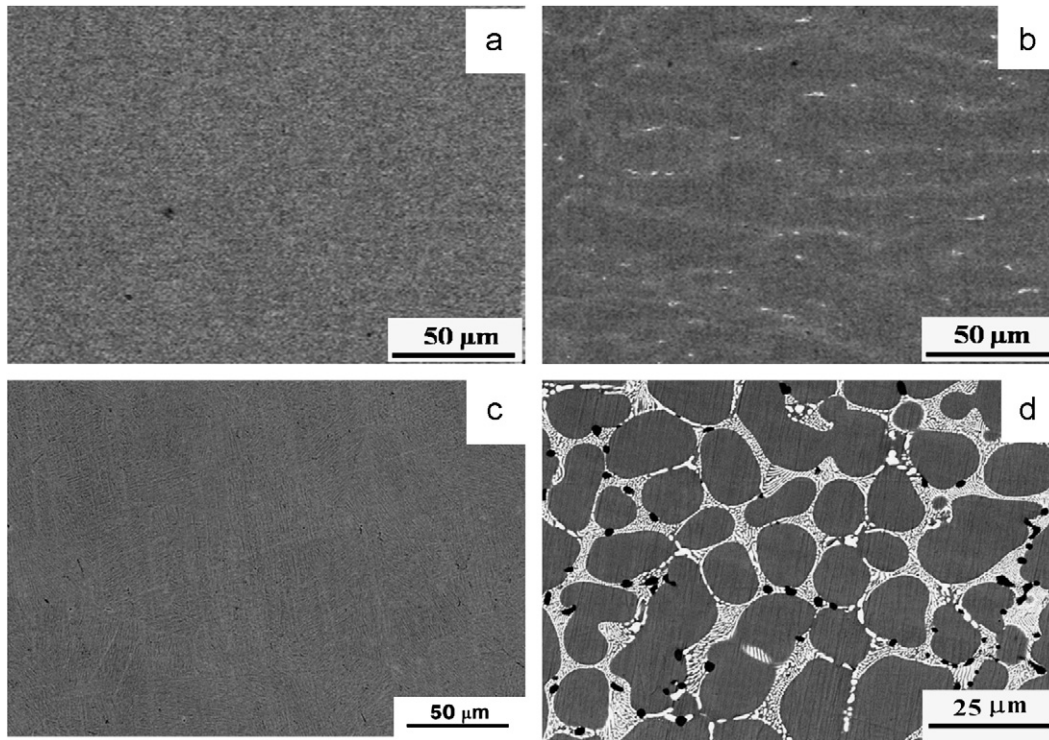


Fig. 1 The microstructures of (a) $\text{Ni}_{50}\text{Ti}_{49}\text{Nb}_1$, (b) $\text{Ni}_{50}\text{Ti}_{47}\text{Nb}_3$, (c) $\text{Ni}_{49.6}\text{Ti}_{45.9}\text{Nb}_{4.5}$ and (d) $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ alloys.

Table 1 Characteristic martensitic transformation temperatures NiTiNb SMAs ($^{\circ}\text{C}$).

Alloy	Ni/Ti	M_S	M_f	A_S	A_f
$\text{Ni}_{50}\text{Ti}_{49}\text{Nb}_1$	1.020	50	–	75	100
$\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$	1.042	16	6	38	65
$\text{Ni}_{50}\text{Ti}_{47}\text{Nb}_3$	1.064	–43	–	–11	27
$\text{Ni}_{49.6}\text{Ti}_{45.9}\text{Nb}_{4.5}$	1.081	–77	–95	–48	–11
$\text{Ni}_{49.8}\text{Ti}_{45.2}\text{Nb}_5$	1.10	–100	–140	–65	–18
$\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$	1.068	–73	–90	–25	–11

$\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ alloy performs a wider intrinsic transformation hysteresis (48°C) than $\text{Ni}_{49.6}\text{Ti}_{45.9}\text{Nb}_{4.5}$ (29°C). As a matter of fact, the intrinsic transformation hysteresis of $\text{Ni}_{49.6}\text{Ti}_{45.9}\text{Nb}_{4.5}$ is quite near to that of binary NiTi SMAs ($20\text{--}30^{\circ}\text{C}$ in general). Hence, considering the microstructural similarity between binary NiTi and $\text{Ni}_{49.6}\text{Ti}_{45.9}\text{Nb}_{4.5}$, as well as the microstructural difference between binary NiTi and $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$, it is reasonable to believe that the wider intrinsic hysteresis of $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ might be associated with its composite microstructure, especially the existence of large amount of $\beta\text{-Nb}$ phase.

3.2. Martensitic transformation involved mechanical behavior of NiTiNb shape memory alloys

3.2.1. Mechanical behaviors of martensite and austenite at the same temperature

Owing to the transformation hysteresis, SMAs could keep different states (martensite or austenite) at a specific temperature within M_S and A_S temperature by cooling the austenite or

heating the martensite to the specific temperature. Accordingly, the deformation behaviors of SMAs in martensite or austenite state could be examined at the same temperature. Fig. 2 shows the stress–strain curves of $\text{Ni}_{50}\text{Ti}_{49}\text{Nb}_1$, $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ and $\text{Ni}_{50}\text{Ti}_{47}\text{Nb}_3$ SMAs in martensite and austenite states, at the specific temperature for each alloy. Taking $\text{Ni}_{50}\text{Ti}_{49}\text{Nb}_1$ alloy for example, its M_S and A_S temperatures are 50°C and 75°C , respectively. In order to make a comparative study of the mechanical behaviors of martensite or austenite state at the same temperature, one $\text{Ni}_{50}\text{Ti}_{49}\text{Nb}_1$ specimen with full martensite was heated to 56°C and another specimen with full austenite was cooled to the same temperature. Then, the stress–strain curves of $\text{Ni}_{50}\text{Ti}_{49}\text{Nb}_1$ in martensite and austenite states were recorded at 56°C . Following similar procedures, the deformation behavior of $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ and $\text{Ni}_{50}\text{Ti}_{47}\text{Nb}_3$ alloys with martensite and austenite states were respectively characterized at 32°C and -27°C . The corresponding stress–strain curves are shown in Fig. 2b and c.

The stress–strain curves shown in Fig. 2 indicate that the yield stress for the reorientation of martensite variants is approximately 100 MPa higher than that for inducing martensitic transformation in austenite, even though the two specimens deform at the same temperature. In addition, it is observable that the martensite yields in different manner from the austenite, i.e. the former performs a flat yielding plateau, and the later exhibits a climbing yield slope. In the early stage of the deformation process, the yield stress for austenite falls behind the yield stress for martensite until the strain reaches approximately 5%. Nevertheless, these NiTiNb SMAs possess almost the same ultimate fracture strength, regardless of their initial states. The reason for the different yielding behaviors of martensite and austenite at the same temperature will be discussed in the following section.

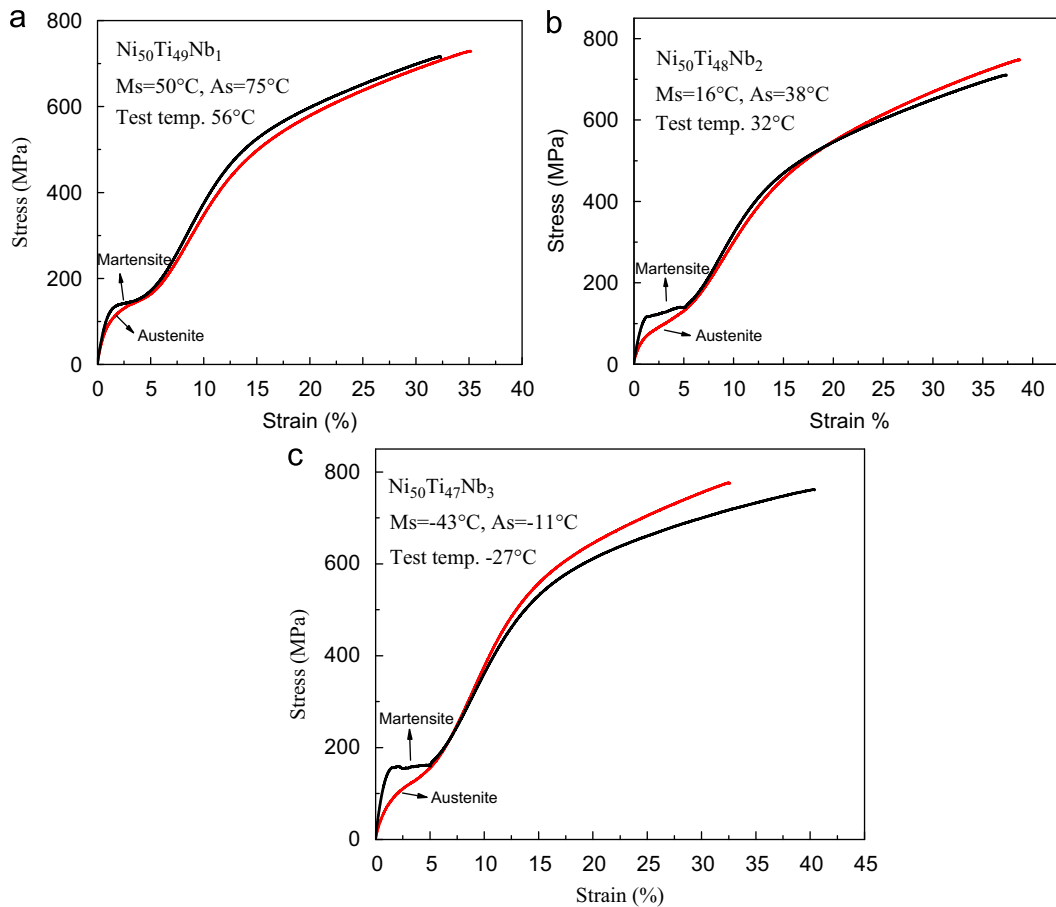


Fig. 2 Stress–strain curves of $\text{Ni}_{50}\text{Ti}_{49}\text{Nb}_1$ (a), $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ (b) and $\text{Ni}_{50}\text{Ti}_{47}\text{Nb}_3$ (c) alloys in martensite and austenite states, at specific temperature for each alloy.

As shown above, even at the same temperature the reorientation of martensite variants requires higher stress than that to induce martensitic transformation in austenite. In order to further examine the influence of test temperature on the yielding behavior of NiTiNb alloys in martensite and austenite, $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ alloy was employed to characterize the yielding behavior difference between the martensite and the austenite. Considering the M_S (16°C) and A_S (38°C) of $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ alloy, 23°C , 32°C and 38°C were selected to investigate the mechanical behavior of the alloy under martensite and austenite states, and the corresponding results are shown in Fig. 3.

When the martensite and austenite of $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ deform at lower temperature, 23°C for example, a significant difference in the yield stress was observed. With increasing temperature, the yield stresses of both the martensite and the austenite increase. On comparison to martensite, the yielding stress for austenite increases more rapidly with the increasing temperature. Consequently, the higher the testing temperature, the weaker the yield stress difference between the martensite and the austenite. In particular, when the testing temperature rises to 38°C , the difference between the yielding stresses for martensite and austenite is negligible. This means that the stress for the reorientation of martensite variants is almost identical to the stress to induce martensitic transformation in austenite at 38°C .

3.2.2. Explanation on the yield stress difference between martensite and austenite

Because of the nature of thermoelastic martensitic transformation, SMAs could possess different phase states, such as martensite, austenite or a mix of martensite and austenite, depending on temperature. However, upon heating or cooling SMAs could keep their original state (martensite or austenite) to a specific temperature located between M_S and A_S , owing to their transformation hysteresis. This means that SMAs could possess martensite state or austenite state at the same specific temperature between M_S and A_S , by heating the specimen in full martensite state or cooling the specimen in full austenite state. In order to energetically explicate the yield behavior of martensite and austenite at different temperature, Fig. 4 represents a schematic of the Gibbs free energy of martensite and austenite as a function of temperature. From an energetic point of view, at a specific temperature between M_S and A_S the martensite is under a superheated state when heated from a temperature at which the SMA is in full martensite state. Based on the same principle, the austenite is under a supercooled state when cooled from a temperature at which the SMA is in full austenite state. In an attempt to explain the temperature dependence of the yield stress difference between martensite and austenite, two characteristic temperature, t_1 and t_2 temperatures ($t_1 < t_2$), were defined. According to Fig. 4, the Gibbs free energy change for austenite to martensite

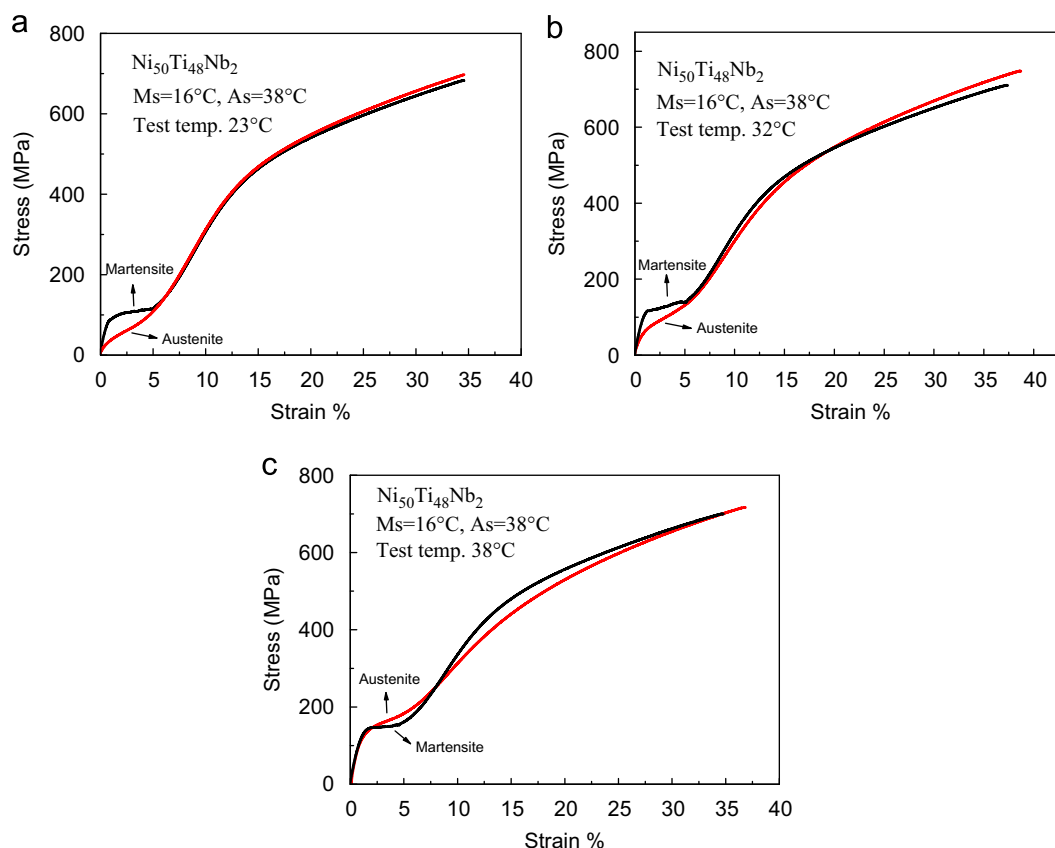


Fig. 3 Stress–strain curves of $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ alloy under martensite and austenite states at 23 °C, 32 °C and 38 °C.

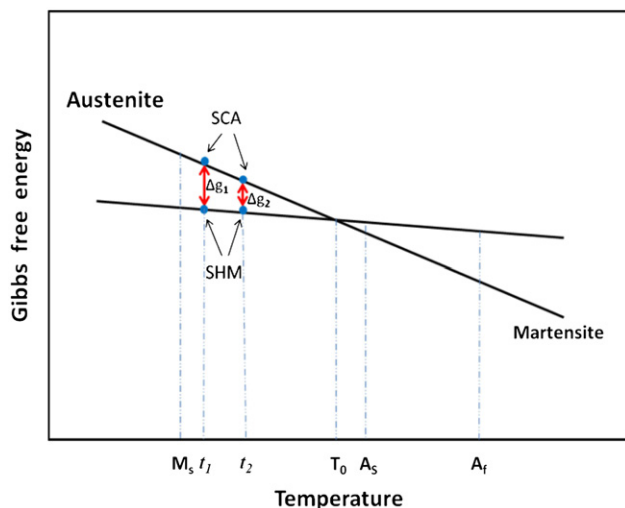


Fig. 4 Schematic of the Gibbs free energy of martensite and austenite as a function of temperature. SCA represents supercooled austenite, and SHM denotes superheated martensite.

transformation decreases with the increasing temperature. Accordingly, under an external stress the transformation from austenite to martensite is more difficult to trigger at t_2 than at t_1 . This might be the reason why the yield stress for inducing martensitic transformation increases rapidly when the temperature increases in the range of M_S and A_S .

Contrary to usual belief, the experimental results of the present study clearly demonstrated that under external

stress the austenite is easier to yield than the martensite at the same temperature. With regard to the lower stress for inducing austenite to martensite transformation than for reorientation of martensite at the same specific temperature between M_S and A_S , the corresponding mechanism is not clear at present.

3.2.3. M_S temperature dependence of the stress for reorientation of martensite

Owing to the nature of thermoelastic martensitic transformation, a specific SMA always perform the lowest stress for inducing martensite transformation at its M_S temperature [2]. However, for different SMAs, there is lack of experimental data on the relationship between the M_S temperature and the stress for inducing martensitic transformation and reorientation of martensite. In the present study, mechanical behaviors of NiTi and NiTiNb SMAs with different M_S temperatures were examined, showing that the yield stress for reorientation of martensite variants is dependent on the M_S temperature of the SMAs. Fig. 5 illustrates the stress–strain curves of $\text{Ni}_{50}\text{Ti}_{50}$, $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ and $\text{Ni}_{49.5}\text{Ti}_{46.5}\text{Nb}_4$ alloys at the temperatures of 15 °C below their corresponding M_S temperature. It is indicated that the yield stresses for reorientation of martensite decrease with the decreasing M_S temperature. That is, an alloy with lower M_S temperature exhibits lower yield stress for reorientation of martensite.

Similar result was achieved in binary NiTi SMAs. Fig. 6 shows the stress–strain curves of $\text{Ni}_{50.9}\text{Ti}_{49.1}$ and $\text{Ni}_{50.2}\text{Ti}_{49.8}$ alloys at their M_S temperature of -28 °C and 18 °C, respectively. It is clearly seen that the stress for inducing martensitic

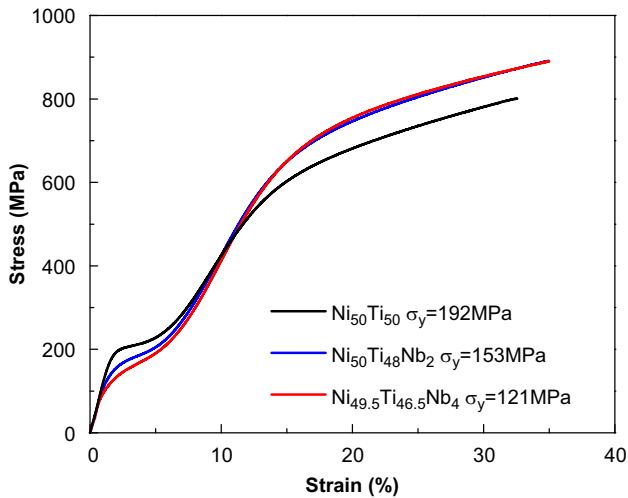


Fig. 5 Stress–strain curves of $\text{Ni}_{50}\text{Ti}_{50}$, $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ and $\text{Ni}_{49.5}\text{Ti}_{46.5}\text{Nb}_4$ alloys at the temperature of ($M_S - 15^\circ\text{C}$), whose M_S temperature is 58°C , 16°C and -10°C , respectively.

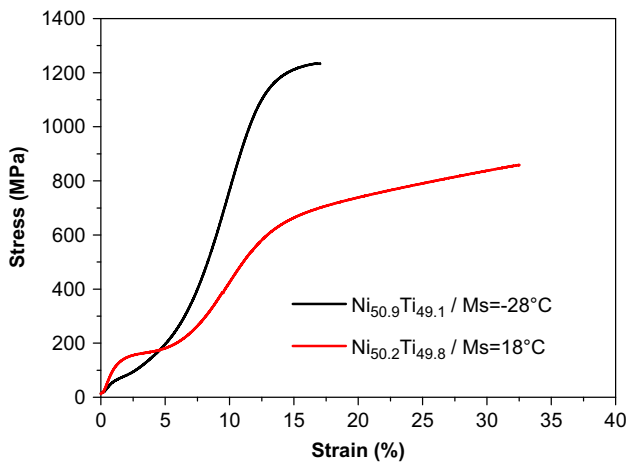


Fig. 6 Stress–strain curves of $\text{Ni}_{50.9}\text{Ti}_{49.1}$ and $\text{Ni}_{50.2}\text{Ti}_{49.8}$ alloys at their M_S temperature.

transformation in $\text{Ni}_{50.9}\text{Ti}_{49.1}$ alloy is much lower than that in $\text{Ni}_{50.2}\text{Ti}_{49.8}$ alloy. The mechanism for this phenomenon is now under investigation, and the detailed explanation will be given in future reports.

3.3. Wide hysteresis of NiTiNb SMAs with low Nb content

As mentioned above, the microstructure of NiTiNb shape memory alloys is closely related to their Ni to Ti ratio and the content of Nb. In the microstructure of $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ SMA, there exist large amount of eutectics of NiTi(Nb) matrix and $\beta\text{-Nb}$. It has been recognized that $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ could perform wide hysteresis, roughly 150°C for example, upon a proper deformation in martensite state or stress-induced martensite state [12,17]. Early researchers considered that the deformed $\beta\text{-Nb}$ particles in $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ inhibit reverse martensitic transformation, playing a key role in the achievement of wide hysteresis [17]. Recent work by Liu et al. indicated that low Nb containing NiTiNb SMAs without large amount of $\beta\text{-Nb}$ phase in microstructure still exhibit wide hysteresis upon a

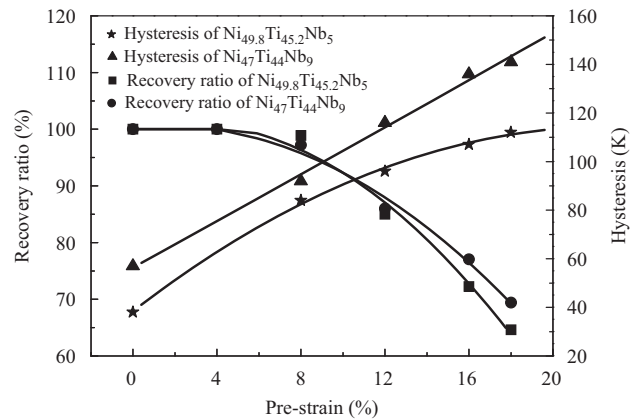


Fig. 7 Dependence of hysteresis and recovery ratio on the deformation strain of $\text{Ni}_{49.8}\text{Ti}_{45.2}\text{Nb}_5$ and $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ SMAs.

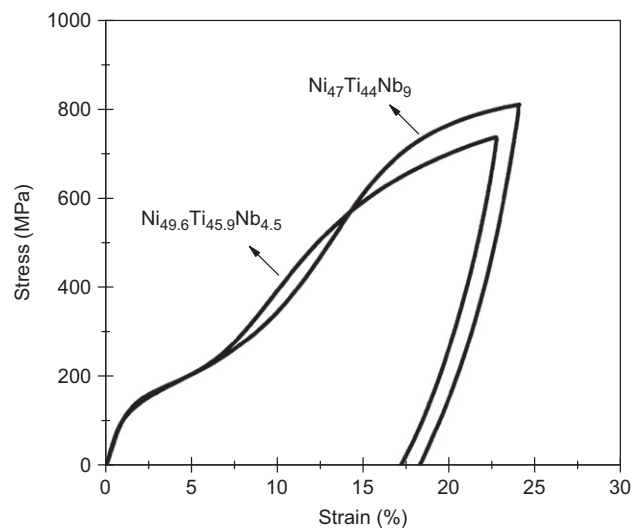


Fig. 8 Stress–strain curves of $\text{Ni}_{49.6}\text{Ti}_{45.9}\text{Nb}_{4.5}$ and $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ alloys at the same temperature of -60°C [20].

proper deformation [19]. Fig. 7 illustrates the dependence of the transformation hysteresis and recovery ratio of $\text{Ni}_{49.8}\text{Ti}_{45.2}\text{Nb}_5$ and $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ SMAs on the predeformation strain. It is indicated that both $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ and $\text{Ni}_{49.8}\text{Ti}_{45.2}\text{Nb}_5$ SMAs perform wide hysteresis and similar recovery ratio upon a predeformation. $\text{Ni}_{49.8}\text{Ti}_{45.2}\text{Nb}_5$ alloy possesses a wide hysteresis of 108°C by a predeformation of 16%, although a little smaller than that of $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ upon the same predeformation (136°C).

Considering the difference in initial hysteresis between $\text{Ni}_{49.6}\text{Ti}_{45.9}\text{Nb}_{4.5}$ (35 K) and $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ (48 K), $\text{Ni}_{49.8}\text{Ti}_{45.2}\text{Nb}_5$ achieved similar net increase in hysteresis compared to $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$, especially for small pre-deformation. Note that there is few isolated $\beta\text{-Nb}$ phase in $\text{Ni}_{49.8}\text{Ti}_{45.2}\text{Nb}_5$. Thus, one can conclude that large amount of $\beta\text{-Nb}$ particles have minor contribution to wide hysteresis, and the Nb resolved in the NiTi matrix might be a predominant aspect. It is reasonable to speculate that the additive Nb resolved in the matrix is considered to change the kinetics of thermoelastic martensitic transformation, resulting in the stabilization of martensite [20].

Fig. 8 shows the stress–strain curves of $\text{Ni}_{49.6}\text{Ti}_{45.9}\text{Nb}_{4.5}$ and $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ alloys at the same temperature of -60°C . It

is found that when deformed at this temperature, $\text{Ni}_{49.6}\text{Ti}_{45.9}\text{Nb}_{4.5}$ and $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ alloys perform similar deformation behavior, particularly almost the same yielding and reorientation behavior. As shown above, $\text{Ni}_{49.6}\text{Ti}_{45.9}\text{Nb}_{4.5}$ contains no $\beta\text{-Nb}$ phase in microstructure. This suggests that the presence of $\beta\text{-Nb}$ phase do not play a considerable role in the deformation behavior.

3.4. Energetic consideration of transformation hysteresis of NiTiNb shape memory alloys

It has been well established that martensitic transformation takes place by nucleation and growth. Energetically understanding the martensitic nucleation is very helpful to comprehend the thermodynamics and kinetics of martensite growth, irrespective of thermoelastic or non-thermoelastic transformation modes. According to classical nucleation theory, the free energy change (ΔG) accompanying the formation of a martensitic nucleus in a shape of oblate spheroid with radius r and semi-thickness c can be expressed by [21]

$$\Delta G = \frac{4}{3}\pi r^2 c \Delta g_c + \frac{4}{3}\pi r^2 c \left(\frac{c}{r} A\right) + 2\pi r^2 \sigma \quad (1)$$

where Δg_c is the chemical free energy change per unit volume of martensite and serves as the driving force for martensitic transformation; σ the martensitic nucleus/parent interfacial energy per unit area; Ac/r the elastic strain energy per unit volume caused by shape deformation, and A the elastic strain energy parameter. Thus, the critical values of radius r^* and semi-thickness c^* of the nucleus can be obtained from Eq. (1) by setting $\partial \Delta G / \partial c = \partial \Delta G / \partial r = 0$. Accordingly, the driving force for formation of a critical nucleus can be related to the elastic energy per unit volume ($\Delta g_e = Ac/r$) by $\Delta g_c = -\Delta g_e/2$. This means that during the nucleation stage of martensite, half chemical free energy will be stored as elastic energy. It is worth noting that this description is applicable to the nucleation event, not suitable to the growth of martensite variants with considerable size.

In the nucleation stage, the interfacial energy contributes greater component than elastic energy to non-chemical free energy which opposes martensite formation. However, once the nucleation barrier could be overcome by thermal or mechanical driving energy, the growth of critical nuclei will lead to a decrease in total free energy and the growth of nuclei proceeds spontaneously. From then on, accompanying the growth of martensite, the proportion of interfacial energy in non-chemical free energy would gradually lessen with respect to elastic strain energy. The net chemical driving force will increase with the growth of martensite, approaching half of the chemical driving force, $\Delta g_c/2$. Here, if the specific interfacial energy could be negligible, the elastic energy could be determined to be $\Delta g_e = -\Delta g_c/2$. At this moment, under the driving force of chemical free energy the martensite variants grow rapidly. The growing martensite phase and the matrix are not in a thermodynamic equilibrium. Therefore during the growth of martensite variants, $\Delta g_e = -\Delta g_c/2$ is not applicable to describe the relationship between the elastic energy and the chemical driving force. With further growth of martensite variants the elastic strain energy increases, and would stop at a balance of chemical free energy with non-chemical free energy [22,23]. In this situation, the specific interfacial energy is negligibly small with respect to elastic energy, and an

equilibrium set up between the elastic strain energy (Δg_e) and the chemical driving force (Δg_c), i.e. $\Delta g_e = -\Delta g_c$.

During the thickening of martensite variants in non-thermoelastic martensitic transformation, most of the driving energy would be consumed in the plastic deformation of the matrix for accommodation of shape and volume changes. In the case of thermoelastic martensitic transformation, the accommodation involves shape change by twinning, not by plastic slip. Elastic strain energy would be stored around the martensite and matrix, which resists forward transformation and assists reverse transformation. If the elastic energy was relaxed by deformation or by other means, the reverse martensitic transformation would be postponed. The reason is that at higher temperature, more driving free energy can be provided to compensate the relaxation of elastic energy to activate martensitic transformation.

The correlation of elastic energy relaxation and hysteresis expansion

In thermoelastic martensitic transformations, the forward and reverse transformation temperatures start and finish in narrow temperature ranges due to their small chemical driving force. In the narrow temperature range, if the difference of specific heat between martensite and austenite phases is not taken into account, the relationship between chemical free energy and temperature should be linear. Fig. 9 schematically illustrates the chemical free energy of martensite and austenite phases as a function of temperature, in which T_0 denotes the temperature at which the Gibbs free energies of martensite and austenite phases are equal.

According to Tong and Wayman [22], the elastic energy caused by martensitic transformation approaches minimum and is negligibly small at M_S and A_f , and increases with the proceeding of forward martensitic transformation from M_S to M_f . When the martensitic transformation completes at M_f , the elastic energy reaches its maximum and balance with the chemical free energy. Assuming the stored elastic energy being fully relaxed by deformation, the reverse transformation start

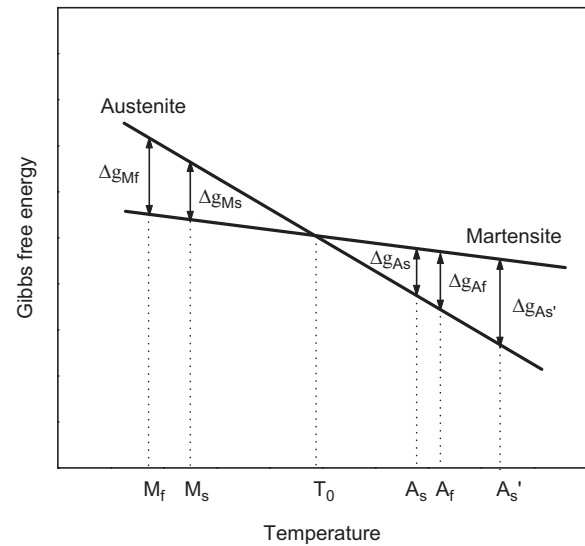


Fig. 9 Schematic illustration of the chemical free energy change of martensite and austenite phases vs. characteristic temperatures.

temperature would rise to higher temperature, A_{Sd} . Accordingly, the chemical free energy change at A_{Sd} can be expressed as the sum of the chemical free energy change at A_S and the elastic energy change at M_f

$$\Delta G_{chem}^{M \rightarrow P}(A_{Sd}) = \Delta G_{chem}^{M \rightarrow P}(A_S) + \Delta G_{el}^{P \rightarrow M}(M_f) \quad (2)$$

Referring to Fig. 9, the relationships between the differences in temperature and the corresponding chemical free energy changes can be geometrically expressed as below

$$\frac{T_0 - M_f}{\Delta g_{Mf}} = \frac{A_S - T_0}{\Delta g_{As}} = \frac{A_{Sd} - T_0}{\Delta g_{Asd}} \quad (3)$$

According to Tong and Wayman [22], for thermoelastic martensitic transformations the T_0 temperature could be represented by $T_0 = (M_S + A_f)/2$. The increase of the reverse transformation temperature ($A_{Sd} - A_S$) can be mathematically formulated as a function of T_0 and M_f

$$A_{Sd} - A_S = T_0 - M_f \quad (4)$$

In order to verify the compatibility of A_{Sd} with the experimental results, data reported in some literatures associated with deformation induced hysteresis expansion of NiTi and NiTiNb SMAs are tabulated in Table 2, in which A_S is defined to represent the experimentally measured reverse transformation starting temperature. As for the NiTi and Ni₄₇Ti₄₄Nb₉ SMAs, only when the specimens were subjected to severe deformation, the hysteresis can reach its maximum. Referring to Table 2, after severe deformation the A_{Sd} temperature is always lower than A_S by several degrees for NiTi and approximately ten degrees for NiTiNb alloys, though the A_{Sd} temperatures are close to the A_S . It is likely that in addition to relaxation of elastic energy, there may be other factors involved in the hysteresis expansion, particularly for NiTiNb alloys, although the influence of these factors are not dominant.

Discussion

As shown above, though the calculated A_{Sd} is not far from the A_S for polycrystalline TiNi and NiTiNb SMAs, A_{Sd} is always lower than A_S , particularly for NiTiNb alloys. It is reasonable to believe that the difference between A_{Sd} and A_S might be related to the severe plastic deformation of SMAs. In fact, drastic plastic deformation of metals or alloys could produce a large number of dislocations or other defects. Consequently, the plastic deformation induced dislocations could strengthen the matrix of NiTi and NiTiNb SMAs and then suppress the martensite recovery to some extent. It has been demonstrated that intense plastic deformation can substantially stabilize martensite and effectively expand the hysteresis of NiTi and

NiTiNb SMAs [10–12]. According to Piao et al. [11], during the deformation of polycrystalline NiTi or NiTiNb SMAs, the stored elastic energy is not readily relaxed due to the constraints of grain boundaries. Only when the pre-deformation caused the pertinent deformation of grain boundaries to occur, the stored elastic energy could be released adequately. This might be the reason why a large elongation is always required to increase the hysteresis of polycrystalline SMAs. Although the dislocations suppress the recovery of martensite to some extent, they do not play an effective role in hysteresis expansion. The research work by Liu and Galvin [16] supports this conclusion. They found that for the specimens with different dislocation structures, the thermal hysteresis of stress induced martensite show little variation. When heating the deformed structures of NiTi or NiTiNb alloys to a temperature above A_S (less than 200 °C), the characteristic temperatures (including A_S) almost return back to the original ones, although the dislocation structures remain [10,11,16].

In early research work [11,12,17] the wide hysteresis of NiTiNb alloys was completely or partially attributed to the existence of Nb-rich phase distributed in the matrix. It was believed that during the deformation of NiTiNb alloys, the Nb-rich particles deform together with the matrix, resisting the shape recovery when heating. It is worth noting that the Nb-rich phase in Ni₄₇Ti₄₄Nb₉ alloy is soft. Its yield strength should be much lower than the yield strength of the austenite phase at elevated temperature. For example, the yield strength of Ni₄₇Ti₄₄Nb₉ in austenite state at room temperature could reach 500 MPa [11,12,24]. Upon heating to above room temperature, the recovery stress of Ni₄₇Ti₄₄Nb₉ is much higher than the yield strength of Nb-rich particles [12,25]. Consequently, the deformed Nb-rich particles could not resist strongly the shape recovery on heating. Hence, it is reasonable to believe that it is the relaxation of stored elastic energy, not the structural factors, which plays effective role in the expansion of the transformation hysteresis upon a predeformation. Although the deformed Nb-rich particles might exert some resistive effect on shape recovery, they could not contribute significantly to the hysteresis expansion.

According to Eq. (4), the increase in reverse transformation temperature ($A_{Sd} - A_S$) due to the relaxation of elastic energy depends on the difference between T_0 and M_f . Furthermore, $(T_0 - M_f)$ consists of two components, $(T_0 - M_S)$ and $(M_S - M_f)$. In general, the magnitude of $(T_0 - M_S)$ is a measure of undercooling when martensite initially forms, and is proportional to the chemical driving force for the transformation [19]. The $(M_S - M_f)$ is closely associated with the elastic strain energy which resists forward martensitic transformation [25]. Previous studies indicated that NiTiNb SMAs perform much greater $(M_S - M_f)$ and $(T_0 - M_S)$ than binary NiTi alloys. For example, the $M_S - M_f$ is approximately 80 °C for Ni₄₇Ti₄₄Nb₉ and 20 °C for NiTi, and $A_f - M_f$ is approximately 55 °C for Ni₄₇Ti₄₄Nb₉ and 30 °C for NiTi [11,12,26]. This means that during martensitic transformation, more elastic strain energy would be stored and more driving force should be provided for NiTiNb than for NiTi alloys. Once the elastic energy is completely relaxed upon predeformation, the NiTiNb alloys would perform a larger thermal hysteresis than for NiTi alloys. Actually, in Ni₄₇Ti₄₄Nb₉ alloy only the NiTi(Nb) matrix performs thermoelastic martensitic transformation and is responsible for the shape memory effect. Considering that the transformation characteristics of NiTi based SMAs

Table 2 The comparison of experimentally measured and calculated reverse transformation temperature after plastic deformation of NiTi and NiTiNb SMAs.

Alloys	A_S (°C)	Elongation (%)	A_S (°C)	A_{Sd} (°C)	Ref.
Ni ₅₀ Ti ₅₀	81	20	122	115	7
Ni ₅₀ Ti ₅₀	74	20	125	121	6
Ni ₄₇ Ti ₄₄ Nb ₉	-65	16	60	50	10
Ni ₄₇ Ti ₄₄ Nb ₉	-55	16	42	28	11

are closely dependent on their chemical composition, the difference in kinetic respects between NiTiNb and NiTi SMAs could be related to the addition of Nb element. It is reasonable to believe that the resolved Nb element in NiTi matrix changes the kinetic characteristics of martensitic transformation and expands the intrinsic hysteresis (T_0-M_S and M_S-M_f) of NiTiNb alloys [26].

4. Conclusions

1. Martensite and austenite of NiTiNb shape memory alloys perform different mechanical behaviors even at the same temperature. The austenite is easier to yield than the martensite under external stress.
2. The yield stress for reorientation of martensite variants is dependent on the M_S temperature of NiTiNb alloys. An alloy with lower M_S temperature exhibits lower yield stress for reorientation of martensite.
3. The presence of β -Nb phase do not have considerable contribution to wide hysteresis and deformation behavior of NiTiNb SMAs. The NiTiNb SMAs with low Nb content could achieve wide transformation hysteresis upon predeformation. The resolved Nb element changes the kinetics of martensitic transformation and leads to the stabilization of martensite.
4. The relationship between the relaxation of elastic energy and the hysteresis expansion was established. The relaxation of elastic energy by plastic deformation plays a dominant role in the hysteresis expansion of NiTi and NiTiNb SMAs.

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