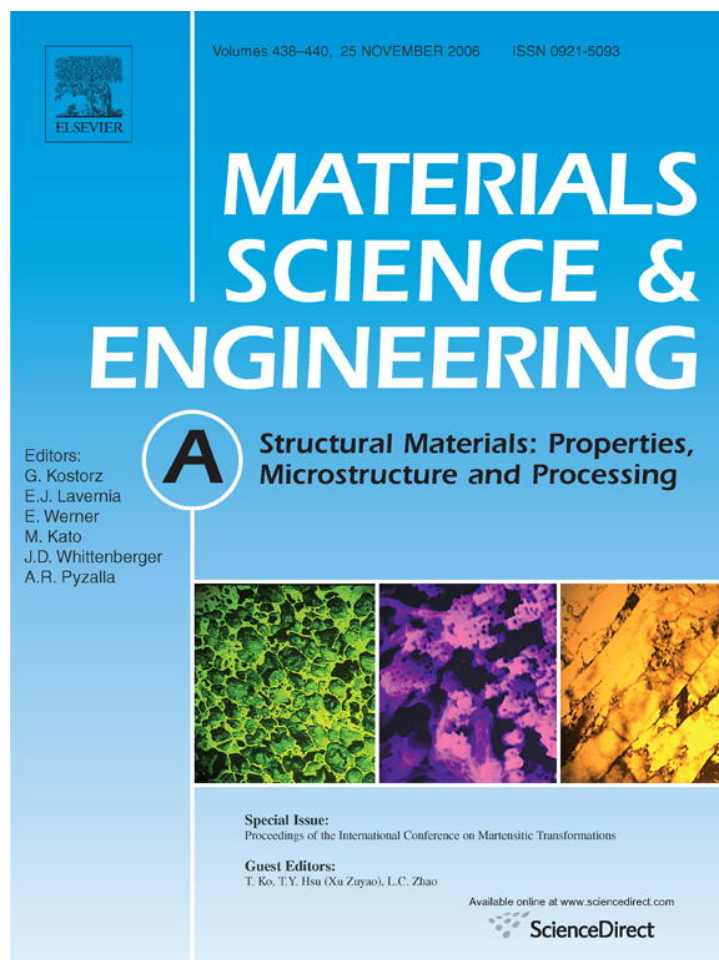


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In situ experimental evidence on R-phase related deformation processes in activated NiTi wires

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Abstract

Although many commercial NiTi wires commonly exhibit sequential $B2 \leftrightarrow R \leftrightarrow B19'$ transformations, their unique stress–strain–temperature behaviors are readily comprehended and modeled as being solely due to the $B2 \leftrightarrow B19'$ martensitic transformation and/or reorientation/twinning processes $B19' \leftrightarrow B19'$ in the martensite phase. Omitting the R-phase is commonly advocated by the fact that the $B2 \leftrightarrow R$ transformation strains are much smaller and not all NiTi alloys exhibit R-phase transformation. However, small strains are commonly utilized in engineering applications and the R-phase is known to be promoted by thermal and/or mechanical cycling. The activity of the R-phase related deformation processes is moreover difficult to detect experimentally and hence the investigators do not have to be always aware of it. Two newly developed experimental techniques (*in situ* neutron diffraction and *in situ* combined ultrasonic and electric resistance measurement) were used to investigate the deformation/transformation processes in the activated NiTi wires related with the R-phase. Activity of individual $B2 \leftrightarrow R$ transformation, $R \leftrightarrow R$ reorientation and $R \Rightarrow$ distortion processes during thermomechanical loads on binary NiTi wires was detected and distinguished from the $B2 \leftrightarrow B19'$ transformation or $B19' \leftrightarrow B19'$ reorientation processes. It is claimed that the involvement of R-phase related processes in thermomechanical behaviors of common binary superelastic NiTi wires is more important than commonly acknowledged.

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1. Introduction

Since shape memory alloys (SMA) are being used in engineering applications for their unique stress–strain–temperature functional hysteretic responses, it is necessary to understand these responses and predict them reliably. A serious problem is that multiple deformation mechanisms become active in various stages of cyclic thermomechanical loads on commercially most attractive NiTi alloy [1]. This complicates the modeling of its unique thermomechanical behavior. It is very challenging to identify experimentally the activity of individual deformation mechanisms in polycrystalline NiTi samples. Naturally, noninvasive *in situ* experimental techniques, which do not disturb the deformation processes occurring in thermomechanically activated samples, are needed. Electrical resistivity measurements

on wire specimens have traditionally been used for this purpose [2]. Although significant variations of electric resistance accompany the phase transitions and martensite reorientation processes, interpretation of the results in terms of the activity of individual deformation/transformation processes is commonly controversial [2]. Hence, alternative *in situ* experimental methods, which provide better links from the activity of deformation processes to macroscopically observed physical quantities are needed.

In this work, two recently developed *in situ* experimental techniques dedicated for SMAs (*in situ* neutron diffraction [3–6] and *in situ* combined ultrasonic and electric resistance measurement [6,7]) were used to investigate the deformation/transformation processes in activated NiTi wires related with the rhombohedral R-phase. The R-phase processes are least explored among all deformation/transformation processes in NiTi and their activity is very difficult to detect just from macroscopic stress–strain–temperature curves due to the small crystallographic strain associated with the R-phase and further peculiar

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features (continuous variation of R-phase distortion below R_f [1,5]). That is why the R-phase has been focused in this work.

2. Experimental

2.1. Neutron-diffraction method

The motivation for using neutron diffraction to follow deformation processes in activated SMAs comes from the facts that the neutrons penetrate through the bulk specimens and provide structure sensitive information averaged over the whole gauge volume of the polycrystalline sample. The neutron powder diffraction data are collected in stopovers during thermomechanical cyclic tests typically at constant temperature and stress or strain. Individual reflections of the austenite and martensite phases are analyzed (single-peak fit) for integrated intensities and peak positions. The experimental results are typically provided in a form of the evolution of the integral peak parameters with the applied stress, strain and temperature in the test.

As the applied stress increases in a mechanical test, the crystal lattice becomes elastically deformed and the lattice spacings change. The elastic strains, ε_{hkl} , in particularly oriented grains, called lattice strains further on, are evaluated from the diffraction measured deviations of d_{hkl} -lattice spacings (Eq. (1)):

$$\varepsilon_{hkl} = \frac{d_{hkl} - d_{0,hkl}}{d_{0,hkl}} = \frac{\Delta d_{hkl}}{d_{0,hkl}} = -\cot(\vartheta)\Delta\vartheta \quad (1)$$

where ϑ is the diffraction angle and $d_{0,hkl}$ and $I_{0,hkl}$ are, respectively, the lattice spacing and integrated intensity of hkl reflections measured at zero stress. Martensite phase fractions, ξ_{hkl} , in sets of equally oriented grains can be evaluated from the integrated intensities of the austenite reflections, I_{hkl} (Eq. (2)):

$$\xi_{hkl} = \left(1 - \frac{I_{hkl}}{I_{0,hkl}}\right) \quad (2)$$

Neutron diffraction on a transforming SMA polycrystal thus works like a multiprobe that uses crystal lattices of the austenite and martensite phases as built in gauges distributed throughout the specimen volume capable to detect lattice strains (stresses) and peak intensities (phase fractions) in suitably oriented grains. This information is interpreted with the help of micromechanics modelling [8,9] in terms of mechanics of martensitic transformation in polycrystal environment (see Refs. [4,6,8,9] for details).

In situ neutron diffraction experiments were made using neutron diffractometer TKSN 400 dedicated to strain measurements at research reactor at NPI Rez, Czech Republic equipped with a tension/compression (T/C) deformation rig and hot air heating systems. Only narrow diffraction patterns (2θ range = $\sim 10^\circ$) in axial geometry (scattering vector parallel to load axis) were measured using monochromatic radiation ($\lambda = 0.224$ nm, instrumental resolution $\Delta d/d = 2 \times 10^{-3}$).

Ni49.5Ti (at.%) (denoted as NiTi-R) alloy bar specimens ($d_s = 5$ mm, $l_s = 50$ mm and $l_s = 15$ mm) were used in the experiments. The specimens exhibited B2 \rightarrow R \rightarrow B19' sequential transformation ($R_s = 25^\circ\text{C}$, $M_s = -13^\circ\text{C}$) in a stress free thermal cycle following heat treatment at $T = 500^\circ\text{C}$ for 1 h and quenching in ice water.

2.2. Combined ultrasonic and electric resistance method

Neutrons are, however, scarce and difficult to use for *in situ* diffraction studies of thin NiTi wires of major application interest. Hence we searched for other signals that can be used to probe noninvasively the deformation processes in activated NiTi. Acoustic waves and electric current sensitive to the variations of elastic and electrical properties accompanying the deformation/transformation processes in the NiTi wires are utilized as such signals in the recently developed *in situ* ultrasonic and electric resistance measurement technique called USERIST [6]. In the USERIST measurement, the speed C_L and attenuation α of ultrasonic waves and electric resistance ρ are simultaneously measured on NiTi wires exposed to thermomechanical loads. Physical reasons behind the observed evolutions of the ρ , α and C_L (more details in Refs. [6,7]) will not be discussed here due to the lack of space. Let us only point out that these quantities vary with: (i) phase composition (volume fraction of B2, R, B19' phases), (ii) texture in martensites—orientation distribution of crystallographic variants of R and B19' phases (elastic and electric properties are anisotropic), and (iii) rhombohedral distortion and elastic properties of the R-phase [6,9] varying continuously below the R_f temperature.

The experiments were carried out on superelastic wires (Fort Wayne Metals, $d_s = 0.18$ mm, $R_s = 18^\circ\text{C}$, $M_s = -92^\circ\text{C}$) and shape memory wires (Memory-Metalle GmbH, $d_s = 0.7$ mm, $R_f = 30^\circ\text{C}$, $M_s = -20^\circ\text{C}$, $A_s = 30^\circ\text{C}$).

3. *In situ* neutron diffraction measurement

Main advantage of the *in situ* neutron diffraction method for the studies of phase transforming materials is that the phases (structures) existing temporarily under stress in bulk SMA specimens can be identified according to their characteristic powder diffraction patterns. Any change of the diffraction pattern evidences either phase transformation or texture change in martensite phase [4]. Let us demonstrate this using Fig. 1. Stress–strain curves measured in two compression tests on NiTi polycrystal bar at temperatures $T = 60$ and 22°C are shown in Fig. 1a. One can distinguish elastic parts and transformation plateau parts on both σ – ε curves but it is not clear why the elastic slopes are so different and which deformation processes are involved. The results of the *in situ* diffraction measurements (Fig. 1b and c) carried out in denoted stress–strain points provide relevant information. It appears that, upon loading at $T = 60^\circ\text{C}$, elastic deformation is the only deformation mechanism activated between points 0–5 (austenite reflection $1\ 1\ 1_A$ shifts towards the lower d -spacings as the compression stress increases in the elastic range). Upon further loading beyond the point 5, the intensity of the $1\ 1\ 1_A$ reflection decreases and $1\ 2\ 0_M$ martensite reflection appears and grows, which suggests progress of the stress induced B2 \rightarrow B19' martensitic transformation. Martensite reflection $1\ 2\ 0_M$ corresponds to stress induced B19' variants in $\langle 1\ 1\ 1 \rangle$ oriented grains with shortest lattice spacing parallel to the load axis [4]. On the other hand, the diffraction patterns recorded at $T = 22^\circ\text{C}$ (Fig. 1c) in stress points 0–8 clearly show that, in the apparent elastic range, there is an exchange of intensity between

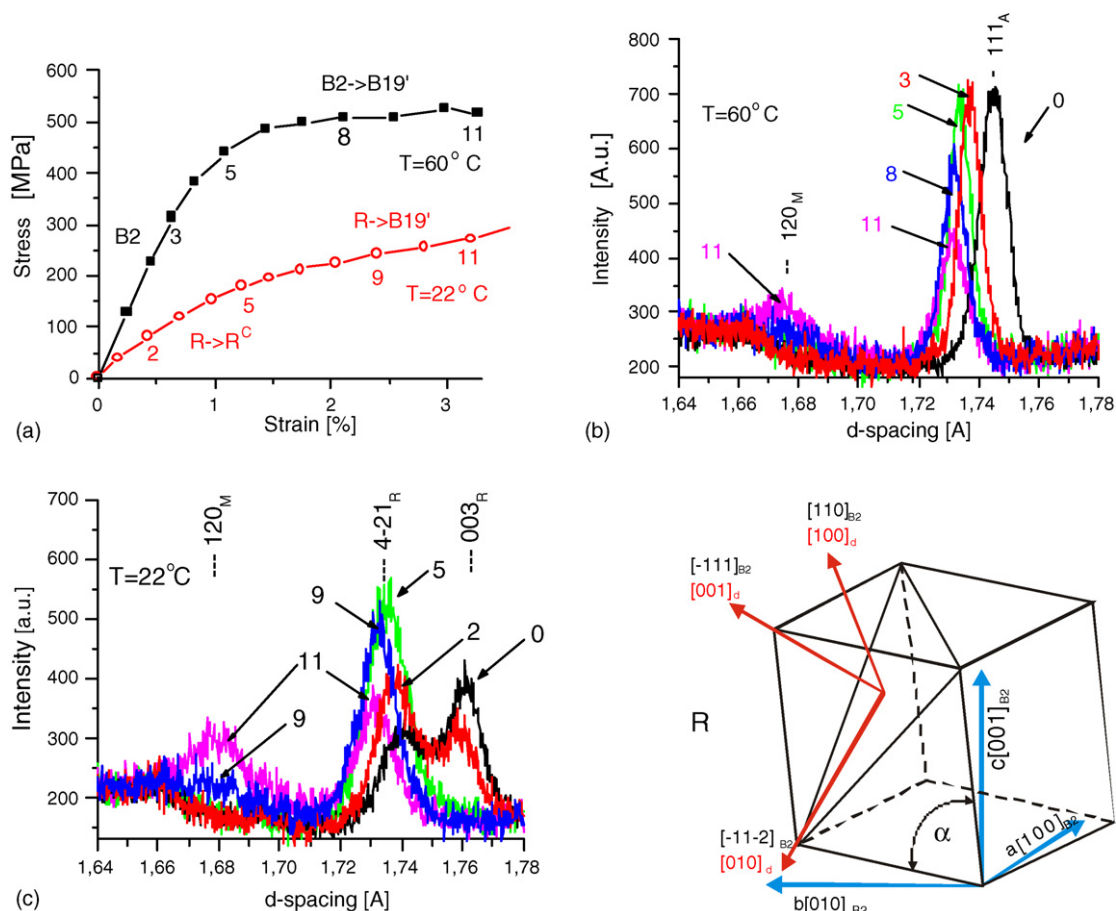


Fig. 1. Results of two *in situ* neutron-diffraction tests on NiTi superelastic bar specimen ($R_s = 25^\circ\text{C}$, $M_s = -13^\circ\text{C}$) during compression at $T = 60^\circ\text{C}$ (b) and $T = 22^\circ\text{C}$ (c). Neutron diffraction patterns in axial arrangement (b and c) were recorded in stress points denoted on σ - ε curves (a). The 111_A austenite reflection (b) splits upon cooling below R_f temperature (c) into two R-phase reflections corresponding to one longer (003_R) and three shorter diagonals ($4\cdot21_R$) of the cube undergoing the rhombohedral distortion along its space diagonal (d).

two R-phase reflections ($003_R \rightarrow 4\cdot21_R$) both originating from the 111_A parent austenite reflection [5]. This evidences that not just elasticity but also twinning reorientation processes in the R-phase towards the variants with lower d -spacings aligned with the load axis are in fact responsible for the lower slope of the apparently elastic part of the compression stress-strain curve at $T = 22^\circ\text{C}$. In total, the activity of four different deformation/transformation processes (elasticity, $R \rightarrow R$, $R \rightarrow B19'$ and $B2 \rightarrow B19'$) were thus distinguished by the *in situ* neutron-diffraction method.

Unusual mechanical phenomena were found in stress-strain tests on the same NiTi alloy performed at various temperatures [5]. In particular, the slope of the apparently linear elastic parts of the compression σ - ε curves was found to decrease with decreasing temperature and an unexpected asymmetry in elastic parts of σ - ε curves in tension and compression was observed. It was confirmed by the neutron diffraction [5] that both phenomena are related with the R-phase activity in the apparently elastic range and later rationalized with the help of micromechanics modelling of NiTi polycrystalline aggregates undergoing $B2 \rightarrow R \rightarrow B19'$ transformation [8,9]. In brief, the larger R-phase distortion at lower temperature results in lowering the slope of the apparently elastic part of the σ - ε curves with

decreasing temperature below R_f and the tension/compression asymmetry of the apparent elastic slopes originates from the fact that the R-phase processes in 111 textured NiTi bars have larger strain capacity in tension than in compression [9].

Fig. 2 shows results of a thermomechanical *in situ* neutron diffraction experiment on the same NiTi-R alloy in which both temperature and stress vary simultaneously. Particularly, generation of recovery stress during heating a sample subjected previously to 1.2% strain in tension, unloaded and constrained at 0.3% tensile prestrain was investigated. The stress increases upon heating (Fig. 2b) with relatively large slope $s = d\sigma/dT = 17$ MPa/K, but the increase saturates after reaching $\sigma \sim 300$ MPa level. The recorded neutron diffraction patterns (Fig. 2a) provide a clear evidence that the R-phase had almost reoriented during the small tensile predeformation (compare the intensity of the R-phase peaks recorded at $T = 22^\circ\text{C}$ prior and after tensile deformation). Upon subsequent heating, there is an extensive exchange of the intensity between the 003_R and 111_A reflections suggesting a massive reverse $R \rightarrow B2$ transformation accompanying the generation of the recovery stress upon heating (Fig. 2b). Once the 003_R intensity decreases to zero (no more R-phase exists in the 111 oriented grains and most likely in the whole sample), the stress does not increase anymore. This

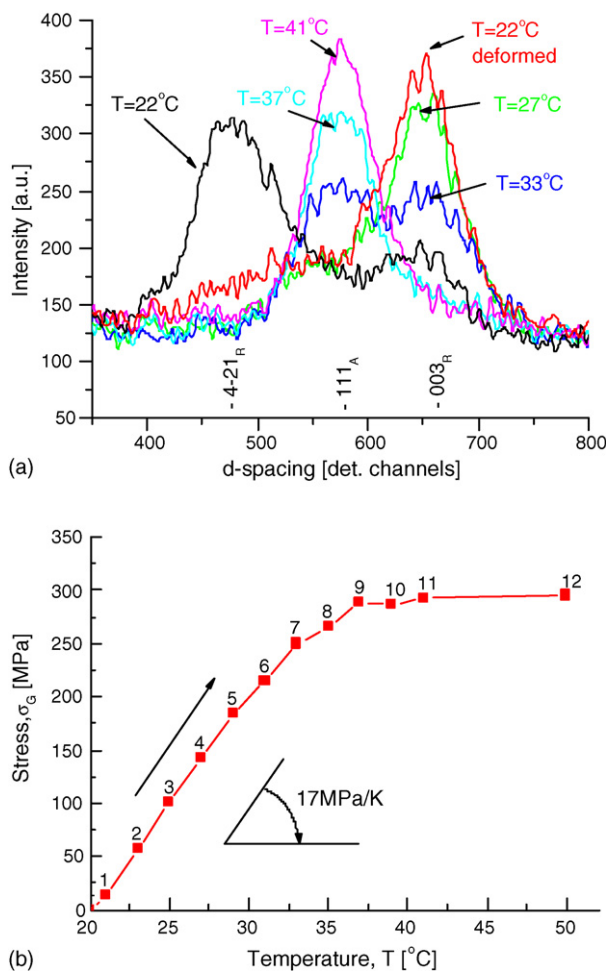


Fig. 2. Results of *in situ* neutron diffraction measurement during recovery stress test. Diffraction patterns (a) and macroscopic stress–temperature response (b) recorded during heating of the deformed NiTi-R bar specimen, the length of which was held constant (0.3% prestrain). The sample was deformed in tension at room temperature $T=22^\circ\text{C}$ up to 1.2% and unloaded prior the experiment.

clearly supports the view that the large slope $s=17\text{ MPa/K}$ is due to the R-phase and that the intrinsic limit on the recovery stress generation originates from the expiration of the R-phase upon heating. Both phenomena are directly related to the small crystallographic transformation strain of the $\text{B2} \leftrightarrow \text{R}$ transformation.

However, one has to be very cautious with interpretation of the diffraction results presented in Figs. 1 and 2, since any information obtained from the analysis of $1\ 1\ 1_A$ reflection concerns only the $\langle 1\ 1\ 1 \rangle$ oriented grains of the sample [4,6]. Different information would be obtained using another hkl_A austenite reflection—looking at another set of $\langle hkl \rangle$ oriented grains. Multi-peak time of flight experiments [4,5] combined with micromechanical model simulation of NiTi polycrystal behaviors [8,9] provided interesting details about the scenario of the load and phase fraction partitioning in the transforming NiTi polycrystals.

Results of systematic *in situ* neutron diffraction studies of NiTi alloys transforming in various thermomechanical cyclic tests via sequential $\text{B2-R-B19}'$ transformation can be found

in Ref. [10] and correspondent modelling work in Ref. [9]. According to simulations of the recovery stress generation due to $\text{R} \rightarrow \text{B2}$ transformation (see Fig. 11 in Ref. [9]), even if the macroscopic recovery stress steeply increases upon heating (Fig. 2b), the local stresses in $\langle 1\ 1\ 1 \rangle$ oriented grains remain relatively low (explains the negligible peak shift with increasing stress (Fig. 2a)) and the R-phase in these grains transforms very late to the B2 phase (explains why $0\ 0\ 3_R$ and $1\ 1\ 1_A$ peak intensities in Fig. 2 exchange later upon heating between points 6 and 11 ($T=31\text{--}41^\circ\text{C}$)).

4. *In situ* ultrasonic and electric resistance measurement

Fig. 3 shows selected results of USERIST tensile tests on a superelastic NiTi wire at three not very different temperatures $T=22, 31$ and 37°C . Trivial effects of dimensional changes on C_L , α and ρ were subtracted from the recorded signals. One can see that the recorded $\sigma\text{--}\varepsilon$ curves are all pseudoelastic and not that much different, although the plateau stress increases with increasing test temperature. The recorded evolutions of the C_L , σ and ρ at different temperatures however, differ significantly. This evidences that different deformation/transformation processes (see labels in Fig. 3) were activated during the tensile tests at different temperatures.

It appears that three distinct processes (elasticity, $\text{B2} \rightarrow \text{R}$, $\text{R} \Rightarrow$) take successively place in early stages on the tensile test ($\varepsilon < 1.2\%$) at $T=22^\circ\text{C}$ (Fig. 3a). It is interesting to note that the strains appearing upon further loading the stress induced R-phase above 300 MPa are accompanied by an unusual steep increase of the C_L (decrease of the attenuation α). We consider this to be due to a third newly revealed deformation process called R-phase distortion (denoted as $\text{R} \Rightarrow$). It reflects a curious elastic behavior of the R-phase—further continuous distortion of its structure with decreasing temperature and/or increasing stress. Its activity in mechanical tests could not have been positively recognized in the earlier neutron diffraction studies [10] due to technical reasons (both distortion and elastic stretching appears as peak shift). Significant variations of C_L and α have never been observed during elastic loading of the austenite (Fig. 3c) or martensite (Fig. 4b) phases. The R-phase distortion takes place upon loading in the temperature range $T=20\text{--}29^\circ\text{C}$ (Fig. 3a). At higher temperatures ($T=31^\circ\text{C}$, Fig. 3b), the stress induced $\text{B2(R)} \rightarrow \text{B19}'$ transformation starts (plateau appears on the $\sigma\text{--}\varepsilon$ curve) before the $\text{B2} \rightarrow \text{R}$ process is completed, so that the $\text{R} \Rightarrow$ distortion process does not occur.

It shall be pointed out that the measured instant values of ρ , α and C_L are in principle average values over a mixture of phases currently existing in the specimen [6]. Since the activity of multiple deformation processes overlap in polycrystalline wires, interpretation of the USERIST data is not straightforward and requires usage of dedicated modelling tools (as e.g. Refs. [8,9]) capable of dealing with multiple deformation mechanisms in SMAs. Let us point out that the $\text{B2} \rightarrow \text{R}$ transformation and $\text{R} \Rightarrow$ processes could not have been mutually distinguished just from the electric resistance measurements, since ρ continuously increases with increasing stress in both cases.

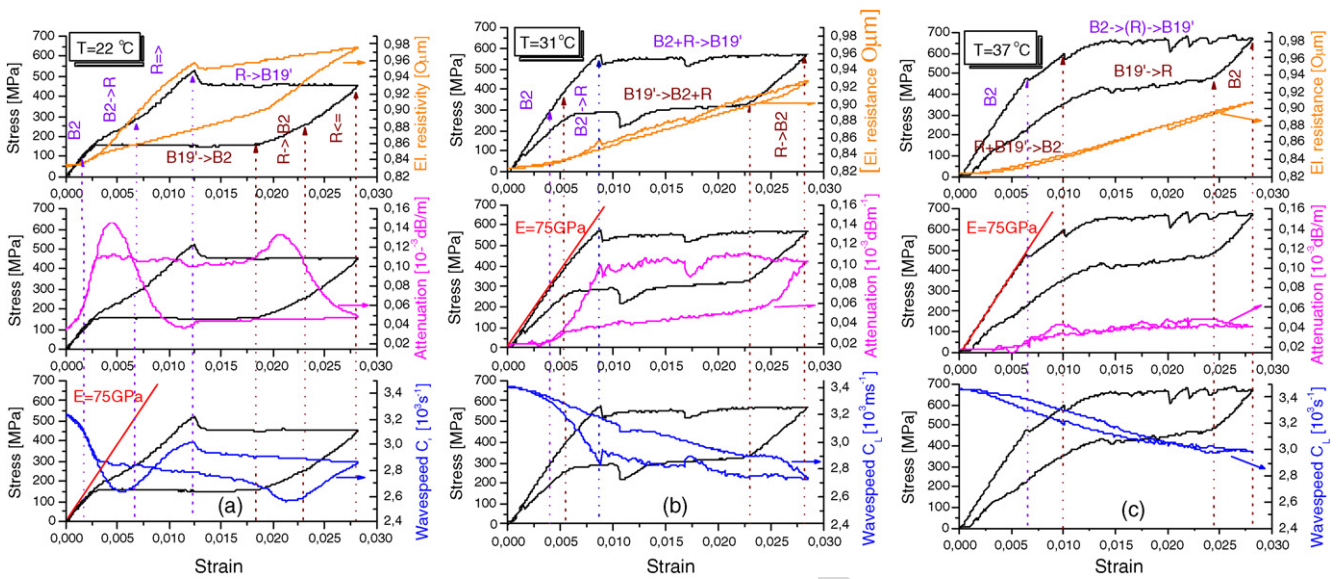


Fig. 3. Results of three USERIST tensile tests on superelastic NiTi wire ($d_s = 0.18$ mm, $R_s = 18$ °C, $M_s = -92$ °C) at: (a) $T = 22$ °C; (b) $T = 31$ °C; (c) $T = 37$ °C. The set of nine graphs shows the recorded the electrical resistance ρ (top), attenuation α (middle) and wave speed C_L (bottom) of the longitudinal acoustic wave propagating through the wire transforming in pseudoelastic tensile tests. Variations of the ρ , α , C_L during the test reflect the activity of distinct deformation/transformation processes (top figures) in the wire.

Fig. 4 shows results of two USERIST tests on a different NiTi wire deformed twice at the same temperature, but in different structural states (in the R-phase (Fig. 4a) and in the B19' martensite phase (Fig. 4b). This could be achieved taking advantage of the thermal hysteresis effect. In spite of the different structural state of the wire at the test start, mechanical responses are not that much different. Nevertheless, based on the USERIST signals C_L , α and ρ , activity of distinct deformation processes in both tests could be distinguished [6] (see labels in top, Fig. 4).

R-phase related processes were also clearly detected in USERIST studies during thermomechanical recovery stress

tests. Selected results are shown in Fig. 5. The superelastic wire was heated to $T = 95$ °C (stage a), deformed at this temperature up to prestrain $\epsilon = 0.85\%$ (b), cooled (c)–heated (d)–cooled (e) while the prestrain $\epsilon = 0.85\%$ was kept constant (Fig. 5a and b). Finally, the wire was finally unloaded at $T = 22$ °C (f). Clearly, as the temperature approaches $T = 40$ °C upon cooling (Fig. 5c and d), the stress starts to decrease. The electric resistance ρ , wave speed C_L and attenuation α drastically change upon cooling below $T = 40$ °C as well, which evidences the start and progress of the $B2 \rightarrow R$ transformation accompanying the stress variation. The natural limit on the recovery stress generation upon

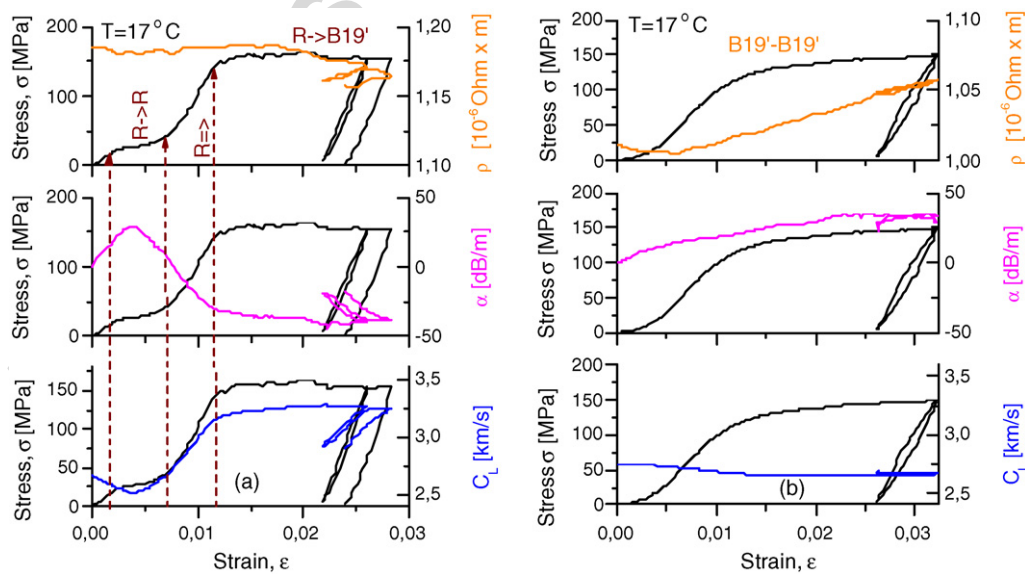


Fig. 4. Results of two USERIST tensile tests on NiTi shape memory wire ($d_s = 0.7$ mm, $R_f = 30$ °C, $M_s = -20$ °C, $A_s = 30$ °C) in R-phase state (a) and in the B19' martensite state (b). Variation of the electrical resistance ρ (top), attenuation α (middle) and wave speed C_L (bottom) of the longitudinal acoustic wave propagating through the wire is compared with the α - ϵ responses of the wires.

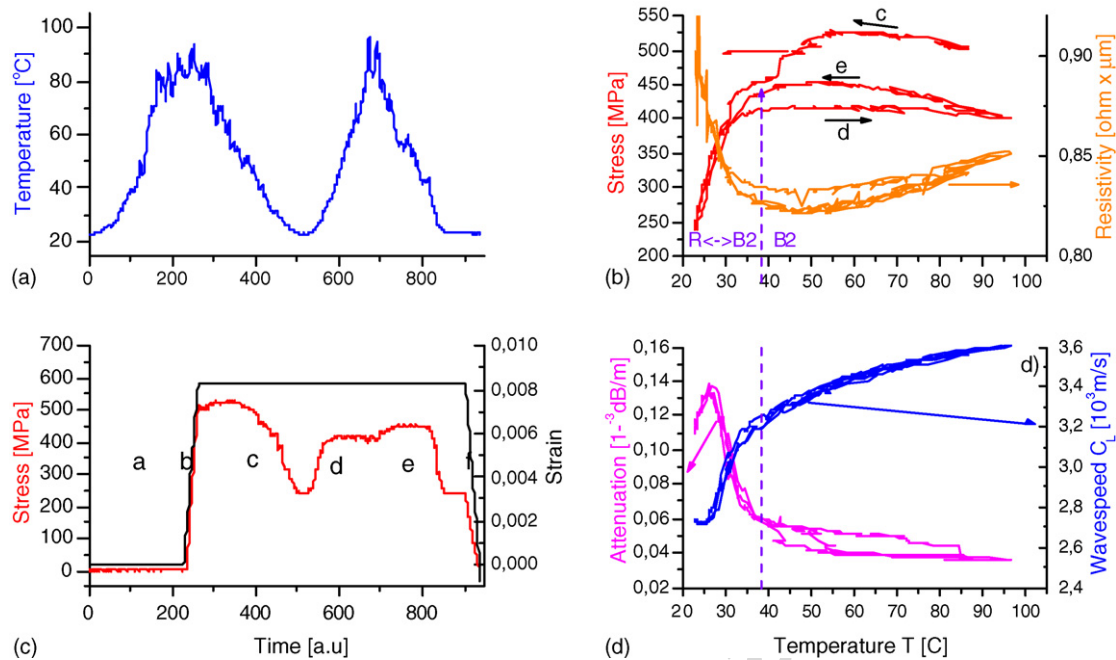


Fig. 5. Result of USERIST experiment during recovery stress test on superelastic NiTi wire ($d_s = 0.18$ mm, $R_s = 18$ °C, $M_s = -92$ °C). Variation of the temperature (a), stress and strain (b), stress and electric resistance (c), wave speed C_L and attenuation α of longitudinal acoustic wave (d) measured during cooling–heating–cooling at tensile prestrain 0.85%.

heating is due to the expiration of the R-phase (as known from diffraction studies [10] (Fig. 2) and modelling [9]).

5. Conclusions

Two *in situ* experimental techniques (*in situ* neutron diffraction and *in situ* combined ultrasonic and electric resistance measurement) were used to investigate the thermomechanical behavior of NiTi wires related with the R-phase. Both techniques are particularly suitable for monitoring the R-phase related processes, the activity of which is otherwise very difficult to trace just from the σ – ε – T responses recorded in thermomechanical experiments.

It was found that the R-phase related processes become surprisingly active during thermomechanical loading of commercial superelastic NiTi wires in a wider range of stresses, strains and temperatures than expected. The R-phase processes were found to be largely responsible for recoverable strains 0–1.5% above the M_s temperature as well as for recovery stress generation with large $d\sigma/dT$ slope and natural upper limit upon heating. Since small strains are commonly used in engineering applications, the R-phase processes should be seriously considered in modelling of thermomechanical behavior of binary NiTi wires.

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