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METASTABLE EFFECTS ON MARTENSITIC TRANSFORMATION IN SMA
PART VII. Aging problems in NiTi

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Shape memory alloys (SMA) are interesting for applications in damping of civil engineering structures. To achieve the SMA as a guaranteed material for damping of structures requires a reliability study of the static and dynamic properties adapted to each type of application. Here we present static (temperature and time effects) and dynamic actions in pseudo-elastic NiTi SMA. We concern with long time effects of temperature and time mainly in beta phase.

NiTi results are presented, including measurements of electrical resistance as a function of temperature and time, DSC to –80°C (TA Instruments), non-conventional conduction calorimetry (to 80 K), and several X-ray diffraction spectra at different temperatures. Diffusion effects are present, and all the measurements show that transformation temperatures change with time of aging even at moderate temperatures (i.e., near 100°C), depending on time and temperature. It is possible to visualize the diffusion change in the R phase transformation via classical X-ray characterization. We include some results of pre-stressing effects applying the stress at different zones of the hysteresis cycle. The experimental analysis shows that coupling between stress and temperature enhances the changes. For long times (10, 20 years) and direct sunny actions, more deep analysis is required. Finally, some dynamic effects in cycling affecting the SMA creep are outlined.

Keywords: *aging, creep, martensitic transformation, NiTi, SMA, temperature effects, time effects*

Introduction

One of the applications of SMA is the damping using their hysteresis cycle. In the pseudoelastic state, they might recover strains of some percent (near 8% for NiTi wire), under stresses of some hundred MPa, with considerable hysteresis. To achieve the SMA as a guaranteed material for damping of structures, it is required a study of the static and the dynamic properties, and its endurance. Here we will present the static temperature and time effects and dynamic actions in pseudoelastic NiTi SMA.

The relevant properties of SMA include both mesoscopic/macroscopic properties for applications, as: self-heating on mechanical cycling, the Clausius–Clapeyron coefficient effects (namely, the direct summer–winter effects on the transformation stress), the internal loops (with hysteresis dependent on amplitude), the SMA creep effects (progressive elongation of a sample when mechanically cycled), and the fatigue life effects, or effective number of cycles a sample can withstand.

In Cu-based alloys, as CuAlZn, there are well established some diffusion effects. For instance, there is the 'classical' effect of martensite stabilization, by which, after transforming to martensite and waiting some time, the reverse transformation (to β) is difficult or even avoided. Also, in Cu-based alloys, phase coexistence between beta and martensite produce changes of properties with time (quantity of martensite tends to increase at constant temperature and applied stresses) [1]. In NiTi, only some limited time effects are noticed [2, 3].

This paper is the seventh one of a series about metastable effects on martensitic transformation in SMA. The first paper of this series was centered in effects induced by the action of thermodynamic forces (stress and temperature) in the parent phase of CuZnAl single crystal (paper 1) [1]. The paper 2 [4] is focused in the heat treatment required for appropriate grain growth avoiding the SMA creep (with extremely reduced accumulative deformation effect in working cycles). The paper 3 [5] is related to diffusion effects induced by aging in NiTi, and the paper 4 [6] is mainly centered on SMA dynamics and simulation in civil engineering structures for damping applications. In paper 5 [7] the fatigue-life required for application in damping of earthquakes in Civil Engineering applications is studied and some conditions to improve the number of working cycles

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previous to fracture are established. In addition, the evolution of the dissipated frictional energy with cycling is analyzed. The study shows some minor effects related to self-heating and subsequent cooling processes, and also associated to atomic diffusion phenomenon. In paper 6 [8] the formalism of the Clausius–Clapeyron coefficient (CCC), in the frame of equilibrium thermodynamics, is considered. In this frame, the thermodynamic conditions for the phase coexistence in one 1-D transformation are established and visualized in practical comparison with the experimental measurements. The experimental procedures are revisited according to the thermodynamic point of view, and the origin of some difficulties is pointed out. Also, an experimental approach for CCC evaluation in CuAlBe and in NiTi is suggested.

In the present paper we are concerned with two actions: first the static long time effects of temperature stress and time mainly in β phase. NiTi results are presented, including measurements of electrical resistance as a function of temperature and time, DSC to 193 K (TA Instruments), non-conventional conduction calorimetry (to 80 K), and X-ray diffraction as a function of temperature. The second action concerns only extremely partial effects on dynamic effects. Diffusion effects are present, and all the calorimetric measurements show that the transformation temperatures (the shape of calorimetric output signal changes) change with time of aging even at moderate temperatures (i.e., near 373 K), depending on time and temperature. It is possible to visualize the aging change in the parent-R phase transformation via classical X-ray characterization.

Some remarks and conclusions can be outlined. First, the aging effects in β phase NiTi are very slow at moderate temperatures. For instance, time constants of several months at 373 K, compared to approximately two days for CuAlBe long time after quenching and only around 1 h for the first time constant of CuZnAl at 373 K. The evaluation of the time constants for NiTi of the evolution at moderate temperatures remain a rough estimation due to the long times implied. Second, the amplitude of the changes in transformation temperature remains uncertain as they are difficult to determine the values due to the time scales involved. In particular, the time scales seems related with the used lower temperature limit in thermal cycles. Further, it is not possible at the actual state to give a reliable upper boundary for the transformation temperature changes. In the Cu-based alloys as CuAlBe or CuZnAl, the amplitude of the Ms changes was found to be around 15% of the change on the aging temperature.

Then, long time applications of NiTi i.e., many years as the standby time previous to earthquake appearance, might encounter difficulties, even in situations as common as when the material is situated under the external conditions, i.e. under the direct sunlight actions. The use of NiTi in engineering in general, or in civil engineering, should only be accepted in well known conditions and with life-time evaluated in the expected conditions, fulfilling the requirements of use. On the other hand, a rough estimation shows that medical applications (as dental wires used at 37°C or 310 K for several months) should expect a time constant larger than 100 years, being, in the actual state of the art, appropriate for use, with respect to any transformation temperature evolution always irrelevant. The diffusion effects in an immediate application to damping near room temperature (some weeks, as in satellite launching, or in damping stayed cables of bridges) have low relevance. In these applications the fatigue-life is the relevant parameter for guaranteed behavior. With strong wind, damping of cables requires 10^5 oscillations/day: the NiTi fatigue-life is the more relevant condition for useful application.

We have also made a partial study of the time effects of pre-stressing actions. Depending on the application this feature can be more or less relevant: for damping cables in bridges, submitted to the action of the wind, the previous time of inactivity is irrelevant (i.e., some hours or days). If the pre-stressed material shall act as a damper for earthquakes, the time of inactivity can reach several years or decades and also it will be submitted to yearly changes of temperature between winter and summer (i.e., 40 K or more). It is necessary to ensure the guaranteed behavior in all cases [6]. We present some results of pre-stressing effects in the different zones of the cycle: in the elastic zone, in the coexistence zone or when all the material is transformed to martensite, for different times and in the last case also for different temperatures.

Experimental

With the aim to quantify low temperature aging effects in NiTi, we have performed different kind of measurements: calorimeters, X-ray diffraction and electrical resistance. Calorimetric measurements have been made with non conventional calorimeter, cooling with liquid N_2, cycling between 320 and 90 K, and also using a TA Instruments [5, 9] Q1000 Differential Scanning Calorimeter using the Tzero technology (TA Instruments) cycling between 313 to 191 K. An X-ray diffractometer INEL was used, with Cu tube, and graphite monochromator (using $K\alpha_1$, λ=0.15406 nm), with detector CPS 120 (5644 channels). For the temperature control we used an Oxford Cryosystems, 700 series cryo-stream plus. The electrical resistance measurements have been made with a four-point technique and computed controlled temperature.

The samples used were of NiTi from Special Metals [10], in pseudoelastic state. Samples ‘as furnished’ of 2.46 mm and around 120 mg have been used for non-conventional calorimeter. Later they have been aged at 100°C and thermally cycled after different aging times. For the DSC calorimetry cycles. For the X-ray and electrical resistance measurements similar wires (diameter of 0.5 mm) are used.

For the study of the pre-stress effect, the used samples are wires of NiTi ‘as furnished’ from Special Metals in pseudoelastic state (55.8 mass% of Ni), of 0.5 mm diameter and 1.01 m of length. The stress-strain-time analysis is realized using a home made ‘like Instron’ machine. We measure the deformation using the nominal position of the sample grip, the force via a digitalized HBM sensor, and the temperature with an OMEGA E thermocouple (chromel-constantan).

Quasi-static: temperature-time effects measurements

In other shape memory alloys, as CuZnAl and CuAlBe, it has been detected diffusion effects at 373 K or at room temperature. Some measurements have been done in order to try to quantify this kind of effects in NiTi, if quantitatively exists. First of all we characterized the behavior of as furnished samples (in pseudoelastic state). Later, to obtain sufficient data, the samples were aged at 373 K for different times, 31, 59, 118, 240, 301 and 361 days, and measured.

In Fig. 1a and b the directly obtained calorimetric output: the roughly heat power signal in Watts from calorimetric measurements is represented against temperature. We can see in Fig. 1 that in the cooling the sample as furnished (or ‘as is’) shows a peak, that we call ‘peak 1’, centered at the temperature Rs corresponding eventually to the β to R phase transformation (see below at the part devoted to resistance and X-rays), and a signal corresponding to the R to martensite change, designed as peak 2 that is not a sharp peak, the shape is largely broader. In the heating, two mean peaks are observed, that we call ‘peak 2’ and ‘peak 1’, that are very close one to each other. The baseline in cooling and heating shows uncertainties related to artifacts of measurements. The peaks 2 and 1 correspond to the retransformation from martensite to R phase, and from R to β phase respectively, as it will be shown in X-ray part. Finally we detected a very small peak, near to 300 K (Fig. 2b) produced by the thermocouple plate.

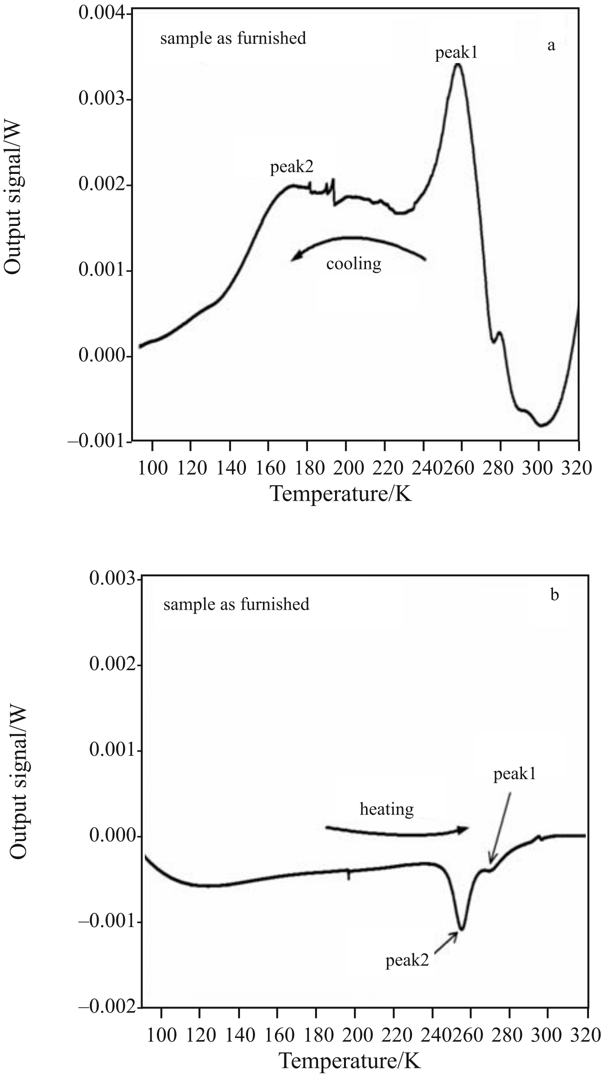

Fig. 1 Calorimetric output signal in a sample of NiTi of 2.46 mm diameter, as furnished, using non-conventional calorimetry. a – cooling, b – heating

We have represented the same graphs in Figs 2a and b, dividing the direct signal by the local temperature rate, and per mass, obtaining in this way the signal in kJ kg^{-1} K^{-1}, and the area comprised between a peak and the baseline gives the dissipated or absorbed energy in the cooling or heating process per mass unit. With this kind of representation the identification of peaks is more relevant. In fact, the direct output signal of calorimeter is modified by the temperature rate modifying the shape. The temperature rate in non-conventional calorimeter that uses spontaneous heating and cooling is, near ‘exponential’.

In Figs 2a and b, corresponding to the cooling and heating of one sample as furnished (without aging), the two peaks of transformation (eventually: β to R phase, and R to martensite), and both peaks of retransformation are well observed. We repeated the calorimetric measurements two times for each sample

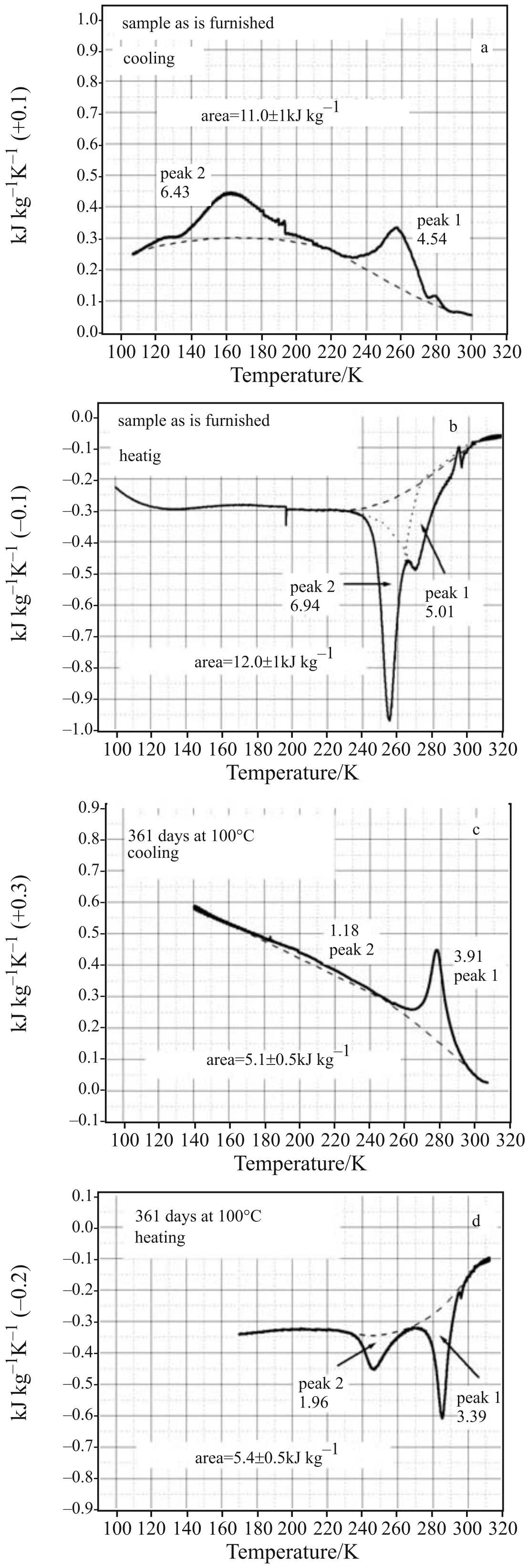

Fig. 2 Energy evolution cycling of NiTi of 2.46 mm diameter. Using the calorimetric curves the baselines are outlined. a and b – NiTi cooling and heating as furnished. c and d – NiTi cooling and heating after 361 days of aging at 373 K

after different aging times at 373 K. Figures 2c and d show the calorimetric curves for cooling and heating after aging 361 days.

Comparing the curves for ‘as furnished’ and aged samples, important features are observed related to the evolution of temperature position of peaks and the evolution of the area of these peaks. Concerning with the areas, applying linear or polynomial fittings to determine the baselines, as shown in Fig. 2, we found the values of dissipated or absorbed energy in the cooling or heating processes per mass unit, in kJ kg^{-1}, with an uncertainty between ±1 and ±0.5 kJ kg^{-1}. We can see in Fig. 2 how the global value decreases after aging, but also it is shown that initially, in the cooling, the peak 1 is lower than the peak 2, and after aging it is greater, and the same happened with both peaks in the retransformation: the peak 1 initially is lower than peak 2, and after aging it is the greatest. It is very remarkable that the two peaks

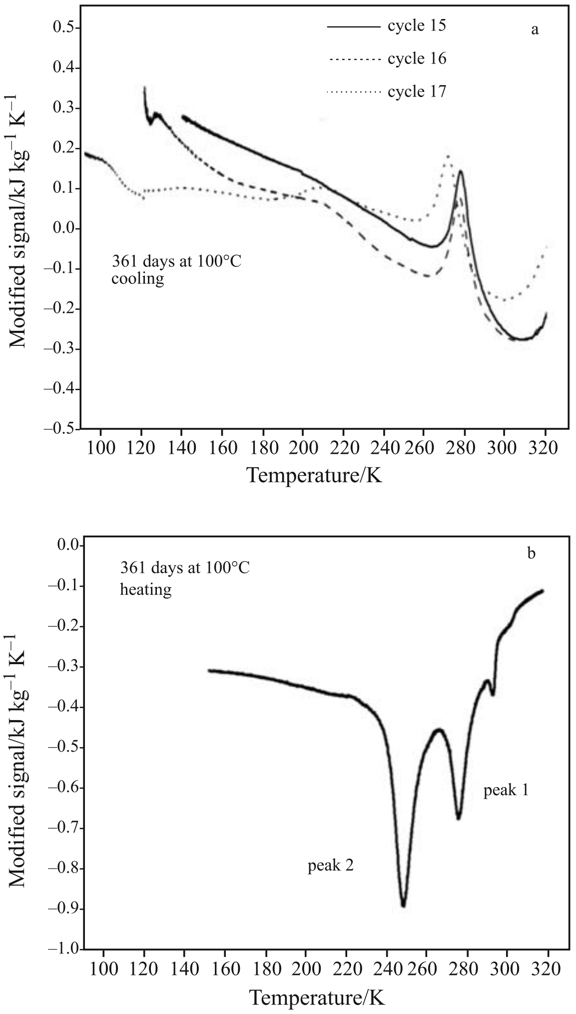

Fig. 3 a – Uncertainty in calorimetric curves (cooling for a NiTi sample of 2.46 mm diameter aged 361 days at 373 K), b – peaks in calorimetric heating for the same sample aged 59 days at 100°C

of the retransformation are present until the last aging time but in the cooling the lower temperature peak progressively reduces to practically disappearance, with an energy value under the error value (~1 kJ kg^{-1}).

In fact, as higher is the aging time, the shape of the peaks and the value of its areas in the cooling depend more on the evolution of the baseline and of the experimental scatter, as it can be seen in Fig. 3a. In this figure the three cooling graphs obtained after the 361 days of aging are shown. The value of the global area is the same in all cases (inside the indetermination range), but the values corresponding to both peaks change slightly. In Fig. 3b we show a graph corresponding to the calorimetric heating after 59 days of aging, to show that the splitting between both peaks, 2 and 1, is related with the aging time (Table 1).

Table 1 Aging time, temperature of peak 1 in heating, and difference of temperature between peak 1 and 2

Time aging/ days	Temperature peak 1/K	Diff. of temp. between peak 1 and 2/K
0	268.5	12.7
31	272.4	20.8
59	277.7	21.5
118	282.7	35.3
240	283.9	37.7
301	284.6	38.5
361	285.1	39.6

Attending to the evolution of the temperature of peaks, in cooling, the first peak (peak 1, corresponding to the Rs temperature, see the X-ray part), displaces to higher temperatures. In Fig. 4a we can see the evolution of the peak 1 to higher temperatures, which is coherent with the evolution already observed in the measurements made with TA Instruments DSC calorimeter in a reduced temperature span but these measurements show a greater time constant (250 days) [5]. In the heating, we can see that the peak of low temperature (peak 2), corresponding to the retransformation martensite to R phase, moves to lower temperatures and the peak 1, corresponding to the retransformation from R phase to β phase, is moving to higher temperatures. The displacement of the peak 1 to higher temperatures was also seen in the previous measurements made with TA Instruments DSC calorimetry [5]. In Fig. 4b (calorimetric heating), shows the evolution of peak 2.

The temperature of peaks is fitted with the following general expression, where τ is the time constant:

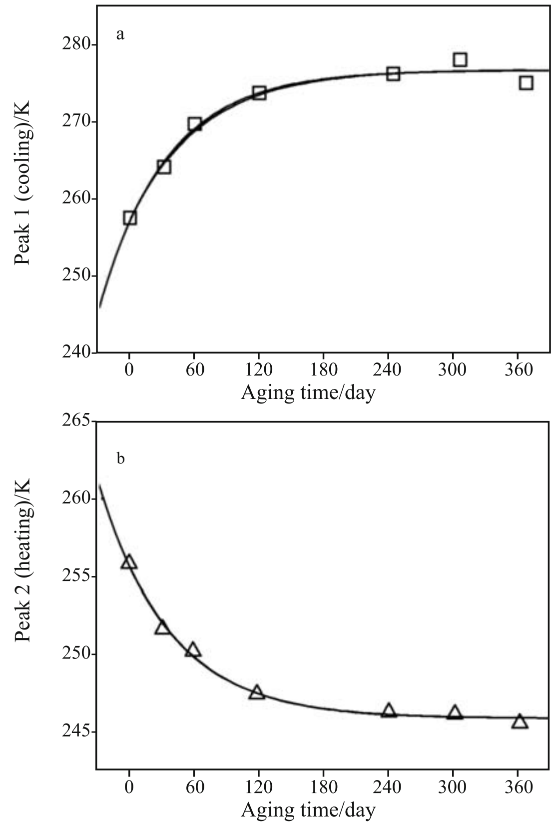

Fig. 4 a – Evolution of peak 1 (or Rs) temperature, when cooling, *vs.* aging time in days at 373 K (non-conventional calorimetry), for NiTi samples of 2.46 mm diameter, b – evolution of peak 2 in heating with aging

Table 2 Fit values for the temperature of centre of peaks

	T_0/K	ΔT/K	τ/day
Peak1 cooling	257.5	19.3	66
Peak 1 heating	267.6	17.2	66
Peak 2 heating	255.7	–9.9	66

$$T_{\text{peak}} = T_0 + \Delta T\left[1 - \exp\left(\frac{t}{\tau}\right)\right]$$

The fitted values for the three peaks are shown in Table 2.

Resistance and X-ray measurements

To improve the experimental behavior of aging of NiTi, we made complementary measurements of resistance and observations by X-ray diffraction. Wires of 0.5 mm diameter were observed at different temperatures, ‘as furnished’ and after aging for 75 days at 373 K. In both cases the three structures, β phase, R phase and martensite have been found. In Figs 5a, b and c, the typical X-ray spectrum of these

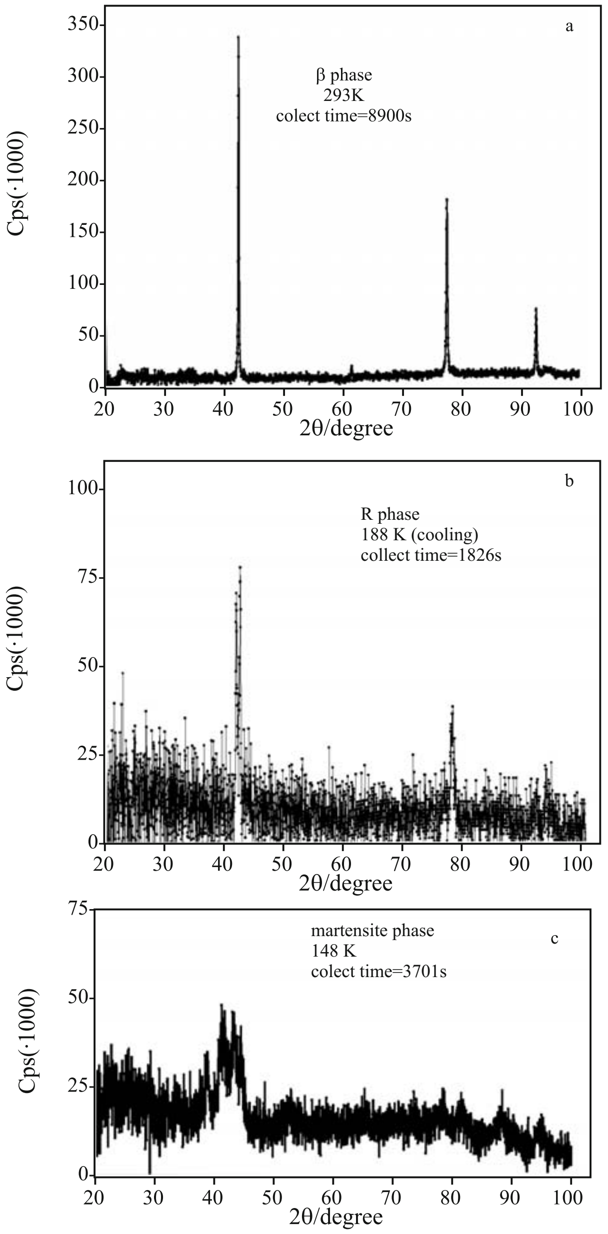

Fig. 5 X-ray diffraction of NiTi sample 0.5 mm diameter. a – as furnished and at room temperature (293 K) the beta phase structure spectrum is observed, b – as furnished, at 188 K (cooling), the R phase structure spectrum is observed, c – as received, at 148 K, the martensite phase structure spectrum is observed

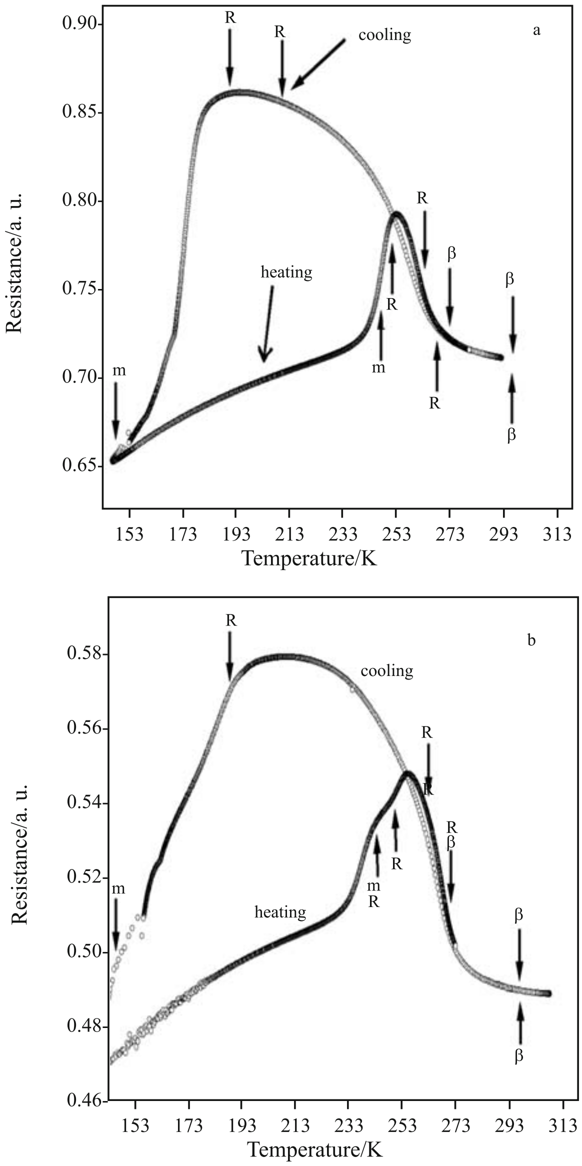

Fig. 6 Resistance measurements and phases observed *vs.* temperature by X-rays. NiTi sample 0.5 mm diameter, first cycle. a – as furnished,. b – after 45 days aging at 373 K

structures, observed in the sample as furnished at different indicated temperatures in cooling, is shown. The signal to noise ratio is extremely reduced in the X-rays spectrum of the martensite phase.

The same wires of 0.5 mm diameter were submitted to resistance measurements as a function of temperature. In Figs 6a and b the results for a sample as furnished and for a sample aged at 373 K for 45 days respectively are shown. In both figures the structures observed at different temperatures by X-ray diffraction observations are indicated. In these graphs of resistance *vs.* temperature, the curves changed from R phase to martensite in the cooling, and these phases have been identified by X-ray observations. The hysteresis between the R to martensite change in cooling is about 100 K.

Stress-time effects measurements

We studied the pre-stressing effects in the different zones of the cycle: in the elastic zone, in the coexistence zone or when all the material is transformed to martensite, for different times and, in the last case, also for different temperatures.

For the study of the hysteresis cycle (extremely slow cycles) we produce deformations in steps of 2.5 mm, and we wait 138 s between each step (a complete cycle stress-strain requires 2–3 h). During this time the stress decay to quasi-static value from the initial stress value produced by the self-heating induced by the latent heat locally released during the transformation (the local temperature recovers the room temperature value). The stress effect ($\Delta\sigma$) is proportional to local temperature change (ΔT) under the action of the phase transformation and the Clausius–Clapeyron coefficient of NiTi (6.3 MPa K^{-1}).

Pre-stress in coexistence zone

In a previous work [6] we found that after near one month of pre-stress in the elastic zone or in the coexistence zone, at room temperature, a step of stress is necessary to be applied to continue the transformation, with increasing values of the step as higher was the applied pre-stress. The step value was observed to reach near 20 MPa when the pre-stress was applied in the coexistence zone. For the present work we measured the pre-stress effect in the coexistence zone for different times at room temperature.

Also we measured the step obtained in the coexistence zone when an immediate cycle is made after pre-stress, as indicated in Fig. 7a. We show two consecutive hysteresis cycles at room temperature: the first one corresponds to the cycle obtained in which a pre-stress is applied in the coexistence zone for 27 days, and the second one is the immediate following one. In Fig. 7b the part of the stress step is amplified to see that the global increase $\Delta\sigma_{tot}$ to be able to continue the second cycle after near one month reaches 35 MPa, corresponding to two contributions: one part $\Delta\sigma_\beta$=20 MPa, corresponds to the increase in parent phase, that needs more stress to be able to continue the transformation, and it means that the critical stress for transformation (CST) has decreased. The second one, $\Delta\sigma_m$=15 MPa, corresponds to a decrease of the necessary stress to transform again in martensite phase, that means an increase in the CST. The global increase is then:

$$\Delta\sigma_{tot} = \Delta\sigma_\beta + \Delta\sigma_m$$

We found that the variation of the necessary stress to continue the transformation when the pre-stress is applied for one month in the coexistence zone, increases with time and can reaches a few tens of MPa. It is a minor effect for one month, but for long times (10, 20 years in the application of SMA for earthquakes) the variation (actually unknown) can become very important.

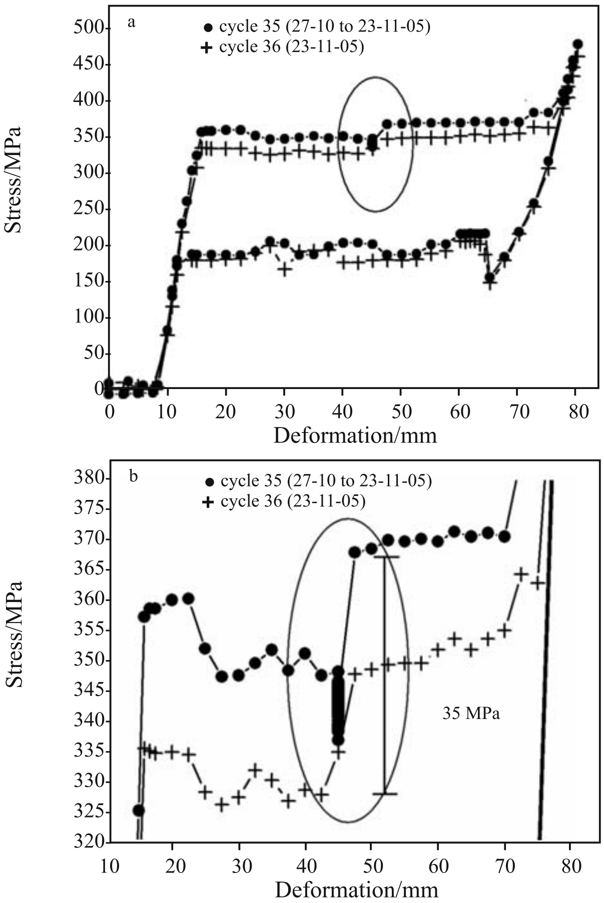

Fig. 7 a – Two consecutive hysteresis cycles at room temperature (293 K), the first one obtained applying a pre-stress in the coexistence zone for 27 days, and the immediate following one, b – global increase of 35 MPa ($\Delta\sigma_{tot}$) to be able to continue the second cycle

Pre-stress in martensite

We have also studied the effect of ageing with applied stress when all the material is transformed to martensite, for different times and temperatures. We made an inner loop after the aging, as shown in Fig. 8a and we measured the change $\Delta\sigma$ in the necessary stress to produce the transformation, between the cycle before the aging and the inner loop after it. The decrease of the stress after the aging indicates that some kind of martensite stabilization takes place after pre-stress in martensite that facilitates the next transformation process (acts in a modified β state). This is one process different of the martensite stabilization obtained after a pre-stress in Cu-based alloys, for which the retransformation process might disappear and is impossible to close the cycle. In Fig. 8b the values obtained in this stress change are represented for different times and also for two temperatures.

The step in the stress with the immediate inner cycle after when the pre-stress is applied in marten-

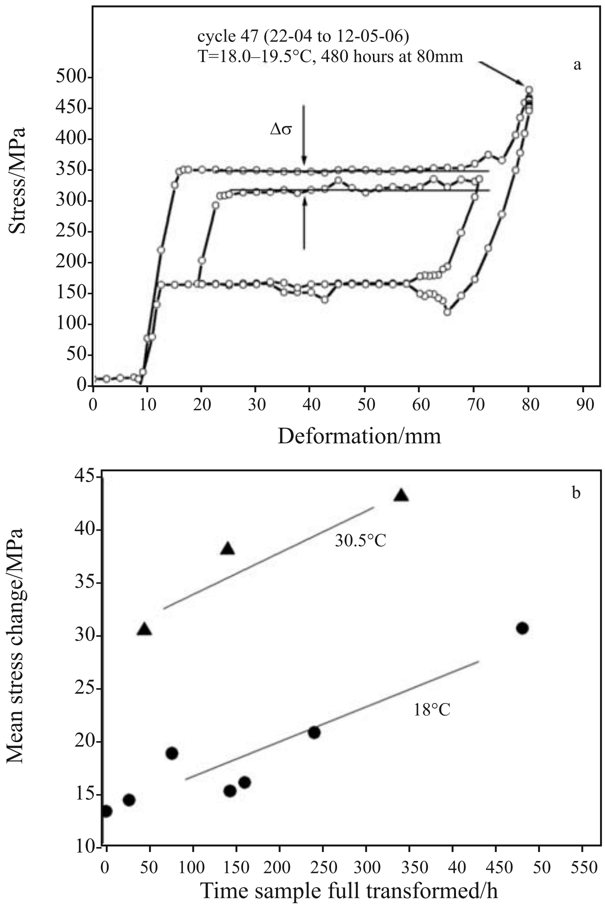

Fig. 8 a – Hysteresis cycle with aging stress in martensite, and inner loop. We measured the mean stress change Δσ between the two arrows, b – mean stress change (as indicated by Δσ in ‘a’) *vs.* time in hours of aging stress in martensite, and for two temperatures

site, increases with time and temperature and can reach a few tens of MPa. It is a minor effect for one month. In fact, the change associated to a temperature change winter-summer (about 40 K) is more important (close to 240 MPa in NiTi, taking into account that its Clausius–Clapeyron coefficient is 6.3 MPa K^{-1}). But for long times (10, 20 years) and for high temperature changes (direct sunny actions), the variation is, in the actual state of the art, unknown, and can be very important. Experimental analysis shows evolution of transformation temperatures with time constants between 70 and 250 days [5]. In conclusion, the effect of pre-stressing is not relevant for an application in which the material is required for damping immediately as, for instance, damping the wind actions, but today cannot be recommended the pre-stressing for SMA dampers of earthquakes.

Dynamic actions: stress-time effects in cycling

Usually, in dampers situated in stayed cables in bridges, the oscillations are separated by pauses of several hours or days. The particular behavior of SMA (if exists) is related to relative fast series of cycles with pauses that need to be quantified. For a preliminary analysis, we made dynamic experiments with the NiTi wire of 2.46 mm diameter and 131.3 mm length, and later on further measures were done.

In Fig. 9 successive series of force-deformation cycles are shown using a NiTi wire of 2.46 mm diameter and 41.5 cm length. In Fig. 9a it is shown that after 20 full cycles at 0.01 Hz, with a deformation of more than 8%, the creep overcomes 7 mm. In Fig. 9b it can be seen that after a pause of 1.5 h, the creep was partially recovered and the cycling starts again from a deformation close to 2.5 mm.

The observations suggest that the SMA creep is the sum of two contributions, one permanent and other recoverable after a pause including thermal effects by

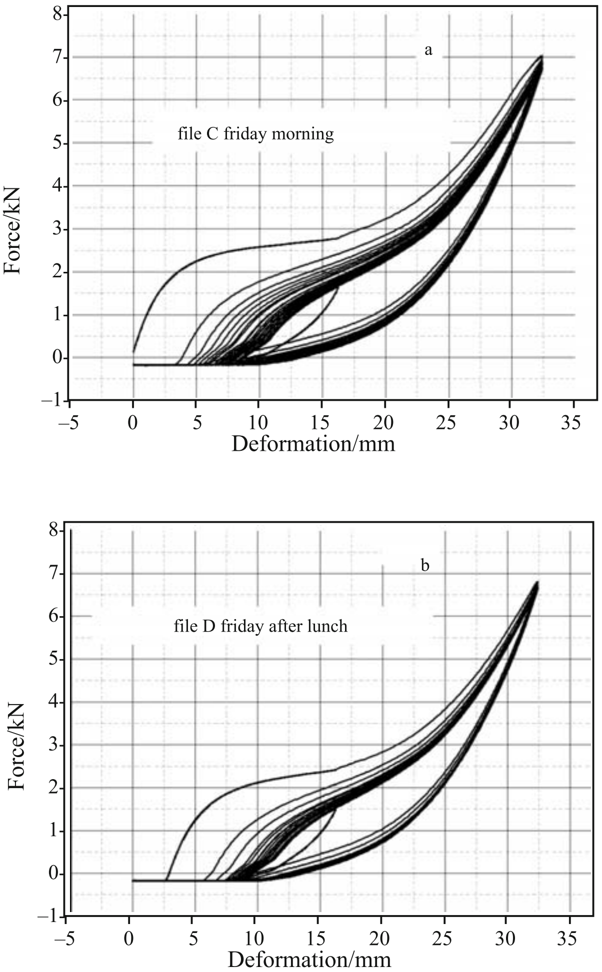

Fig. 9 SMA creep effects in a NiTi wire of 2.46 mm diameter. a – progressive creep in cycling, b – after a pause of 1.5 h, the initial creep is reduced to 2.5 mm

release and absorption of latent heat. The phenomenon is actually in deep study. In fact, in series of continuous cycles the frictional contribution progressively decreases. The experimental analysis furnishes the progressive evolution of the frictional behavior with continuous cycling. The behaviour is monotonic, if it was completely true, is easy to simulate and, can be introduced in the bridge behavior simulation. In the actual state of the art, the parasitic conditions induced by cycles and eventually pauses require deeper quantitative analysis of their relevance.

Conclusions

From the measurements of the effect of aging in temperature in parent phase we found the existence of very slow static changes in NiTi. It means that it is necessary to avoid the direct sun exposition of NiTi if it is used as dampers. On the other hand, the use of pre-stressed materials requires deep knowledge of the material properties at long time, nowadays unknown, and their coherence with the expected applications. For earthquakes, after 10 or 20 years of inactivity, static pre-stressed effects can be relevant. The pre-stress seems not relevant in the case of use in stayed cables of bridges under the effect of wind and rain. The simulation study of damping in the case of cables requires predictable hysteresis behavior (strong wind *vs.* lull). The hysteresis evolution seems a mixed system of irreversible and recoverable effects.

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