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Influence of pre-strain on recovery stress of annealed NiTi thin wire during isothermal holding

Xiaojun Yan, Jan Van Humbeeck*

Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, Kasteelpark Arenberg 44 bus 2450, B-3001 Heverlee, Belgium

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ABSTRACT

The present research aims to understand the recovery stress of NiTi wires generated during heating and isothermal holding under constrained condition. Both pre-strain and isothermal holding temperature have significant effects on the evolution of recovery stress during heating and isothermal holding. In general, increasing isothermal holding temperature and/or pre-strain causes an increase of recovery stress reduction or relaxation. This effect can be attributed to different dislocation densities and mobility of dislocations generated in those conditions.

1. Introduction

It is well known that if a pre-strained shape memory alloy (SMA) is constrained during transformation from martensite to austenite, large recovery stress is generated. It is an important functional property of SMA and has long been the object of study from a scientific and engineering point of view. This property makes SMA ideally suited for use as fasteners, seals, connectors and clamps [1]. The generation and evolution of recovery stresses strongly depends on thermomechanical treatments [2], annealing [3,4], pre-strain [5–7], thermocycling [8–11], matrix [12–15], etc. Meanwhile, the constrained phase transformations of SMAs associated with recovery stress have been investigated [16–19].

However, some problems should still be investigated and resolved. One of these issues is the stress relaxation phenomenon due to long-term sustaining of constrained stress. Depending on the way the SMAs are designed to operate, frequent, long-term periods of high temperature exposure are common in some applications. A high temperature curing process, for example, is needed to produce NiTi fiber reinforced polymer matrix composites [16]. These periods can last from several minutes to several hours. Microstructural changes in the SMA can occur during these times of long-time high temperature exposure. Stress relaxation of SMA is a major issue which must be considered under these circumstances. These features will reduce the usage life of the components and impede their applications. Hence, the understanding of the stress relaxation phenomena of NiTi is important. Up to now, few experimental data on recovery stress relaxation have been reported in the literature [20–22].

In the present study, we aim at investigating the influence of pre-strain and temperature on the recovery stress of annealed NiTi thin wire during heating and isothermal holding.

2. Experimental procedure

The experiments were performed on a commercial NiTi wire provided by SAES Getters (Italy) with a diameter of 0.076 mm and a normal composition of 50.2 at.% Ni. The as-received wire (35% cold-worked) with a length of 100 mm was annealed in argon atmosphere at 450 °C for 10 min. The transformation temperatures of the annealed specimen were determined by differential scanning calorimetric measurement to be $R_s = 62\,^\circ\mathrm{C}$, $R_f = 58\,^\circ\mathrm{C}$, $M_s = 43\,^\circ\mathrm{C}$, $M_f = 33\,^\circ\mathrm{C}$, $A_s = 76\,^\circ\mathrm{C}$ and $A_f = 87\,^\circ\mathrm{C}$.

All thermomechanical experiments were performed on a dynamic mechanical analyzer (DMA) instrument (TA Q800). The recovery stresses were investigated as a function of pre-strain, isothermal temperature and time. All samples were dipped in liquid nitrogen to ensure a full martensite state prior to tests. The thermomechanical loading consisted of:

(1) loading the sample under uniaxial tensile stress at 25 °C up to the required strains, $\varepsilon = 2$, 4, 6 and 8%, respectively, at a strain rate of 0.5%/min;
(2) unloading the sample until a force equal to 5 MPa;
(3) fixing the clamps after unloading and heating the sample under constrained condition up to 150, 200, 250 and 300 °C at the rate of 3 °C/min, respectively. Keeping the temperature at 150, 200, 250, 300 °C for 60 min followed by
(4) cooling down to 25 °C at a rate of 3 °C/min;
(5) repeating (3) and (4) one more time;

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* Corresponding author. Tel.: +32 16 321281/270; fax: +32 16 321992.
E-mail address: Jan.VanHumbeeck@mtm.kuleuven.be (J. Van Humbeeck).

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(6) measuring the free shape recovery behavior of the sample by heating to 180 °C and cooling down to 25 °C at a constant load of 5 MPa.

3. Results

3.1. Characteristics of the material deformed in martensitic state

Fig. 1 shows tensile stress–strain curves of the annealed NiTi wire. The tests are conducted at 25 °C, which is lower than A_s, so the specimens are martensitic also because of the prior cooling in liquid nitrogen. The stress–strain curves can be divided into four regions. In a very basic approach these regions correspond to the inelastic deformation of self-accommodated martensite twins (stage I), martensite reorientation over the stress plateau (stage II), the further reorientation and inelastic deformation of the reoriented martensite following the reorientation deformation (stage III), and the plastic deformation of the reoriented martensite (stage IV), respectively [23]. Some defects are generated in region II to accommodate the detwinning and martensite reorientation processes [23].

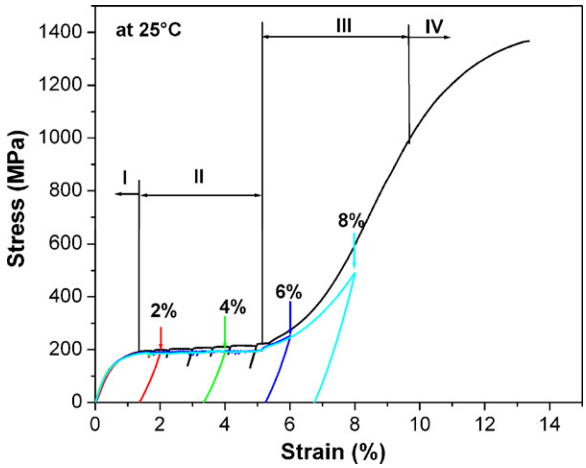

Fig. 1. Tensile stress–strain curves at 25 °C of annealed NiTi wire.

3.2. Constrained recovery and free recovery

Fig. 2(a)–(d) shows the recovery stress–temperature curves of the specimens upon heating to 300 °C with different pre-strained levels of 2%, 4%, 6% and 8%, respectively. It is seen that the 2% pre-strained specimen has a maximum recovery stress at about 170 °C. After continuously heating the specimen to 300 °C, no significant change in recovery stress is observed. It is stable at the temperature range of 170–300 °C. For larger pre-strained specimens, recovery stresses steadily increase and reach maximum values at around 200 °C and then decrease for higher temperatures. It should be taken into account that the NiTi wire is expanding due to the linear

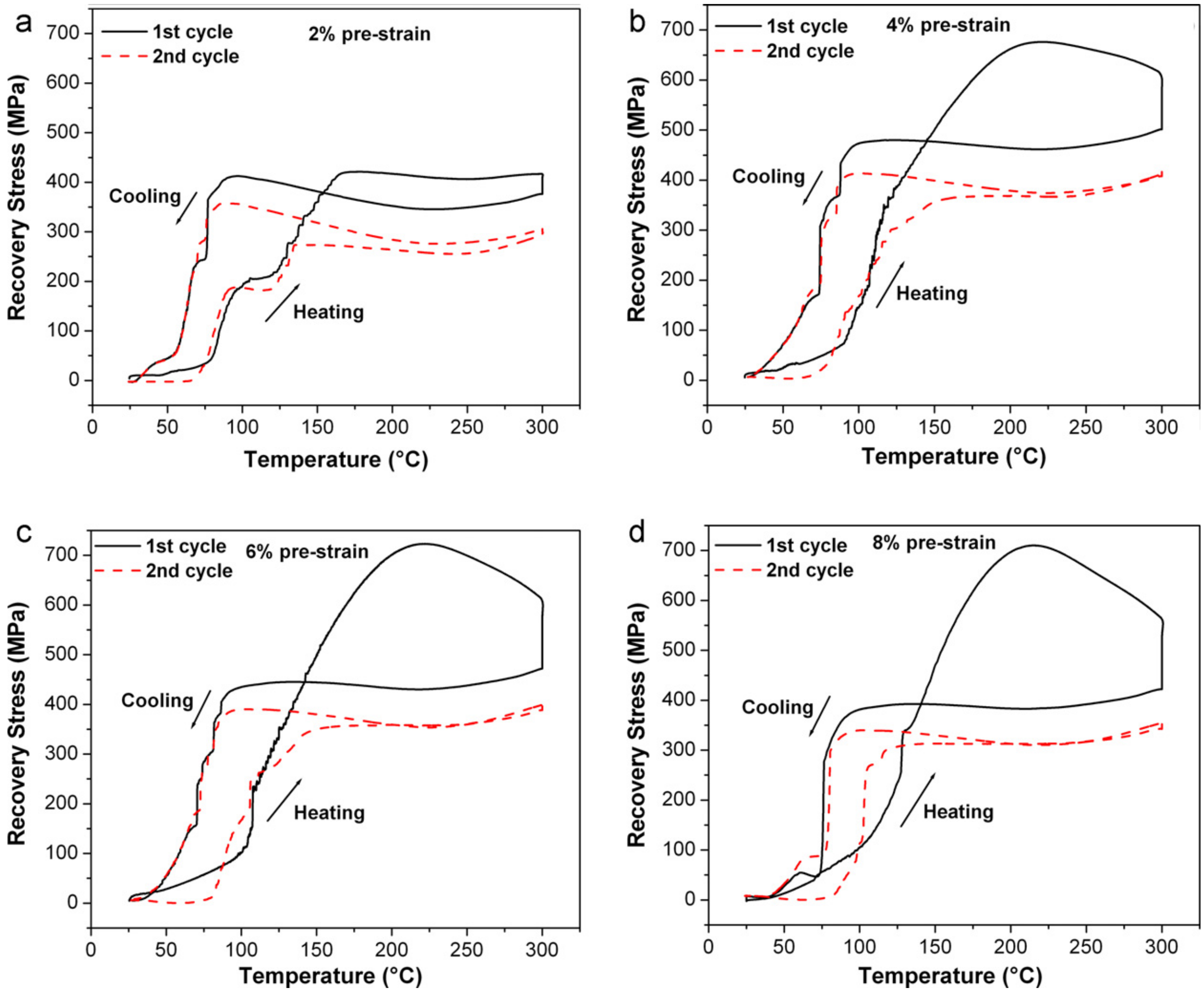

Fig. 2. Recovery stress–temperature curves of the pre-strained specimens heated to 300 °C. (a) 2% pre-strain; (b) 4% pre-strain; (c) 6% pre-strain; and (d) 8% pre-strain. First cycle is in solid line and second cycle is in dash line.

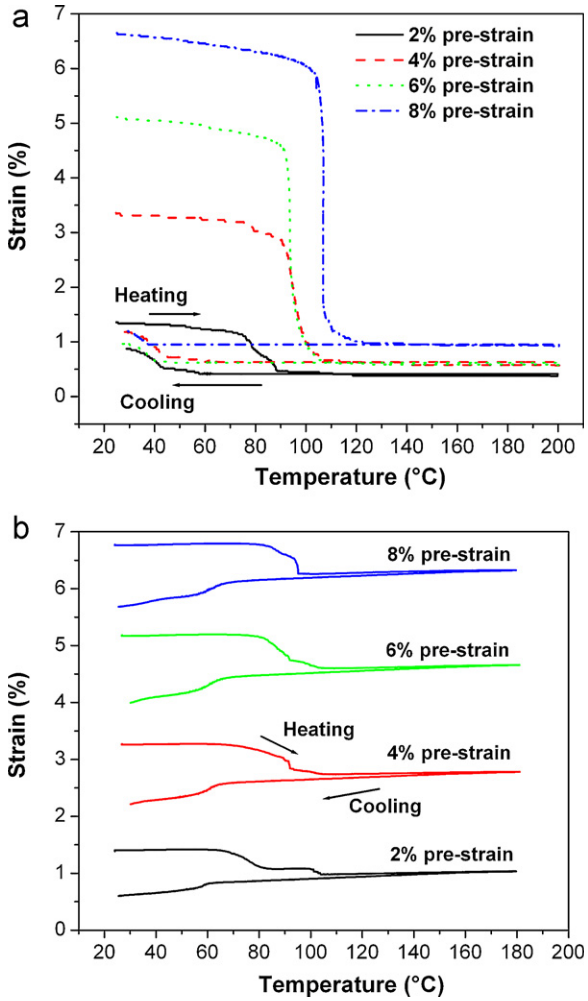

Fig. 3. Strain–temperature curves of free shape recovery measured after: (a) loading to different pre-strains and then unloading at 25 °C in Fig. 1; (b) the second cooling down to 25 °C during thermal cycles to 300 °C for recovery stress measurement in Fig. 2.

thermal expansion process of the sample and clamps. This might cause some stress relaxation. In these cases, it is noticed that the slopes of recovery stress–temperature curves vary with the pre-strains. The larger the pre-strain, the higher the recovery stress change rate both before and after reaching the maximum recovery stresses. This could indicate that other mechanisms are involved in the stress relaxation at high temperatures.

Recovery stresses decrease during isothermal holding at 300 °C for all pre-strain levels. Upon cooling, recovery stresses remain relative stable above the transformation temperatures and decrease drastically below it. During the second heating, recovery stresses reach maximum values at about 150 °C and slightly increase after continuously heating to 300 °C. Isothermal holding during the second cycle has no significant effect on recovery stress.

Fig. 3(a) and (b) shows the strain–temperature curves of the NiTi wire under free recovery condition. The residual strains cannot be completely recovered in these conditions. Thermal recoverable strain associated with the reverse martensitic transformation after two thermal cycles is much smaller than that without thermal cycles. It is also seen that specimens deformed at martensitic state show two-way shape memory effect. This is in good agreement with a previous study [23]. However, two-way shape memory effect disappears after two thermal cycles. The evolution of recoverable strain during each thermal cycle was investigated in [24].

3.3. Recovery stress relaxation

Special attention should be paid to the evolution of recovery stress during isothermal holding at different temperatures.

Fig. 4(a)–(d) shows the stress–time curves of the pre-strained specimens during isothermal holding at 150, 200, 250 and 300 °C, respectively. For ease of comparison, all the recovery stress–time curves have been normalized to 1, the recovery stress at the beginning of the test. Evidently, both pre-strain and isothermal holding temperature are important for the evolution of recovery stress during isothermal holding. Three tendencies can be identified. First, it is seen that recovery stresses increase with time during isothermal holding at 150 °C and their magnitudes decrease with increasing pre-strain, as shown in Fig. 4(a). Second, for the specimens with 2% pre-strain isothermal holding at 200 and 250 °C, recovery stresses increase to maximum values and then decrease. After isothermal holding for 1 h, recovery stresses are still a little higher than those before the isothermal holding. The same tendency is observed for the sample with 4% pre-strain isothermal holding at 200 °C. The third last important feature is that at the larger pre-strain and higher isothermal temperature, the recovery stress shows an exponential decrease during isothermal holding. The reduction rate of recovery stress strongly depends on the isothermal temperature and pre-strain. For the same pre-strain, the higher the isothermal temperature, the more the recovery stress decreases during isothermal holding. For the same isothermal temperature and the larger pre-strain, the more the recovery stress is reduced.

Fig. 5 shows the recovery stress at the end of isothermal holding for 1 h as a function of pre-strain.

It is also noted that at the very beginning of the isothermal holding, the temperature is not stable and has a small oscillation, which causes the change of recovery stress when holding at low temperature, as shown in Fig. 4(a) and (b). The same phenomenon was also found in [24]. This small temperature oscillation has no perceivable effect on recovery stress when holding at higher temperature, as shown in Fig. 4(c) and (d).

Recovery stress relaxation and free shape recovery in different conditions were measured for the specimens with 4% pre-strain upon heating to 150, 200, 250, and 300 °C.

Fig. 6 schematically illustrates two different methods. The unloading was done before and after isothermal holding, corresponding to the point 1 and point 2 in Fig. 6, respectively. After relaxation, recoverable strain (ε_r), unloading modulus and free shape recovery were measured.

Fig. 7(a)–(d) shows the results from free shape recovery measurement. It is seen that the recoverable strain does not show any significant change during isothermal holding at 150 °C. However, the recoverable strain decreases during isothermal holding at 200, 250 and 300 °C. The recoverable strain at 200 °C, for example, is 1.38% before isothermal holding and decreases to 1.08% after isothermal holding. At the same time, the slope of the stress–strain unloading curve increases after isothermal holding. The results are shown in Table 1. The decrease of recoverable strain and increase of unloading modulus indicate that plastic deformation takes place during recovery stress generation and isothermal holding.

Fig. 8(a) and the (b) shows the tensile stress–strain curves of the specimens at high temperatures and strain–temperature curves during free shape recovery after unloading, respectively. The specimens were loaded and unloaded under force control. The initial strain at the beginning of loading is due to the thermal expansion and reverse martensitic transformation of the specimen upon heating to the testing temperature. After unloading and cooling down to 25 °C, free shape recovery was measured. The specimen was loaded to 500 MPa at 150 °C, which corresponded to the maximum recovery stress at this temperature for different pre-strain levels. For other temperatures, the specimens were loaded to 630 MPa, which

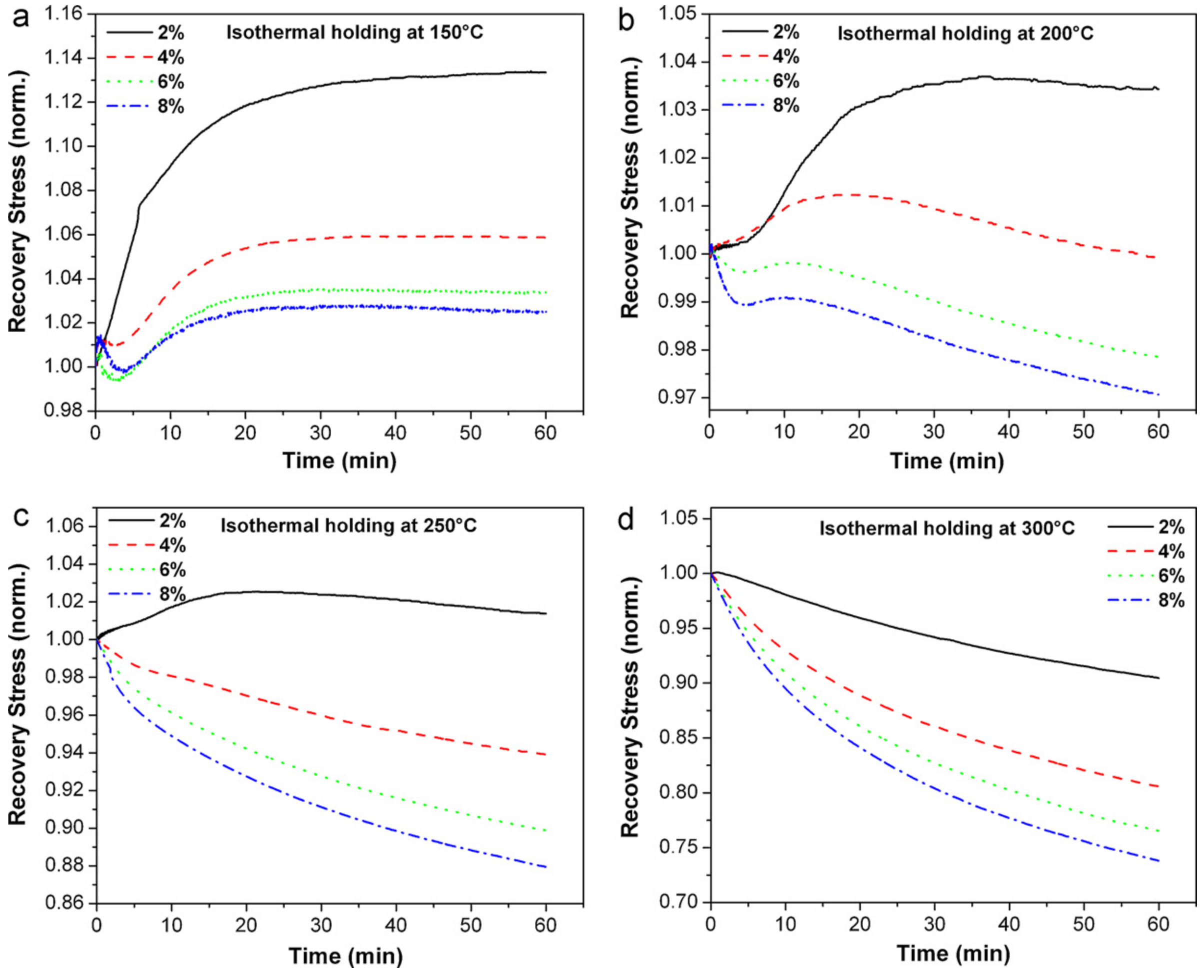

Fig. 4. Recovery stress–time curves during the isothermal holding at different temperatures. (a) Isothermal holding at 150 °C; (b) isothermal holding at 200 °C; (c) isothermal holding at 250 °C; and (d) isothermal holding at 300 °C.

Table 1
Recoverable strain and unloading modulus of annealed NiTi wires before and after isothermal holding at different temperatures.

	Recoverable strain (%)			Unloading modulus (GPa)		
	200 °C	250 °C	300 °C	200 °C	250 °C	300 °C
Before isothermal	1.38	1.09	1.01	52	72	78
After isothermal	1.08	0.95	0.83	66	75	82

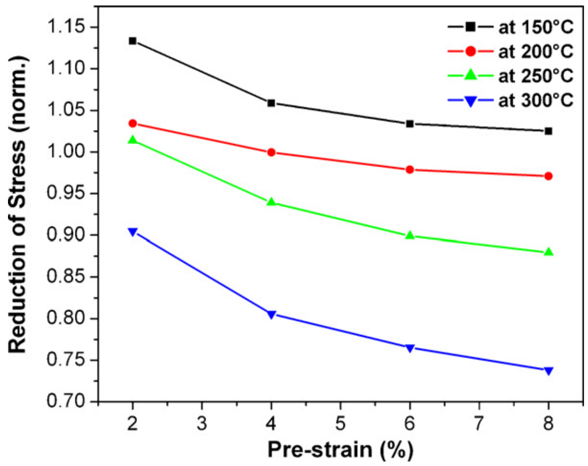

Fig. 5. Reduction of recovery stress after isothermal holding for 1 h as a function of pre-strain at different temperatures.

is slightly lower than the maximum recovery stresses in these conditions. For all specimens, there are residual strains after unloading at testing temperatures, as shown in Fig. 8(a). However, the residual strains disappear upon cooling down to 25 °C and two-way shape memory effects are observed during the following thermal cycle, as shown in Fig. 8(b).

4. Discussion

The experimental results in this study show that both pre-strain and temperature play important roles in the evolution of recovery stress during heating and isothermal holding. The pre-strain can induce dislocations and internal stresses in the matrix; the temperature affects the mobility of dislocations. The combination of both factors causes the different behaviors of recovery stress during heating and isothermal holding. A permanent strain of 0.4–0.6% was measured in the specimen deformed within the stress-plateau region, as shown in Fig. 3(a). This indicates some plastic deformation has occurred during the reorientation deformation in stage II.

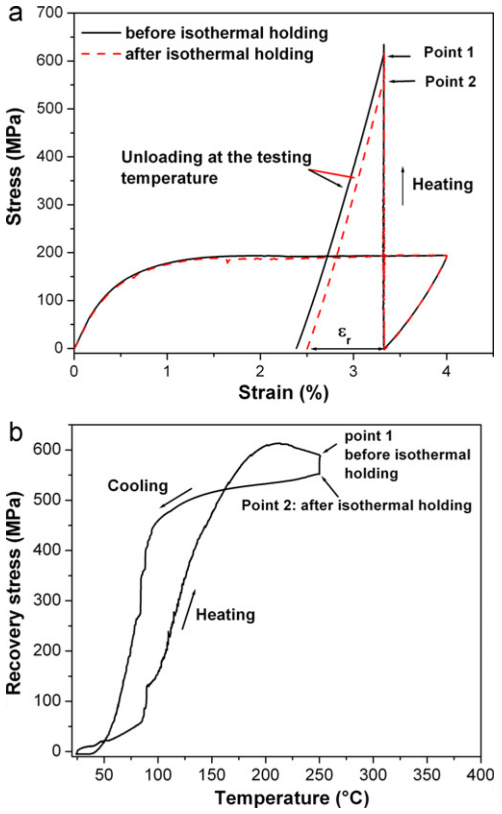

Fig. 6. Comparison of unloading behavior and recoverable strain before and after isothermal holding: (a) stress–strain curves and (b) stress–temperature curve.

Deformation beyond the stress plateau (regions III and IV) results in the further detwinning of martensite and increased dislocation density. Internal stresses in the directions of the preferentially oriented variants of the deformed martensite are created during deformation [23]. It is reasonable to presume that the larger pre-strain levels the higher dislocation densities and internal stresses. Upon heating under constraint, transformation from the oriented martensite to austenite starts, and a recovery stress is generated. Due to the recovery stress, the oriented martensite cannot totally transform to the parent phase even when the temperature is higher than the reverse transformation finishing temperature A_f. Therefore, there is always some oriented martensite retained in the NiTi wire, but its volume fraction varies according to the heating temperature. Comparing Figs. 1, 2, and 8, one can see that the recovery stress levels are almost in the elastic limit of austenite deformation at high temperature but may exceed the stress level of the martensitic reorientation at this high temperature. It is reasonable that the recovery stress will lead to a larger strain (more than pre-strain) in the remaining martensite and to an elastic strain in the parent. This is also confirmed by comparing residual strains under different conditions, as shown in Figs. 3 and 6. The amount of strain generated during heating or isothermal holding, which decides the reduction of recovery stress, is related to the pre-strain level and temperature. The specimens with the same pre-strain should have the same dislocation density and internal stress. However, the mobility of dislocation increases with increasing temperature. Therefore, a larger permanent strain is produced at a higher isothermal temperature, corresponding to higher recovery stress reduction. On the other hand, the specimens with different pre-strains have the same mobility of dislocations at a given temperature, but dislocation density and internal stress increases with increasing pre-strain. Therefore, a larger permanent strain is produced. So, the recov-

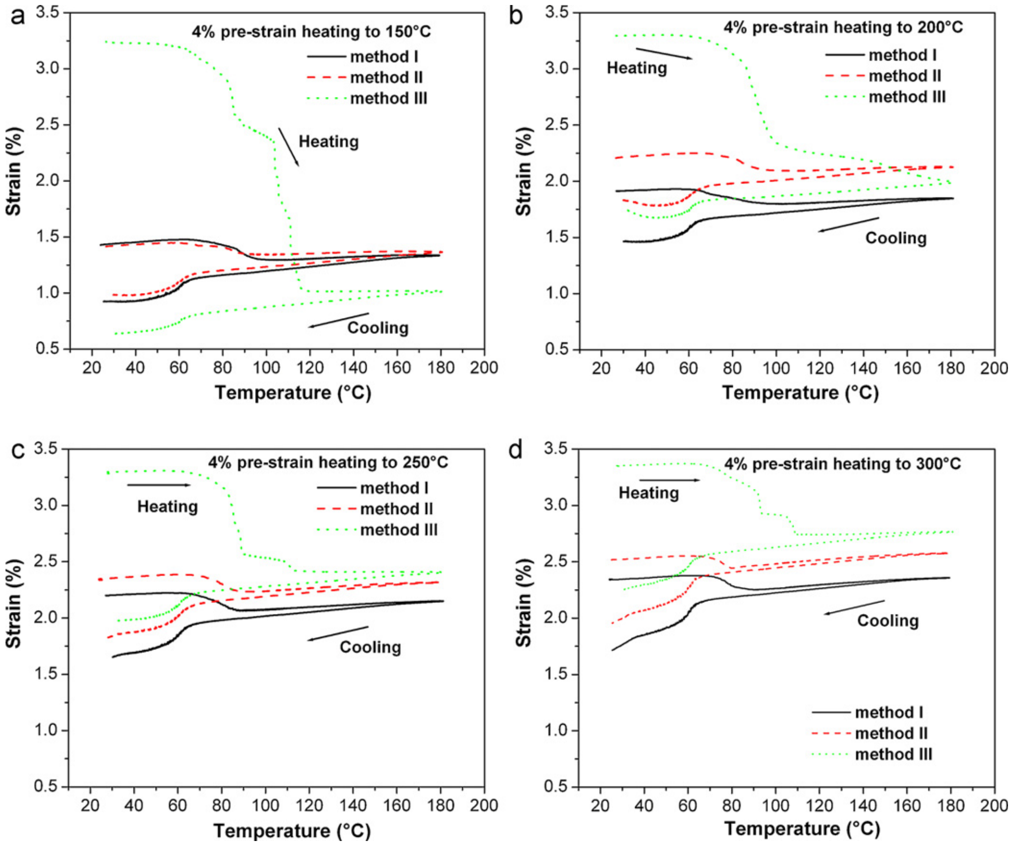

Fig. 7. Free shape recovery measurements after method: (I) recovery stress relaxation at high temperature before isothermal holding (point 1 in Fig. 6) followed by cooling down to 25 °C; (II) recovery stress relaxation at high temperature after isothermal holding (point 2 in Fig. 6) followed by cooling down to 25 °C; (III) the end of one thermal cycle of recovery stress measurement at 4% pre-strain (including heating from 25 °C to 300 °C, isothermal holding at 300 °C for 1 h and cooling down to 25 °C).

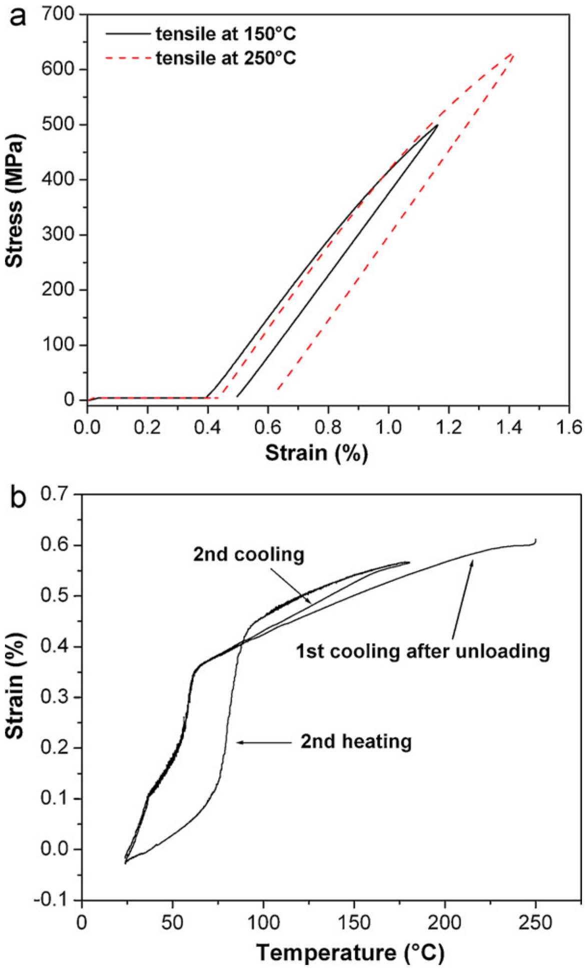

Fig. 8. Stress–strain curves of the specimens at high temperature (a) and shape recovery (b).

ery stress relaxation during isothermal holding can be attributed to dislocation movement caused by the recovery stress assisted by internal stresses.

5. Conclusions

The evolution of the recovery stress of constrained annealed NiTi wires as a function of pre-strain and temperature were investigated. The important conclusions are as follows:

(1) The recovery stress increases upon isothermal holding at 150 °C for different pre-strain levels.
(2) With 2% pre-strain, isothermal holding at 200 and 250 °C, the recovery stress after isothermal holding is a little higher than that before isothermal holding. The same tendency is also seen with 4% pre-strain upon isothermal holding at 200 °C.
(3) Under conditions in this study, the recovery stress decreases during isothermal holding. Increasing isothermal holding temperature and/or pre-strain causes the increase of recovery stress reduction. This effect can be attributed to a different dislocation density and mobility of dislocations generated in different conditions.

Acknowledgement

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References

[1] J. Van Humbeeck, Mater. Sci. Eng. A 273–275 (1999) 134–148.
[2] I.Yu. Khmelevskaya, J. Phys. IV France 11 (2001) 41–46.
[3] X.J. Yan, J. Van humbeeck, Funct. Mater. Lett. 2 (2009) 1–6.
[4] H. Sadiq, M.B. Wong, R. Al-Mahaidi, X.L. Zhao, Smart Mater. Struct. 19 (2010) 1–7.
[5] P. Šittner, D. Vokoun, G.N. Dayananda, R. Stalmans, Mater. Sci. Eng. A 286 (2000) 298–311.
[6] D. Vokoun, V. Kafka, C.T. Hu, Smart Mater. Struct. 12 (2003) 680–685.
[7] W. Cai, C.S. Zhang, L.C. Zhao, J. Mater. Sci. Technol. 10 (1994) 27–30.
[8] W. Cai, C.S. Zhang, L.C. Zhao, J. Mater. Sci. Lett. 13 (1994) 8–9.
[9] Y.J. Zheng, L.S. Cui, J. Schrooten, Mater. Lett. 59 (2005) 3287–3290.
[10] V. Brailovski, E. Clément, P. Terriault1, F. Trochu, J. Phys. IV France 112 (2003) 231–234.
[11] P. Sittner, P. Lukas, V. Novak, D. Neov, M. Ceretti, J. Neutron Res. 9 (2001) 143–150.
[12] K.A. Tsoi, J. Schrooten, R. Stalmans, Mater. Sci. Eng. A 368 (2004) 286–298.
[13] K.A. Tsoi, J. Schrooten, R. Stalmans, Mater. Sci. Eng. A 368 (2004) 299–310.
[14] J. Schrooten, K.A. Tsoi, R. Stalmans, Y.J. Zheng, P. Sittner, Proc. SPIE 4234 (2001) 114–124.
[15] D. Vokoun, R. Stalmans, Proc. SPIE 3667 (1999) 825–835.
[16] Y.J. Zheng, J. Schrooten, L.S. Cui, J. Van Humbeeck, Acta Mater. 51 (2003) 5467–5475.
[17] K.A. Tsoi, R. Stalmans, J. Schrooten, Acta Mater. 50 (2002) 3535–3544.
[18] D.Q. Jiang, L.S. Cui, Y.J. Yan, X.Q. Zhao, Y. Li, Mater. Sci. Eng. A 515 (2009) 131–133.
[19] Y. Li, L.S. Cui, H.B. Xu, D.Z. Yang, Metall. Trans. A 34 (2003) 219–223.
[20] H.C. Lin, T.P. Wang, K.M. Lin, C.Y. Chung, P.C. Wang, W.H. Ho, J. Alloys Compd. 466 (2008) 119–125.
[21] P. Papps, D. Bollas, J. Parthenios, V. Dracopoulos, C. Galiotis, Smart Mater. Stuct. 16 (2007) 2560–2570.
[22] Y.Q. Fu, H.J. Du, Surf. Coat. Technol. 153 (2002) 100–105.
[23] Y. Liu, Y. Liu, J. Van Humbeeck, Acta Metall. 47 (1999) 199–209.
[24] P. Molnar, J. Van Humbeeck, Recovery stress and shape memory stability in NiTiCu ultrathin wires at high temperatures, Scripta Mater., submitted for publication.