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Recoverable strain induced by martensitic transformation during holding of NiTi-based shape memory alloys under constant stress and temperature

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Abstract: The aim of the present paper was to study the strain variation in the NiTi-based shape memory alloys during isothermal holding under stress. The recoverable strain of $Ni_{51}Ti_{49}$ and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloys was studied on holding under stress after cooling (Regime 1), after active loading (Regime 2), or during holding without stress in the sample that demonstrates the two-way shape memory effect (Regime 3). The strain variation was found during holding under a stress in all regimes. This strain was recovered on subsequent heating or unloading, thus, the strain variation on holding was caused by the isothermal martensitic transformation. This isothermal strain depended on the chemical composition of the alloy, the regime for the isothermal holding, the stress, and the holding temperature. The maximum isothermal strain was 3.4% in $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ (Regime 1) and 6.1% in $Ni_{51}Ti_{49}$ (Regime 2). Holding in Regime 3 was accompanied by a small strain (less than 0.3%). The influence of the stored elastic energy on isothermal martensitic transformation on holding was discussed, and it was shown that a large isothermal strain was found if the transformation was accompanied by a small stored elastic energy.

Key words: isothermal martensitic transformation; recoverable strain; superelastic strain; NiTi-based shape memory alloys

1 Introduction

NiTi-based shape memory alloys are widely used in various applications for engineering, aerospace, robotics, heat engines, and medicine [1−5] because of their unique ability to recover the strain on heating (the shape memory effect) or unloading (superelasticity) [6]. The nature of these phenomena is the thermal elastic martensitic transformation that is characterized by athermal kinetics. This means that the martensitic transformation can be initiated by the temperature or stress variation and it does not occur if both temperature and stress are constant [6]. However, it was found that in NiTi-based alloys with non-stoichiometric composition, the forward martensitic transformation could occur upon holding at a constant temperature under zero stress [7−18]. The realization of the $B2\rightarrow B19'$ [7,9,10,12,14−18], $R\rightarrow B19'$ [7,18] and $B2\rightarrow R$ [8,11,13,18] transformations on isothermal holding was confirmed by the resistivity variation [7,9−13,18], differential scanning calorimetry [8,14−17] and direct observation by scanning electron microscopy [18]. The volume fraction of the martensite that appeared during isothermal holding depended on the chemical composition of the alloy and the maximum value of 80% was found in the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$

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alloy [17]. It was assumed that the martensitic transformation changed the kinetics from athermal in equiatomic NiTi alloys to isothermal in non-stoichiometric alloys [7,9,10,12]. However, it was concluded that the martensitic transformation in the NiTi-based alloys remained athermal but it was controlled by the isothermal migration of substitutional atoms [17].

It is well known that the formation of the oriented martensite on cooling under stress or loading in the austenite state is accompanied by the strain variation that recovers on subsequent heating or unloading. One may assume that the oriented martensite must appear during the holding of the non-stoichiometric NiTi-based alloys under stress and this process should be accompanied by strain variation. This assumption was experimentally confirmed in Refs. [19,20], where the $Ni_{51}Ti_{49}$ and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloys were cooled under stress to a temperature close to M_s and held. The additional strain variation was observed on holding under stress in both alloys and this strain completely recovered on subsequent heating. The isothermal strain depended on the holding temperature non-monotonically and the maximum was found if the holding was carried out at temperature in the M_s−M_f range. The maximum isothermal strain of 0.4% was found in the quenched $Ni_{51}Ti_{49}$ alloy on holding under stress of 50 MPa. In the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy, the holding was carried out at a stress of 235 MPa and the maximum isothermal strain was 2.9%. Thus, it was first shown that the isothermal martensitic transformation in the NiTi-based alloys on holding under stress was accompanied by the recoverable strain variation. This opens an opportunity to realize a new scheme for the recoverable strain variation in the NiTi-based alloys besides the well-known regimes (cooling and heating under stress, superelasticity, pre-deformation in the martensite state and heating). To develop a new regime, it is necessary to know how the strain variation on holding under stress depends on the holding parameters such as stress, temperature and pre-holding conditions. This knowledge cannot be found in Refs. [19,20], because the strain variation was studied solely in the "cooling under stress–holding–heating" regime and holding was carried out under 50 MPa for the $Ni_{51}Ti_{49}$ alloy and 235 MPa for the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy. Thus, the present works aims to study the recoverable strain induced by the isothermal transformation during the holding of NiTi-based alloys under stress in various holding regimes.

According to Ref. [17], the isothermal formation of the martensite on holding was observed solely in the NiTi alloy with substitutional defects. The maximum volume fraction of the isothermal martensite (φ=80%) was found in the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy. As the recoverable strain variation is proportional to the volume of the martensite, hence one may expect that the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy should demonstrate the best recoverable strain variation on holding. At the same time, the isothermal transformation on holding was found not only in the ternary and quaternary NiTi-based alloys but also in the binary Ni-rich NiTi alloys which were widely used [17]. It was shown that the maximum volume fraction of martensite (45%) appeared on holding in the quenched $Ni_{51}Ti_{49}$ alloy, hence, it might be expected that this alloy demonstrated the recoverable strain variation. Thus, in the present work, the recoverable strain variation was studied in a binary quenched $Ni_{51}Ti_{49}$ alloy and a quaternary $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy that underwent an isothermal transformation during holding. This allowed one to find the common features, as well as the distinction in the strain variation on the holding of the NiTi-based alloys with various compositions.

2 Experimental

Wire samples of the $Ni_{51}Ti_{49}$ alloy with a diameter of 2 mm and a length of 100 mm were water quenched at 850 °C (15 min). After heat treatment, the samples were subjected to 100 thermal cycles from −196 to 100 °C to stabilize the temperatures of the martensitic transformation. The $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ amorphous thin ribbon was subjected to control crystallization in a differential scanning calorimeter (DSC) at a temperature of 470 °C for 30 min (details in Ref. [21]). The samples had a length of 15 mm, a width of 1.6 mm and a thickness of 40 μm. Both $Ni_{51}Ti_{49}$ and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloys underwent the $B2$→$B19'$ transformation on cooling and the reverse $B19'$→$B2$ transition on heating. The samples were cooled and heated in the DSC (cooling/heating rate was 10 °C/min) to measure the transformation temperatures according to ASTM standard F2004-05R10 (Table 1). The maximum volume fraction of the isothermal martensite was 80% in the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy and 45% in the $Ni_{51}Ti_{49}$ alloy [15−17].

Table 1 Temperatures of martensite transformations measured in $Ni_{51}Ti_{49}$ and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloys on cooling and heating without stress (M_s and M_f are the start and finish temperatures of the forward transformation; A_s and A_f are the start and finish temperatures of the reverse transformation)

Alloy	M_s/°C	M_f/°C	A_s/°C	A_f/°C
$Ni_{51}Ti_{49}$	−43	−63	−24	−9
$Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$	−7	−13	29	52

In the present work, the variation in the strain was studied during isothermal holding in three regimes:

(1) Regime 1, holding under stress after cooling under a stress;

(2) Regime 2, holding under stress after cooling without stress and loading;

(3) Regime 3, holding without stress in the sample that demonstrates the two-way shape memory effect.

To study the isothermal strain variation in Regime 1, the technique, described in Refs. [19,20] was used. The samples were cooled under constant stress to holding temperature T^*, held for 60 min under stress and heated through the temperature range of the reverse transformation (Fig. 1(a)).

To study the isothermal strain variation in Regime 2, the sample was cooled to holding temperature T^* without stress, loaded to stress σ, held for 60 min under stress, unloaded and heated through the temperature range of the reverse transformation (Fig. 1(b)).

To study the isothermal strain variation in Regime 3, the samples were preliminarily deformed in the fully martensitic state and heated through a temperature range of the reverse transformation to initiate the one-way shape memory effect. Then, the sample was cooled and heated through the temperature range of the transformation (cooling/heating rate was 1 °C/min) to measure the value and temperatures of the two-way shape memory effect. After that, the sample was cooled to holding temperature T^* under zero stress, held for 30−60 min without stress, and heated through the temperature range of the reverse transformation (Fig. 1(c)).

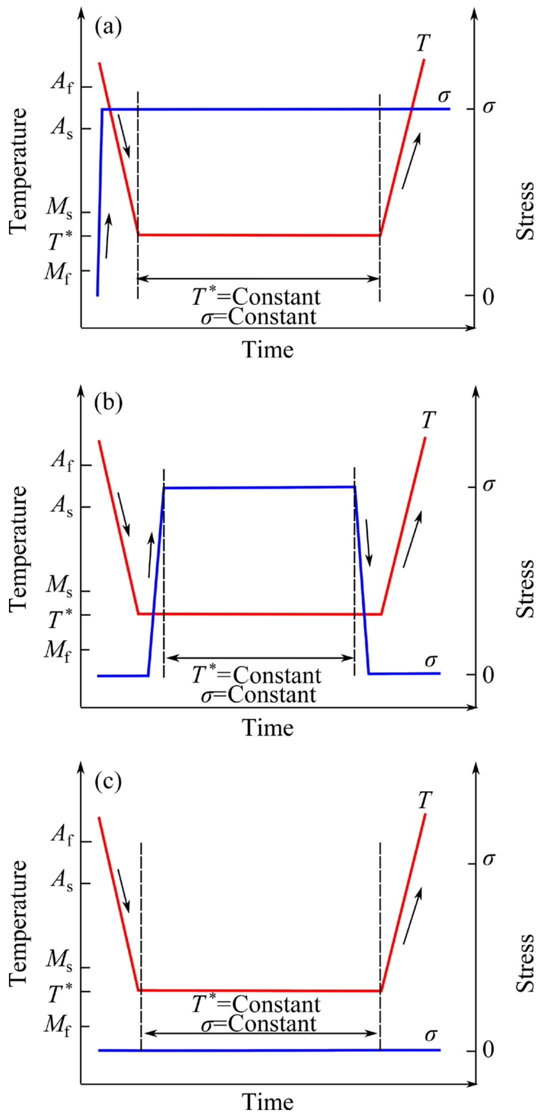

Fig. 1 Schemes for stress and temperature variations in Regime 1 (a), Regime 2 (b), and Regime 3 (c)

In Regimes 1 and 2, holding temperature T^* was close to the M_s measured under the stress at which the holding was carried out. In Regime 3, the sample was held at a temperature close to the M_s found on the $\varepsilon(T)$ curve obtained for the two-way shape memory effect. In Regimes 1 and 2, the holding stress was varied from 100 to 300 MPa for the $Ni_{51}Ti_{49}$ alloy and from 160 to 400 MPa for the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy. The $Ni_{51}Ti_{49}$ alloy was not loaded over 300 MPa because a large plastic strain was observed after heating or unloading.

All experiments were carried out using testing machines equipped with thermal chambers. The stress was measured by a standard force cell. The strain was measured by a video extensometer as the variation in the distance between two white stripes on the sample surface. The temperature of the samples was measured by a K-type thermocouple.

3 Results

3.1 Isothermal strain variation during holding in Regime 1

In Regime 1, the samples were loaded in the austenite state to stress σ, cooled under stress to temperature T^*, held at T^* under stress σ and heated through a temperature range of the reverse transformation (Fig. 1(a)). Figure 2 shows the strain variation on cooling and heating under stress

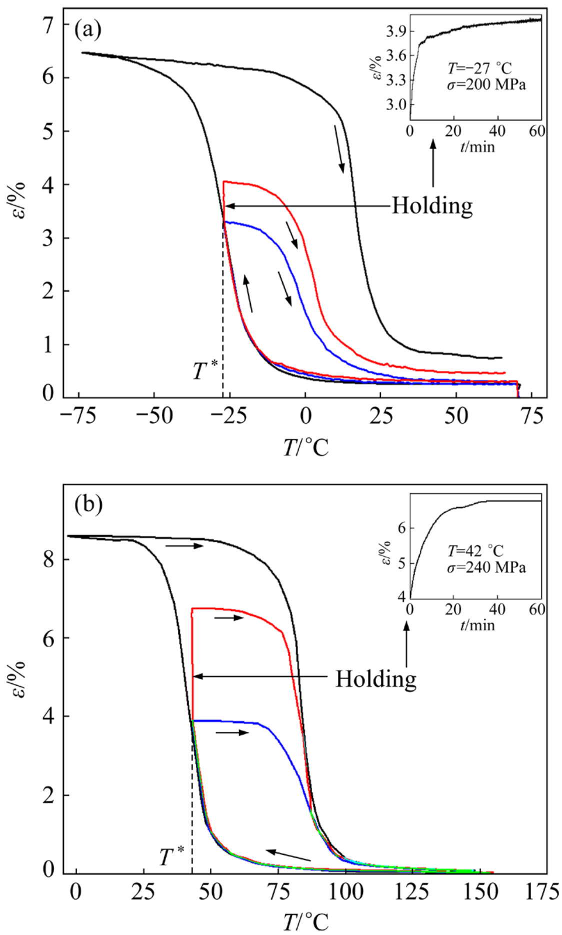

Fig. 2 Strain variation on cooling and heating under constant stress over full temperature range of martensitic transformation (black line), on cooling to temperature of T^* and heating under stress (blue line) and on cooling to temperature T^*, holding and heating under stress (red line) in quenched $Ni_{51}Ti_{49}$ (a) and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ (b) alloys (Inserts show the strain variation during holding under constant stress and temperature)

through the full temperature range of the martensitic transformation (black curve), on cooling to the T^* temperature and heating under stress (blue curve) and on cooling to the T^* temperature, holding and heating under stress (red curve) for both the $Ni_{51}Ti_{49}$ and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloys. It is seen that the strain increased on cooling under stress that is expected; however, an increase in strain is observed on further holding under the same stress that is not typical for the shape memory alloys. On subsequent heating, strain recovers and it shows that both the strain variation on cooling under stress and the strain varied during holding under stress are induced by the formation of the oriented martensite. The strain during holding increased within 10−15 min and then hardly varied or attained the saturation (see inserts in Fig. 2). The saturation value depended on the alloy composition: the strain variation during holding under stress in the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy was twice larger than that in the $Ni_{51}Ti_{49}$ alloy.

The isothermal strain was determined as the strain variation during holding, and the influence of the holding temperature and stress on the isothermal strain (ε_{iso}) was studied. Figure 3 shows that the dependence of the ε_{iso} on holding temperature T^* is non-monotonic, regardless of the holding stress. A comparison of the temperature range of the forward martensitic transformation that occurred during cooling under stress (Table 2) and the temperature ranges where the isothermal strain variation was found during holding (Fig. 3) showed that these temperature ranges coincided. Thus, an isothermal strain variation was observed during holding under stress if the holding temperature ranged from M_s to M_f. An increase in stress increased the temperatures for the isothermal strain variation and the position of temperature at which the maximum isothermal strain was found. This was caused by an increase in the transformation temperature on stress according to the Clausius−Clapeyron relation [6,22,23]. An increase in the holding stress affected the maximum isothermal strain (maximum value on the $\varepsilon_{iso}(T^*)$ curves). In the $Ni_{51}Ti_{49}$ alloy, an increase in the stress increased the maximum isothermal strain (Fig. 3(a)). This is expected because the larger the stress was, the larger the volume fraction of the oriented martensite appeared on holding and the larger the recoverable strain was observed. In the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy, an increase in stress

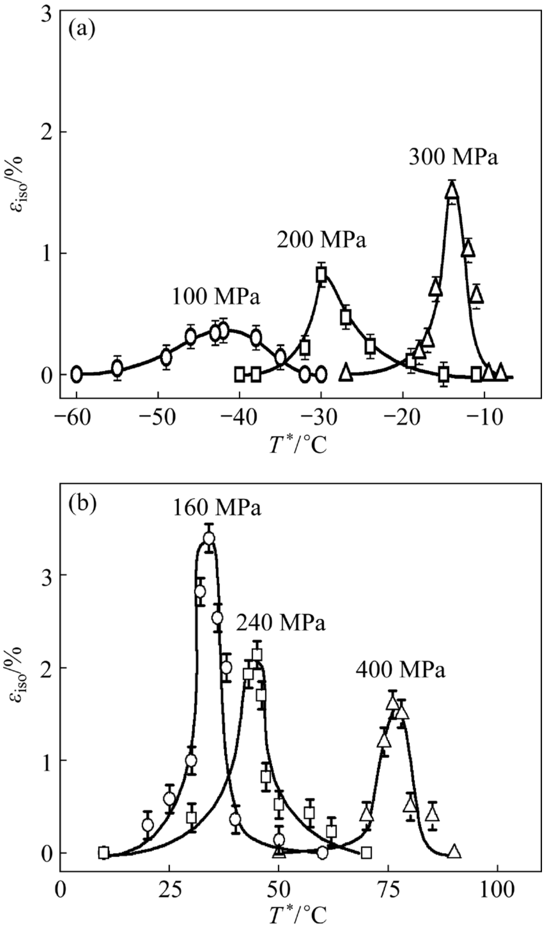

Fig. 3 Dependence of isothermal strain on holding temperature under various stresses for $Ni_{51}Ti_{49}$ (a) and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ (b) alloys in Regime 1

Table 2 Start and finish temperatures of forward martensitic transformation occurring on cooling under stress σ (Temperatures are measured as the intersection of tangent lines on $\varepsilon(T)$ curves obtained on cooling and heating under stress in a full temperature range of martensitic transformation)

Alloy	σ/MPa	M_s/°C	M_f/°C
$Ni_{51}Ti_{49}$ alloy	100	−36	−58
	200	−18	−32
	300	−9	−23
$Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy	160	40	30
	240	52	37
	400	82	68

decreased the isothermal strain (Fig. 3(b)), such behaviour was not clear and should be studied elsewhere. The maximum value of the recoverable strain in Regime 1 was equal to 3.4% and was found during holding the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy under a stress of 160 MPa. In the $Ni_{51}Ti_{49}$ alloy, the maximum recoverable strain of 1.5% was found under a stress of 300 MPa.

3.2 Isothermal strain variation during holding in Regime 2

In Regime 2, the samples were cooled to a temperature of T^* without stress, loaded to stress σ, held at a constant temperature T^* under stress σ and unloaded (Fig. 1(b)). Figure 4 shows the stress−strain curves obtained during a loading−unloading cycle (blue line) and a loading–holding–unloading cycle (red line). In both alloys, the strain variation was observed on holding under stress after active loading that had never been found previously. The isothermal strain was recovered on unloading and subsequent heating of both alloys (a plastic

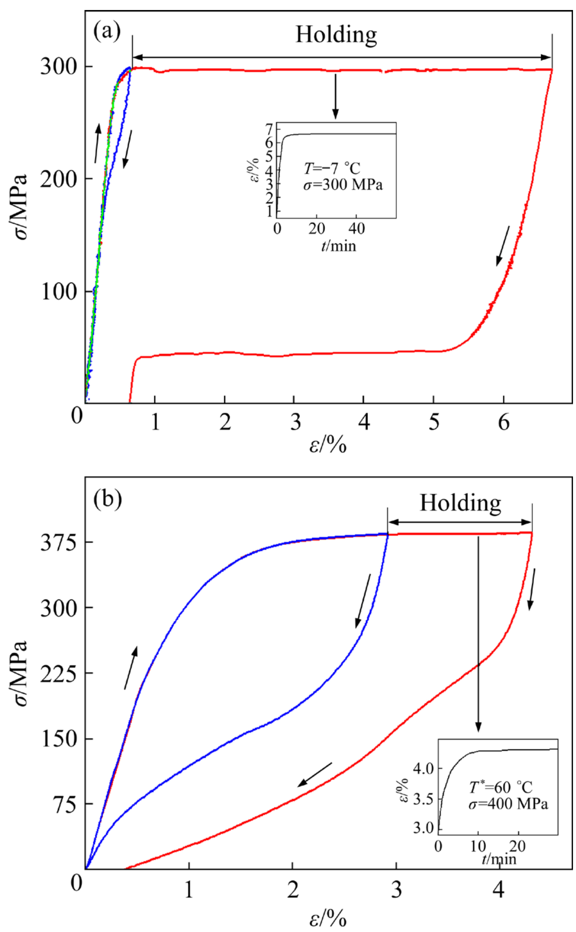

Fig. 4 Strain variation during loading and unloading (blue line) and during loading, holding under stress and unloading (red line) in quenched $Ni_{51}Ti_{49}$ (a) and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ (b) alloys (Inserts show the strain variation during holding under constant stress and temperature)

irrecoverable strain of 0.7% was found in the $Ni_{51}Ti_{49}$ sample after holding under 300 MPa), hence it was induced by the isothermal martensitic transformation. Inserts in Fig. 4 show that during holding under stress, the strain increased within 5−10 min up to saturation, as for Regime 1. At the same time, in Regime 2, the isothermal strain in the $Ni_{51}Ti_{49}$ alloy was larger than that in the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy.

The dependence of the isothermal strain on the holding temperature is shown in Fig. 5. In both alloys, the isothermal strain depended on the holding temperature in a non-monotonic way. As was found for Regime 1, the temperature ranges of the isothermal strain variation in Regime 2 were close to the M_s temperature (see Table 2), except for the results obtained during holding of the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy under a stress of 400 MPa. An increase in the stress increased the temperatures at which the strain variation was observed. In the $Ni_{51}Ti_{49}$ alloy, an increase in the holding stress

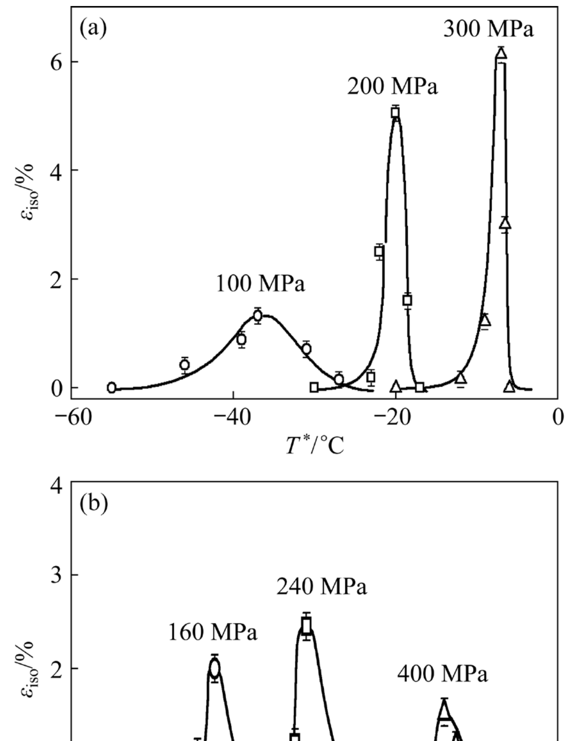

Fig. 5 Dependence of isothermal strain on holding temperature obtained under various stresses for $Ni_{51}Ti_{49}$ (a) and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ (b) alloys in Regime 2

increased the maximum value on the $\varepsilon_{iso}(T^*)$ curves and decreased the temperature range where the isothermal strain variation was found (Fig. 5(a)). In the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy, an increase in the stress affected the maximum value of ε_{iso} non-monotonically and hardly changed the temperature range for the isothermal strain variation (Fig. 5(b)). The maximum value of the recoverable strain in Regime 2 was equal to 2.5% on holding of the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy under 240 MPa and 6.1% on holding of the $Ni_{51}Ti_{49}$ alloy under a stress of 300 MPa.

3.3 Isothermal strain variation during holding in Regime 3

After a preliminary deformation, NiTi-based alloys can demonstrate a recoverable strain variation during thermal cycling through a temperature range of the martensitic transformation without stress (the two-way shape memory effect). In the present study, the isothermal strain variation was studied during the realization of the two-way shape memory effect. The $Ni_{51}Ti_{49}$ and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy samples were pre-deformed in the martensite state by tension and heated to initiate the shape memory effect. After that, the samples were subjected to cooling and heating to observe the two-way shape memory effect. As shown in Fig. 6, the recoverable strain variation was found on cooling and heating without external stress for both alloys, with a value of 2.2%. Strain variation on cooling and heating was stable on thermal-cycling and no degradation of the two-way shape memory effect was observed.

To study the isothermal strain variation during holding, the samples were held for 30−60 min without stress at different temperatures, as shown in Fig. 6 with red arrows. Figure 7 shows that the strain increased during holding without stress, but its variation was significantly less than that during holding under external force (in Regime 1, Fig. 2). This was caused by a less significant effect of the oriented internal stress on the formation of the oriented martensite that led to a small strain variation. In Regimes 1 and 2, the maximum isothermal strain was different between the $Ni_{51}Ti_{49}$ and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloys. At the same time, in Regime 3, this parameter was comparable for both alloys.

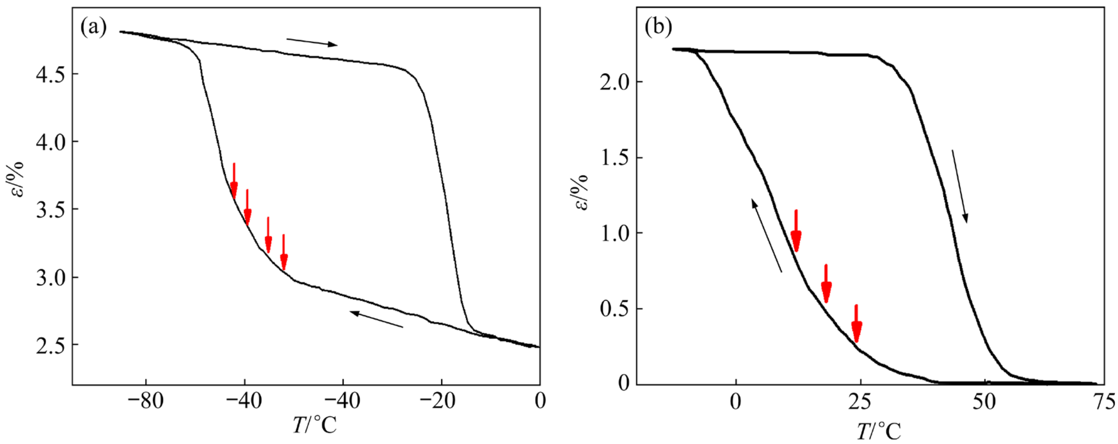

Fig. 6 Strain variation on cooling and heating of $Ni_{51}Ti_{49}$ (a) and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ (b) alloys without stress (The samples were pre-deformed in the martensitic state. The red arrows show the temperatures at which the isothermal holding without stress was carried out)

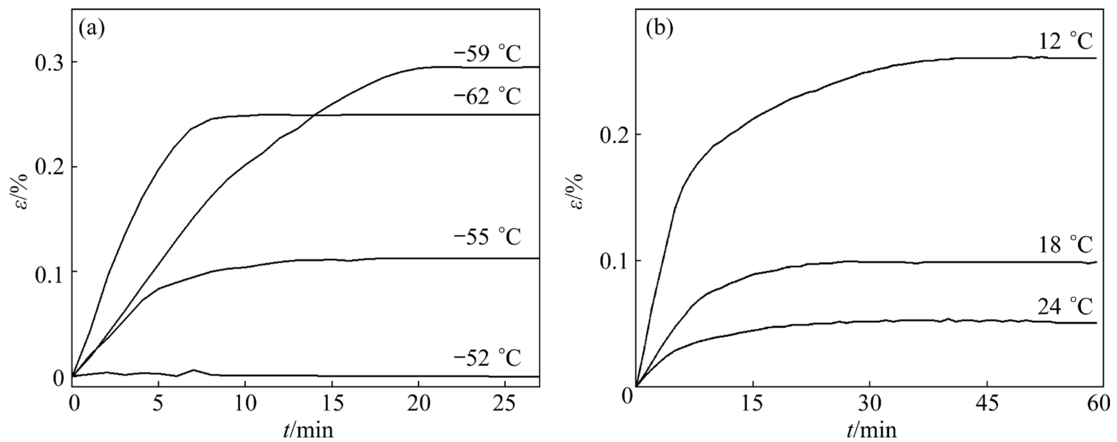

Fig. 7 Strain variation during holding of $Ni_{51}Ti_{49}$ (a) and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ (b) alloys in Regime 3

4 Discussion

In this study, NiTi-based alloys with a non-stoichiometric chemical composition demonstrated a strain variation during holding under constant stress in all studied regimes. The strain variation during holding under constant temperature and stress was caused by isothermal martensitic transformation. According to Ref. [17], the origin of the isothermal transformation was the thermally activated migration of the substitutional atoms. In NiTi-based alloys with a non-stoichiometric chemical composition, excess Ni atoms in binary alloys or Hf and Cu atoms in quaternary alloys are the substitutional defects that prevent the shifting of the atoms needed for the formation of the martensite phase. During holding, the substitutional atoms migrate, and the thermodynamic condition for the forward transformation is fulfilled in local volumes, which allows the martensitic transformation to occur (see details in [17]). One may assume that the different concentration of substitutional defects in binary and quaternary alloys is responsible for the influence of the chemical composition of the alloys on the isothermal strain variation. For instance, in the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy, the concentration of doped elements is larger than the number of excess Ni atoms in the $Ni_{51}Ti_{49}$ alloy, as a result, the isothermal strain in the quaternary alloy was larger than that in the binary alloy in Regime 1 (Fig. 3). However, in Regime 2, the opposite behaviour was observed, and the isothermal strain in the $Ni_{51}Ti_{49}$ alloy was 2.5 times larger than that in the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy.

The reason for the differences in the isothermal strain found in Regimes 1 and 2 may be the different elastic energy stored during the transformation. According to Refs. [24−27], the stored elastic energy E_{el} is equal to

$$E_{el}=(M_s-M_f)\Delta S \tag{1}$$

where ΔS is the entropy change during the transformation. This energy is proportional to the temperature range of the forward transformation, hence, the M_s-M_f value may be used as a measure of the stored elastic energy. The M_s and M_f may be easy determined on cooling under stress (in Regime 1). However, these temperatures cannot be measured directly during the loading–unloading experiments (Regime 2). At the same time, these temperatures correlate to the σ_s and σ_f – the start and finish stress for the stress-induced martensitic transformation. To initiate forward martensitic transformation during loading, the M_s and M_f should be increased by stress to the deformation temperature [6]. Usually, the stress increases the start and finish temperatures of the forward martensitic transformation according to the Clausius-Clapeyron relation (Fig. 8(a)). In this case, the relationship between the M_s-M_f and $\sigma_f-\sigma_s$ values may be found as

$$\frac{d\sigma}{dT}=\frac{\sigma_f-\sigma_s}{M_s-M_f} \tag{2}$$

hence, the M_s-M_f may be estimated as

$$M_s-M_f=\left(\sigma_f-\sigma_s\right)\frac{dT}{d\sigma} \tag{3}$$

where $dT/d\sigma$ is the Clausius-Clapeyron ratio which is determined as the slope for the dependence of the critical stress for martensite formation (σ_s) on the deformation temperature. Such dependences were found for the studied alloy, and the $dT/d\sigma$ was estimated (Fig. 8(b)). This value was equal to 0.139 °C/MPa for the $Ni_{51}Ti_{49}$ alloy and 0.094 °C/MPa for the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy.

For Regime 1, the M_s-M_f values were measured using the $\varepsilon(T)$ curves found on cooling and heating under constant stress over the full temperature range of the martensitic transformation. For Regime 2, the M_s-M_f values were measured according to expression (3), where the σ_s and σ_f values were measured using the $\sigma(\varepsilon)$ curves found during loading to 10% and unloading at temperatures at which the holding was carried out (the σ_s and σ_f values were determined as the intersection of tangent lines). The M_s-M_f values found for both regimes are given in Table 3. For the $Ni_{51}Ti_{49}$ alloy, the temperature range of the forward transformation in Regime 1 was 4−11 times larger than that in Regime 2. Thus, the formation of the same volume fraction of martensite in Regime 1 was accompanied by a larger elastic energy variation than that in Regime 2. This means that the formation of martensite during holding in Regime 1 was hardened; however, the martensite may appear easily during holding in Regime 2. As a result, 1.5% of the isothermal strain was observed in Regime 1, and 6.1% was observed in Regime 2. In the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy, the elastic energy in Regime 1 was 2−3 times larger than that in Regime 2, and the isothermal strains were comparable.

The difference in stored elastic energy may explain the difference in the isothermal strain found in the $Ni_{51}Ti_{49}$ and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloys. In Regime 1 under a stress less than 200 MPa, the

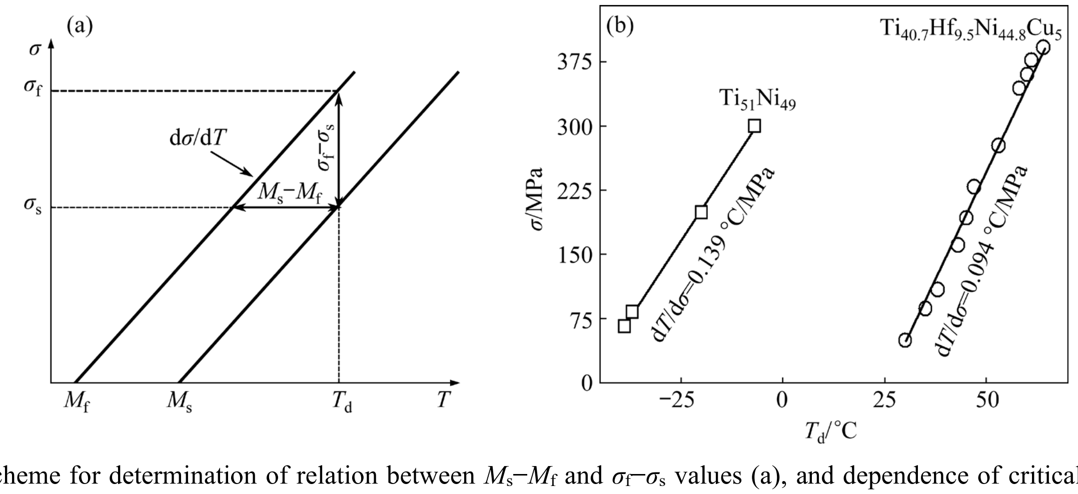

Fig. 8 Scheme for determination of relation between M_s-M_f and $\sigma_f-\sigma_s$ values (a), and dependence of critical stress for martensite transformation (σ_s) on deformation temperature (T_d) in $Ni_{51}Ti_{49}$ and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloys (b)

elastic energy in the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy was less than that in the $Ni_{51}Ti_{49}$ alloy; as a result, the isothermal strain in the quaternary alloy was larger than that in the binary alloy. At the same time, in Regime 2, under a stress of 200 MPa or more, the stored elastic energy in the binary alloy was less than that in the quaternary alloy, which led to a larger isothermal strain in the $Ni_{51}Ti_{49}$ alloy than in the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy.

Thus, the holding under stress of the NiTi-based alloys undergoing the isothermal transformation may be used as a new way for the observation of the recoverable strain variation which may be realized in two regimes. In the first regime, the sample should be cooled under stress to a temperature close to the M_s, held for 10−15 min, and then heated (Fig. 9(a)). In the second regime, the sample should be loaded to the σ_s stress, held for 10−15 min, and then unloaded (Fig. 9(b)). Using these regimes facilitates a decrease in the temperature range for strain variation on cooling and heating under stress, or the stress range of loading and unloading, which may be useful for certain applications.

5 Conclusions

(1) A large strain variation was observed on holding of the $Ni_{51}Ti_{49}$ and $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloys under stress after cooling the sample to a temperature close to the M_s (Regime 1) or loading of the sample to the σ_s stress (Regime 2). Stress-free holding of the samples which demonstrates the two-way shape memory effect (Regime 3) was accompanied by a small isothermal strain (0.3%). The strain variation on holding under stress was recovered on heating (Regimes 1 and 3) or unloading (Regime 2).

(2) The strain increased on holding under stress up to saturation, which depended on the chemical composition of the alloy, the holding temperature, stress and holding regime.

(3) In the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy, the maximum isothermal strain was 3.4% on holding under a stress of 160 MPa in Regime 1 and 2.5% on holding under a stress of 240 MPa in Regime 2. In the $Ni_{51}Ti_{49}$ alloy, the maximum isothermal strain was observed on holding under a stress of 300 MPa

Table 3 M_s−M_f values measured in Regime 1 and Regime 2 under various stresses

Alloy	σ/MPa	Regime 1		Regime 2	
		(M_s-M_f)/°C	ε_{iso}^{max} / %	$[(\sigma_f-\sigma_s)\cdot(dT/d\sigma)]$/°C	ε_{iso}^{max} / %
$Ni_{51}Ti_{49}$	100	22	0.4	4.5	1.3
	200	14	0.8	2.1	5.1
	300	14	1.5	1.2	6.1
$Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$	160	10	3.4	4	2
	240	15	2.1	4.5	2.5
	400	14	1.6	7	1.5

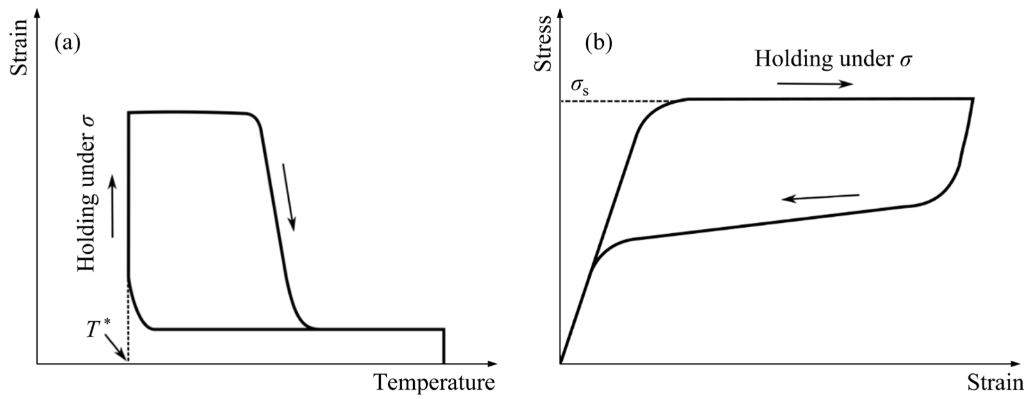

Fig. 9 New working regimes for strain variation in NiTi shape memory alloys: (a) Regime 1: cooling–holding–heating under stress–heating; (b) Regime 2: loading–holding under stress–unloading

with 1.5% in Regime 1 and 6.1% in Regime 2.

(4) The difference in the isothermal strain observed during holding under various regimes was attributed to the difference in stored elastic energy. A small isothermal strain was observed under regimes with a large stored elastic energy. A larger isothermal strain was found on holding under stress in regimes with a small stored elastic energy.

(5) Holding under stress can be used as a new way for the observation of the recoverable strain variation in NiTi-based shape memory alloys.

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NiTi 形状记忆合金在恒定应力和温度下保温过程中马氏体相变诱发的可恢复应变

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摘　要：研究 NiTi 形状记忆合金在应力下等温保温过程中的应变变化。为了研究可恢复应变，对 $Ni_{51}Ti_{49}$ 和 $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ 合金进行 3 种制度的保温处理，分别是：应力下冷却后在应力下保温(制度 1)；无应力和载荷下冷却后在应力下保温(制度 2)；具有双向形状记忆效应的样品在应力下保温(制度 3)。结果表明，所有制度中，在应力下保温后样品均会发生应变变化。该应变在后续热处理或卸载后能恢复，因此表明应变变化是由等温马氏体相变引起的。这种等温应变取决于合金的化学成分、等温保温制度、应力和保温温度。$Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ 合金(制度 1)和 $Ni_{51}Ti_{49}$ 合金(制度 2)的最大等温应变分别为 3.4% 和 6.1%。制度 3 中的保温伴随着较小的应变(小于 0.3%)。讨论储存弹性能对等温马氏体相变的影响，结果表明，当相变伴随着较小的储存弹性能时，等温应变较大。

关键词：等温马氏体相变；可恢复应变；超弹性应变；NiTi 形状记忆合金；保温

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