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METASTABLE EFFECTS ON MARTENSITIC TRANSFORMATION IN SMA
Part III. Tentative temperature effects in a NiTi alloy

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The applicability of shape memory alloys (SMA) for dampers in civil engineering requires guaranteed behavior with well controlled or irrelevant changes after several years of inactivity and/or under the action of daily or seasonal temperature effects. The long time analysis of the aging temperature effects on a NiTi alloy shows similar behavior to other SMA but with higher time constants at temperatures near 373 K: 1.9 days at 410 K and near 100 days at 363 K with an activation energy value near 12500 K (RT=104 kJ mol^{-1}). At the present state of the art, the measurements show that the change of transformation temperatures under the action of the external temperature (or 'room temperature' change) is close to 15 K. The direct use of the as furnished material can suffer relevant changes of working properties in devices under the action of direct sunlight or high room temperature working conditions.

Keywords: *diffusion, martensitic transformation, NiTi, nitinol, SMA, temperature effects, time effects*

Introduction

The shape memory alloys (SMA) are smart materials that can be used for damping, acting simultaneously as a sensor and as an actuator, without auxiliary power or computing requirements [1]. The particular properties of SMA are produced by a martensitic transformation between metastable phases [2, 3]. The interest in SMA for damping in civil engineering applications as, for instance, for protection from the quake actions, requires appropriate materials with several years (10 to 20 years) of guaranteed and well controlled behavior. Also, for higher and semi-permanent loads (rain, wind) in big towers or in bridges of stayed cables some permanent supervision is necessary as in magnetoreological damping devices. On the other hand, the possibility to work without continuous supervision is highly interesting in small buildings as family houses [4, 5].

The study of the thermodynamic forces (i.e., temperature and stress) on diffusion effects has shown that well established changes appear in CuAlZn under the action of temperature and stress [6, 7]. In the more recent literature [8, 9] it is determined that the aging at 373 K cannot produce parasitic effects as precipitation in NiTi at the transmission electron microscopy resolution level. In fact, minor changes in atomic order can produce detectable effects on transformation temperatures clearly under the standard resolution level of structural possibilities [10, 11].

When the application interest is focussed in the eventual use of dampers by SMA under the action of the external weather (i.e., wet weather, direct rain) the NiTi furnishes again a preliminary advantage in comparison with the moisture sensitive Cu-based alloys. The NiTi alloys show an excellent corrosion behavior, as in stents and other surgical applications, and their applications have been enhanced in the last 10 to 20 years [1, 12]. However, for long time applications it is required that the eventual changes are avoided or well established and controlled. It is, also, needed that the transformation hysteresis does not evolve significantly with cycling.

The general target of these series of papers is focused on the difficulties associated with the SMA applications. In particular, when SMA are used as a damper in civil engineering applications. Paper I [7] describes the time dependent and recoverable effects of the thermodynamic forces (temperature and stress) on the CuZnAl single crystal. In fact, the CuZnAl single crystal alloy can be considered as a prototype of SMA, with relatively faster diffusion effects. Paper II [13] describes the behavior of the CuAlBe polycrystalline SMA. It focuses on the experimental sample preparation: homogenization in beta (parent) phase at high temperatures and the appropriate long time aging at 373 K that ensures a reduced accumulative permanent deformation on cycling.

The present work (paper III) shows some 'preliminary tests' (more than one year of measurements) ana-

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lyzing the time and temperature evolution of a NiTi alloy. This SMA alloy has potential advantages for working in the outside of buildings, for instance, in not protected conditions for external weather actions. This work outlines the eventual diffusion effects (a time dependent process) in NiTi. The evaluation of the aging effects near room temperature is first established via a standard TA Instruments calorimetric device. The measurements show a change of the transformation temperature with the aging time at 373 K with an excellent reproducibility. For appropriate confirmation of these preliminary observations more complete measurements (resistance and unconventional calorimetric measurements with an extended temperature span) were performed and, then, seven months of continuous measurements of electrical resistance with controlled temperature at 363 K. The analysis shows changes related to aging in NiTi wires in pseudoelastic state. At this preliminary level, the measurements suggest that the alloy cannot be situated at direct sunlight actions for long time (several years) to avoid progressive and spontaneous increase of the transformation temperature (i.e. 15 K or higher).

Experimental

Two types of wires of NiTi are used as furnished [14]. Mainly wire of 0.5 mm of diameter in pseudoelastic state and finished in ‘black oxide’, and wire of 2.46 mm of diameter finished in ‘light oxide’. Four different measuring devices are used in this study ensuring the measurement coherence, three for the 0.5 mm wire and one for the 2.46 mm wire. The first one, a TA Instruments [15] Q1000 Differential Scanning Calorimeter using the Tzero technology (TA Instruments) has been used. The instrument uses the heat flow measuring principle which is based in two thermocouples placed symmetrically inside a furnace and measuring the temperature of a sample and a reference. The Tzero technology adds the contribution of another Chromel–Constantan thermocouple placed between the sample and the reference (Fig. 1) then a four-term equation [15] is applied to measure the heat flow. A purge of 50 mL min^{-1} of nitrogen is used in order to optimize the temperature uniformity. The furnace and its heating coil are hold in a cold environment (179 K) that permits the required control of temperature inside the chamber by adjusting the power applied to the coil. In our measurements the thermal cycling was performed between 191 and 313 K.

The second one is a classical four-point resistance device [16] with spontaneous cooling by liquid nitrogen and heating by an external furnace working between 143 and 313 K. The third apparatus was a non-conventional four wires resistance measurement device that permits some better resolution in resistance (resistance values with 4 or 5 figures) *vs*. time with a well controlled and programmable temperature scan from 235 to 410 K [17, 18]. As the device performs an efficient cooling, it permits intermediate and frequently evaluation of the transition temperature. Two devices are used. One of them measuring the resistance *vs*. time and aging temperature and the other realizing also, the evaluation of transformation temperature.

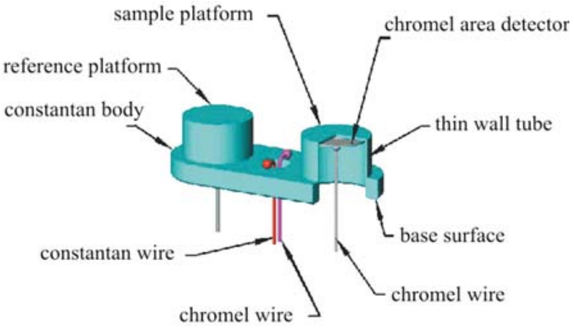

Fig. 1 Outline of the TA instruments calorimetric device sensor

The fourth experimental system for the study of the 2.46 mm diameter was a non-conventional calorimeter working between 90 and 325 K. In a flat surface of a copper block two plates of MELCOR bismuth telluride (usually used for Peltier effects) furnishing efficient Seebeck effect are mounted in differential form. On the flat free side of the MELCOR plates the sample and a reference material are respectively placed (Fig. 2). The sample was a piece of wire having a length of 4 mm in vertical position. As a reference, a Cu cylinder of 2.2 mm diameter and 3.2 mm length, having a similar mass and position as the sample, was used. The differential calorimetric signal is fed into a computer as is also the temperature of the device, measured by means of a platinum resistance. The calorimeter temperature was let to freely evolve between 90 and 325 K by alternatively putting the device in a cold and in a warm Dewar flask (i.e. around

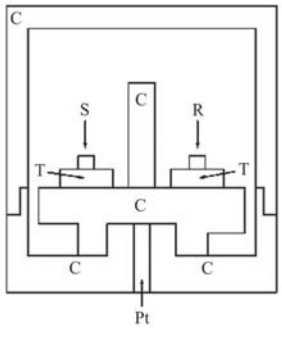

Fig. 2 Outline of the non-conventional calorimeter. C – parts built in copper, T – thermobatteries (MELCOR), Pt – platinum resistance thermometer, S – sample, R – reference mass. The system has a cylindrical shape: diameter 60 mm and height 70 mm approximately

4 L). Typical scanning rates implied $3\cdot10^4$ s to sweep the before mentioned temperature range. The non-conventional calorimeter has been described in details elsewhere [19]. Use of non-conventional calorimeters is relatively classic in SMA analysis to study the thermodynamic behavior on the hysteresis cycle [20], the after quench effects [21], an approach to direct measurements in stress induced transformation [22] or recently in phase stability analysis [23].

The samples were used as furnished or aged for different time intervals at 373 K. In general the calorimetric measurement compares samples as furnished with samples aged for several days/months in a furnace at 373 K. Only the third device, measuring the resistance (the aging is realized at 363 K) can realize the ageing analysis and, also, intermediate measurements of the transformation temperature by appropriate cooling and subsequent heating. For instance, the measurement can be realized each one or, eventually, several days. The system realizes a relative ‘fast’ cooling and subsequent ‘fast heating’: the thermal cycle from 363 to 248 K and subsequent heating to 363 K requires near 3 h for each measurement.

Results and discussion

In a standard calorimetric device the heat delivery during the first part of the transformation was recorded. A peak, which is currently attributed to the formation of the *R* phase [2], appears during the cooling run. The curves, obtained from NiTi wires of 0.5 mm of diameter, were quite reproducible for cooling and heating, for consecutive cycles and for different samples. The calorimetric outputs on cooling are presented in Fig. 3. For the available cooler possibilities the temperature cycles were situated between 313 and 191 K and the used temperature rate was of 2 K min^{-1}.

The output signal denoted as ‘arbitrary units’ correspond, according to TA device to mW mg^{-1}. In the present case the baseline effects were not taken into account and therefore the quantitative value is of reduced relevance. Figure 3 shows the output signals (cooling curves), two cycles for each sample, two samples without aging (a), two samples after 48 days of aging at 373 K (b), two samples after 158 days at 373 K (c), and one sample after 270 days at 373 K (d). It can be observed that the aging induces a shift in the peak position towards higher temperatures (it occurs also in heating); and some changes in the shape of the peak also take place.

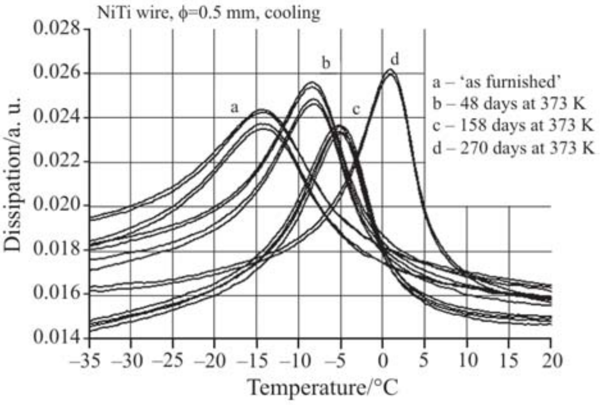

Fig. 3 Calorimetric measurements for NiTi wire samples aged at 373 K (see the text)

Wires of 0.5 mm diameter were also subjected to resistance measurements as a function of temperature. The results for an ‘as furnished’ specimen as, also, for a sample aged at 373 K during 45 days are shown in Fig. 4, left and right, respectively. Several changes are observed in the transformation behavior after aging. First of all, the inflexion point at the first part of the cooling curve moves to higher temperature after aging. This is clearly observed in the slopes of the resistance (d*R*/d*T*) shown in Fig. 5 (cooling). The martensitic transformation temperature, *Ms*, which is usually associated with the maximum of the resistance curves [2], also moves to higher temperature after aging. During heating a unique resistance peak is observed from the fresh specimen (Fig. 4a). However, some kind of splitting of such peak is observed after aging 45 days at 373 K (Fig. 4b) and its maximum shifts to higher temperatures. These peaks on heating are related to both martensite and *R* phase retransformation and it is difficult to assign a clear interpretation of the peak splitting.

NiTi wires of 2.46 mm diameter, of the same composition, were also analyzed using a non-conventional calorimeter. Three different events are indicated (Fig. 6 and Table 1). While event 1 corresponds very nearly to the observations in Fig. 3, shifting to higher temperatures on aging, an opposite behavior is observed for event 2. The effect seems coherent with measurements on electrical resistance (minor splitting in the retransformation as shown in Fig. 4) and on preliminary time-dependence studies in stress induced transformations [unpublished experimental measurements 2006].

In this work, the evolution of the transformation peak on aging will be analyzed with some detail. In Fig. 7 the position of the peak as a function of the aging time was plotted for both specimens (0.5 and 2.46 mm diameter). In addition, the position of the inflexion points from the resistance measurements in Fig. 5 is

Table 1 Changes (K) in the position of ‘events’ for 2.46 mm wire in the three indicated zones or events (Fig. 6)

Event	1	2	3
Before aging	257.2	254.9	269.0
After aging	264.4	250.3	272.2
Shift	7.2	–4.6	3.2

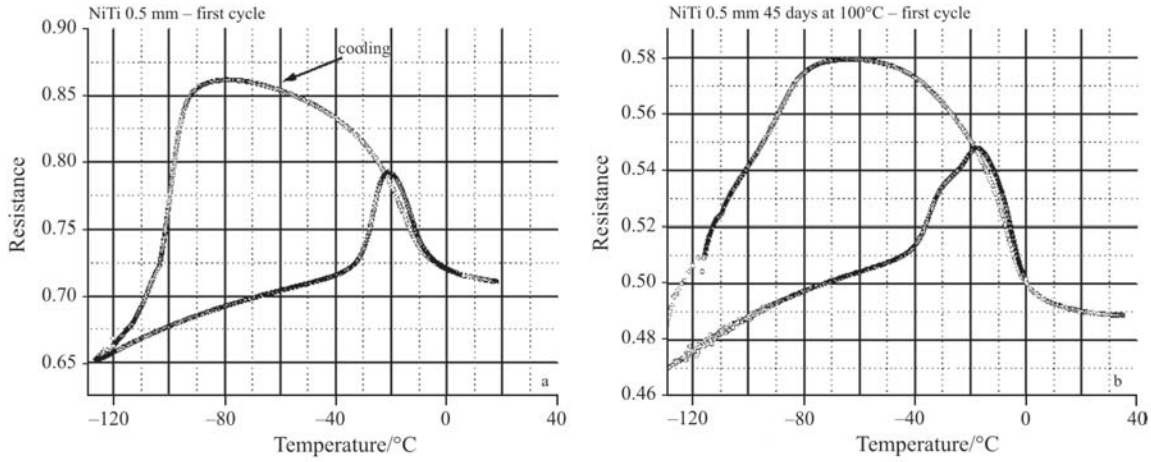

Fig. 4 Experimental measurements of resistance *vs*. temperature (wire diameter 0.5 mm); a – as furnished, b – after 45 days at 373 K. A displacement to higher temperatures and, simultaneously, a splitting of the retransformation curve with lower value of As temperature, can be observed

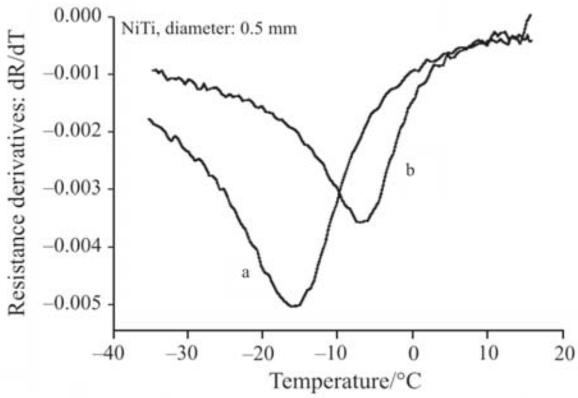

Fig. 5 Resistance derivative *vs*. temperature for the data corresponding to Fig. 4. a – as furnished, b – aged of 45 days at 373 K

also included (squared symbols). It can be observed that the position of the inflexion points corresponds quite well with the position of the calorimetric peaks. Figure 7 shows that the position of the calorimetric peak, normally associated to the *R* phase transformation [2], evolve following some kind of exponential curve with the aging time. All the points plotted in Fig. 7 were used to fit a first order exponential function. It should be remarked that a time constant of τ_1=52 days is obtained with high uncertainty. Using only the four points obtained via TA Instruments calorimeter the time constant approaches 250 days.

Evolution of the inflexion point position, associated to the phase transformation, in the resistance measurements, were also carefully followed for a 0.5 mm of diameter wire aged at 363 K. A series of cooling–heating cycles were done in the temperature programmed resistance device. The set of measurements of the inflexion points of the resistance *vs*. temperature curves on cooling (the lower attained temperature was 248 K) are plotted in Fig. 8. A rough analysis of the results (an exponential fit) establishes that the amplitude overcomes 10 K and a time constant over 100 days is obtained (affected by some parasitic cycling effects).

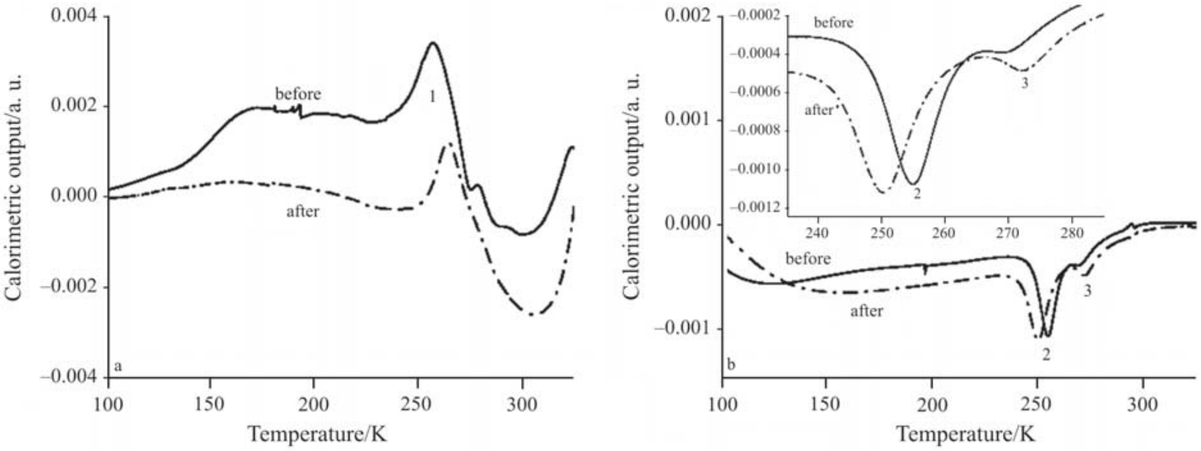

Fig. 6 Calorimetric output on a – cooling and b – heating *vs*. temperature, before and after the aging action in NiTi wire with 2.46 mm of diameter. In the heating, the upper part shows enlarged the relevant peaks

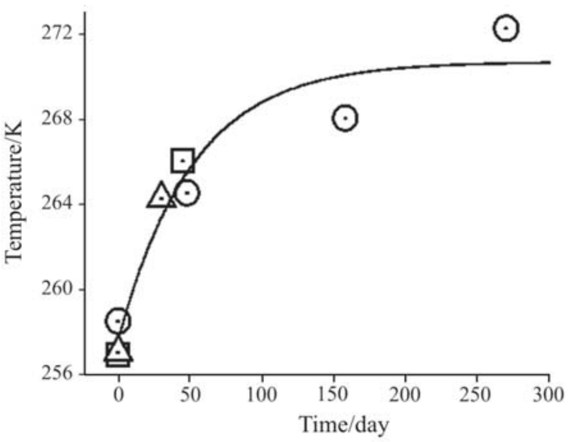

Fig. 7 Position of the transformation peaks as a function of aging time at 373 K. The circles correspond to calorimetric measurements of a NiTi wire of 0.5 mm diameter. The triangles are from a 2.46 mm diameter wire. The squared symbols corresponds to the inflexion points from resistance measurements of a 0.5 mm diameter wire

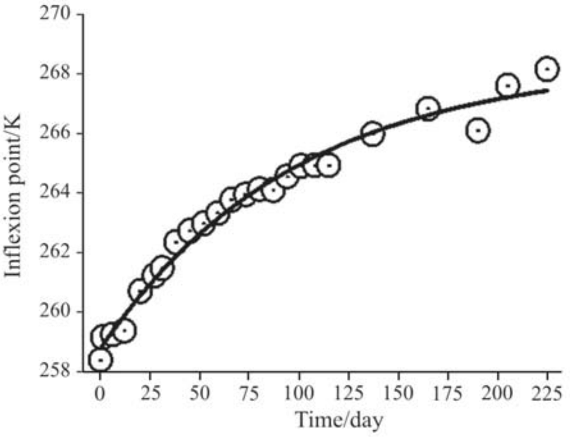

Fig. 8 Inflexion point positions *vs*. the time; NiTi alloy, aging at 363 K, time constant near 100 days

Using the time evolution of the resistance measurements at higher temperatures (time constant near 1.9 days at 410 K) the actual expected value of the activation energy is tentatively close to 12500 K (RT=104 kJ mol^{-1}). Even this value should be considered a very crude approach to the real behavior. Its extrapolation to lower temperatures (i.e., around 40°C) gives a time constant of more than 70 years, and so, any effects would be hard to detect at human body or room temperature.

The resistance measurements are coherent with the calorimetric analysis, establishing changes with aging for the 'as furnished' NiTi. The observations found the appearance of a change without a clear approach (probably related to extremely slow diffusion time scales) to some steady state. For the same reason, the predictable up or down fluctuations found in Cu-based alloys [6, 7] were not yet observed. The splitting process that appears in resistance and in calorimetric measurements requires further analysis, probably a comparison with stress effects and, eventually, with X-rays against temperature analysis. The aim to 'accelerate' the phenomena by means of higher temperatures seems not appropriate. In fact, after several hours at 573 K, the appearance of precipitates has been recently detected [8, 9].

Conclusions

The calorimetric and resistance measurements established the appearance of, apparently, accumulative aging effects in NiTi at temperatures close to 373 K. In fact, the change of transformation temperatures shows a remarkable evolution against aging time. At the present state of the art after one year of continuous measurements, the results does not permit to distinguish between irreversible processes, such as a precipitation, and recoverable ones, such as ordering by atomic diffusion. The experimental measurements suggest some splitting between R-phase transformation (with temperature increase) and the martensitic transformation with temperature decrease.

A quantitative evaluation of the asymptotic values seems convenient when the interest for a particular alloy is their capability to work for long times in direct sunlight. At the actual state of the art, it seems that the transformation temperatures can increase more than 15 K, that represents, via the Clausius–Clapeyron coefficient, a change of stress over 90 MPa. As the aging proceeds quite slowly, it is difficult to evaluate the evolution precisely. The time constant extrapolated to the human body temperature is larger than seventy years, and then no significant effects are expected in most medical and room temperature applications of the alloy. The results suggest that the eventual accumulative aging induced by daily direct sunlight actions cannot be ignored for long time applications.

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