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GUARANTEED BEHAVIOR IN SHAPE MEMORY ALLOYS

Short- and long-time effects related to temperature and phase coexistence

V. Torra[*], *A. Isalgue and F. C. Lovey*[**]

CIRG-DFA-ETSECCPB-UPC, Campus Nord B-4, E-08034 Barcelona, Spain

Abstract

A phenomenological approach, in the parent phase of Cu–Zn–Al shape memory alloy, establishes a predictable model (or mathematical equations) relating the dependence of *Ms* with the temperature over a long period of time (i.e. seasonal or yearly room temperature). High-resolution resistance and temperature measurements *vs.* time are used. The long time *Ms* tracks the external room temperature via two temperature dependent time constants. In steady state, the changes in *Ms* approach 17 per cent of the 'room' temperature change. The detailed analysis shows the puzzling disappearance of the after quench effects.

Keywords: aging effects, guaranteed behavior, martensitic transformation, phase coexistence, predictable behavior, resistance, shape memory alloys, temperature

Introduction

In shape memory alloys (SMA), among which Cu–Zn–Al alloys can be considered as a prototype, the martensitic transformation is considered a first order phase transition. The transformation originates a number of particular properties like the thermoelasticity or pseudoelasticity, the one-way memory behavior and the two-way memory effect. The martensitic transformation in copper-based alloys is thermoelastic, i.e. the transformation progresses following the undercooling below the equilibrium temperature (T_0). The applicability of the material for on-off actions needs only a poor reliability. Reliable industrial applications in long-time intervals (several years) and/or dozens of thousands of cycles are relatively difficult.

In Cu–Zn–Al alloy, the parent phase (bcc structure) is a metastable phase at room temperature obtained by quenching from higher temperature [1]. Avoiding other parasitic effects as grain boundaries or arrays of dislocations, the equilibrium temperature T_0 (and the *Ms* value) is a function of the atomic order. In the present

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[*] Author for correspondence: E-mail: vtorra@fa.upc.es

[**] Permanent address: Instituto Balseiro and Centro Atomico, 8400 S.C. de Bariloche, Argentina

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state of the art, the main order effects on parent phase are related with the near and the next near neighboring atoms (namely B2 and $L2_1$ atomic order in standard Cu–Zn–Al). After quench, several parasitic effects are observed. One among them is the stabilization of the martensite phase. The direct quench into the martensite phase from disordered β-phase induces changes on the retransformation temperature near 100 K (martensite stabilization), with fast evolution in one or two days. Some other, minor, effects are: the phase coexistence effects as the micromemory related to the internal loops in stress-strain or temperature-strain processes and the martensite recoverable creep related to an increase of the strain at constant load or to a reduction of the stress at constant strain. Also, changes on the transformation temperature, stochastic or progressively related to room temperature aging, are reported in recent years. To all effects, the existence of a martensitic transformation between metastable phases supposes an intrinsic evolving capacity. Moreover, the complexity of the transformation and the great number of domains of martensite facilitate the evolution of the alloy. Application of SMA as continuous actuator (as 'SMART' system) relates the permanent coexistence between the phases, the displacement of interfaces, the appearance, the disappearance, the nucleation and the coalescence of parent and martensite domains [2].

The temperature extension in temperature induced transformation without external stress attains several tens of degrees. The associated internal stress between different variants can overcome the critical stress for plastic deformation of martensite. The evolution of the alloy has created substantial difficulties in the domain of practical application and on fundamental studies. Particularly because of the difficulty of treating and separating each phenomenon from all the simultaneous processes that take place in the material. Classical thermodynamics is an appropriate and sensitive tool in macroscopic and mesoscopic analysis: reversible behavior can be well described but recoverable, irreversible (with or without internal changes) and time dependent path are more difficult and have to be carefully treated. The classical equilibrium thermodynamics has been applied to the martensitic transformation. It is a topic of permanent interest and, in some extent, a conflictive subject even in simple formulations of the entropy production related to the 'frictional work' dissipated in the hysteresis cycle [3–4]. Thermodynamics is only partially adapted to describe the behavior of the actual material. The complexity of the system with the metastable phases, the coexistence of a great number of phases of parent and martensite plates, the ease creation of dislocations and the local evolution of the material with the coexistence or with the changes of the external room temperature requires a local description.

It is usually considered that a few days after the quenching process, the sample has reached a 'steady state'. However, it has been shown that a weak evolution of the transformation temperature can take place during the years. Changes are related with unexpected or stochastic effects associated with each sample. Experimental operation routines have been established to minimize these parasitic effects: in reference [5] are described procedures reducing the Ms fluctuations to ±2 K for one year. Because of the metastabilities and the evolving phenomena of the shape memory properties suggested above, this material is frequently considered unsuitable for sophisticated applications. In practice, it is believed that other alloys (as TiNi) have well determined transformation temperatures. Probably this is an unclear hypothesis. In fact, some characteristics can be masked by others or by lower instrumental resolution. For instance, it has been observed that the TiNi presents some evolution (in the coexistence zone and, also, in parent phase) partially hidden by the larger hysteresis width [6]. In literature, TiNi evolution [7] does not include explicitly the time effects. However, very recently, in improved fatigue life analysis, the enhancement of working properties in TiNi rods relates some cycling evolution [8]. The described strain hardening seems similar to the one observed in Cu–Zn–Al with relevant time effects [9].

The reproducible behavior supposes a guaranteed combination of time and working cycles. In SMA applied to stochastic events – as their potential use in damping of scarce earthquake waves, in civil engineering – the potential SMA advantages compared to other damping equipment's should be consolidated by achieving guaranteed behavior after many years in the high temperature phase. SMA appears advantageous once the damping action is guaranteed during many years. Indeed, they do not require the repeated attention of the classic dampers.

This work, mainly based on careful resistance measurements, is devoted to establish the predictable analysis of the long-term behavior in parent phase. The target centers on the link between the long time effects via the room temperature actions in parent phase. The experimental analysis includes two main aspects. The first one, the disappearance of the residual effects after quenches for eventual application to dynamic structural studies. The second one, the predictable *Ms* evolution *vs.* time and temperature from parent phase. By means of long time experimental resistance measurements the phenomenological rules that relate the transformation temperature with the aging temperature and time are established. The observations visualize the residual effects remaining long time after quench.

The observation of hysteresis cycles, either by the action of the temperature or mechanical stress, shows that they are sensitive to the corresponding rates of change of the external actions and to the complexity induced in the material. The hysteresis width changes with the sample complexity: single crystal in parent phase with one or many variants of martensite or polycrystal. These ‘complex’ effects, related to dislocation creation and annihilation, induced by thermomechanical cycling, are only briefly considered.

Experimental

Several single crystals of Cu-based alloys are used. Mainly Cu–Zn–Al alloys were selected with electron concentration close to 1.48. The crystals were grown by a modified Bridgmann technique. The homogenization thermal treatments were 1123 K for 15 min followed by quenching in water at room temperature (293 K) (or, eventually, air quenched). The samples were cut with a low speed diamond saw and then were chemically polished with diluted nitric acid to remove the deformed surfaces.

In the resistance measurements, prismatic samples of near 0.5×1×20 mm or disks of 6 mm diameter and near 0.5 mm thick were used. Resistance values range between 2.5 and 0.3 mΩ. Electrical resistance measurements were carried out with a computer-controlled device, operating continuously for several years in a thermostated room. The resistance measurement uses a squared signal (positive and negative) to avoid parasitic e.m.f. By using a computerized switching a cheaper Hewlett Packard DC power supply produces stabilized positive and negative DC current. Using the computerized system, the temperature is controlled and programmed and their reproducibility is close to (or better than) 0.01 K [10–11]. Through 256 readings of positive and negative DC in samples with resistance near 2 mΩ, the resistance resolution becomes close to 1/20000 (near 0.1 μΩ).

After quench behavior

The temperature rate effect is a well-known effect on SMA behavior. A fast cooling (the quench type) is necessary to freeze the high temperature phase. The classical interpretation suggests that the cooling rate affects the microstructure and the atomic order of the sample. As a transformation temperature, *Ms* value changes with the sample order. Some calorimetric measurements of the dissipated heat power associated to the ordering carried out during the first day after the quench suggest the contribution of several exponential terms in the dissipation [12], quench type and mass dependent. The resistance measurements show a similar behavior to the calorimetric curves. Also, the high-resolution thermomicroscopy (resolution in temperature near

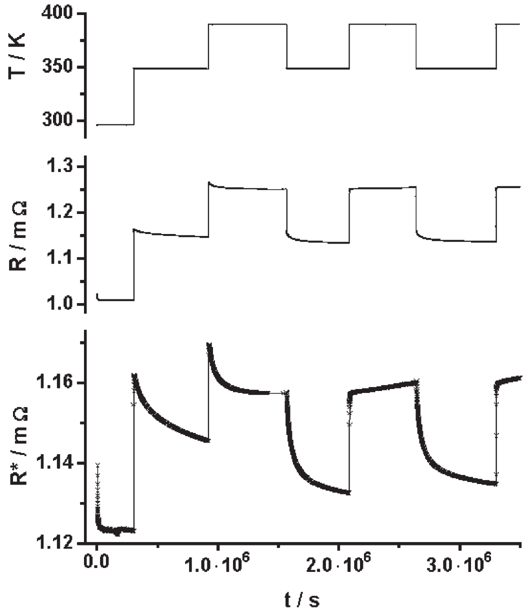

Fig. 1 After quench behavior from high-resolution electrical resistance measurements. Top: temperature *vs.* time ($T(t)$). Center: resistance *vs.* time ($R(t)$). Bottom: reduced resistance *vs.* time ($R^*(t)$)

0.003 K) analyzing a single martensite plate has established that *Ms* evolves with time during several days after quench [2], and their value and time dependence is related to the quench type. Also, classically, it has been established that the after quench effects can be suppressed or strongly reduced via appropriate thermomechanical treatments, i.e., by aging for several hours in boiling water [5]. For a general survey see, for instance, reference [13].

Figure 1 shows aging corresponding to the first 40 days immediately 'after quench effects' via continuous resistance measurements. A slight temperature increase shows an overshoot in resistance measurements related to remnant effects from previous high temperature history. Only after some 9 days at 389 K the steady state seems really achieved. This result suggests that the conditioning treatments [5, 13] of one or few h at 373 K (boiling water) should clearly be extended to some days (close a week) to achieve a situation with 'completely' vanished after quench effects. The standard time in boiling water (one or several h) is, probably, too reduced to suppress the residual effects established by quench.

The main phonon effect in resistance variation is 'suppressed' via the subtraction of a linear relation between resistance and temperature.

$$R^*(t)=R(T,t)(1-\alpha(T-T^0)) \qquad (1)$$

where α is the mean macroscopic linear temperature dependence of resistance (i.e. some 0.002 K^{-1} at T^0=350 K in the studied alloys). In Fig. 1, the $R^*(t)$ clearly visualizes the remnant effects and their disappearance. Probably related to an evolution of the atomic disorder inherited from the quench.

Using the time and 'room' temperature dependence of the resistance measurements, it is possible to establish the time constants (temperature dependent) describing the dynamic evolution of the samples. This suggests the possibility to analyze the structural (crystallographic, atomic order, …) evolution with time and temperature. Recent observations are coherent with this working hypothesis [14–15].

Time effects on parent phase

Careful observations suggest that the 'stochastic' fluctuations on the *Ms* value referred in [5] could be quantitatively associated to internal processes related to the time and temperature history of the sample. The electrical resistance measurements show that, even far from the quench process, and once reached a 'steady state', exists an evolution in the beta phase when a temperature step is done.

To determine quantitatively the evolution of *Ms* in parent phase several samples were used. In particular, one sample has carried out $1.5\cdot10^3$ transformation – retransformation cycles at an average temperature rate of 0.6 K min^{-1}, during three years, with continuous measurements of the electrical resistance and the temperature control. The computerized set-up, controlling the sample temperature, permits cooling (to 263 K) and heating to determine the *Ms* value. It has been observed that, for cycled samples, and after long time in parent (austenite) phase at a given temperature *T*, *Ms* converges to a well-defined value dependent only on temperature *T*.

When the material undergoes a change of the temperature (step like) the electrical resistance changes quickly but only reaches the end value at constant temperature (the ‘steady’ state) in an exponential way. Long time after quench, the approach to the steady state is described satisfactorily by means of two exponential terms [2, 11, 14]. The two time constants ($\tau^{(1)}$ and $\tau^{(2)}$) relate activated processes since they depend strongly on the temperature. The activation energy is relatively high. This suggests a non-classical process. See, for instance, an atomic order process related to divacancy phenomena. For a cycled sample of single crystal in Cu–Zn–Al:

$$\tau^{(1)}/s=\exp\left(-29.304+\frac{13630\ \mathrm{K}}{T}\right);\ \tau^{(2)}/s=\exp\left(-16.933+\frac{10330\ \mathrm{K}}{T}\right) \qquad (2)$$

The time constant values associated with the activated processes in the material are relatively high: from 373 K to 298 K, the $\tau^{(1)}$ changes from 1400 s to 155 days, where the related $\tau^{(2)}$ changes from 0.54 days to 1.6 years.

The experimental analysis establishes that the resistance gives the evolution of the internal microstructure of the material. It is potentially representative of the *Ms* dependence with the time and the temperature.

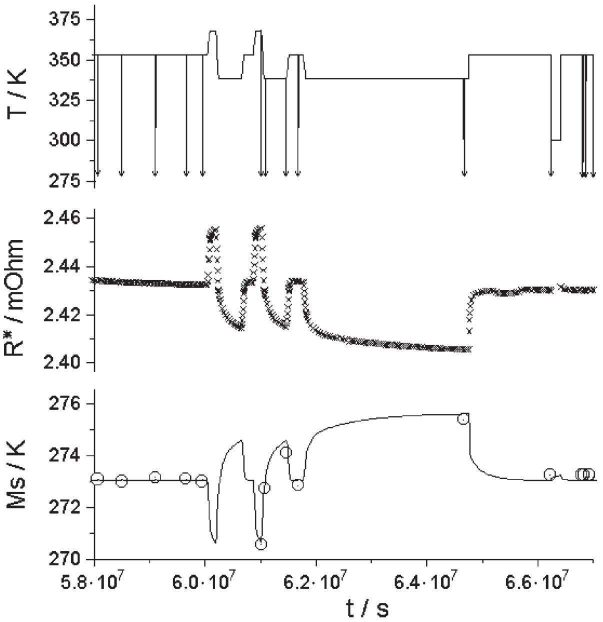

Fig. 2 Long time evolution in parent phase. Top: ‘room’ temperature *vs.* time, arrows indicates the cooling-heating cycle to determine the *Ms* experimental values; Center: reduced resistance (R^*) *vs.* time with ‘similar’ path to *Ms* evolution; Bottom: effects of external temperature *vs. Ms*; open dots: experimental *Ms* measurement (only one cycle); continuous line: calculated value. Differences between calculated and experimental values do not overcome ±0.015 K

Figure 2 shows that R^* time behavior is similar (but with an opposite sign) to the experimental evolution of *Ms* (see the open dots in Fig. 2). This suggests [2, 11, 14] the introduction of two hidden internal 'order' temperatures $T^{(1)}$ and $T^{(2)}$, in the sample, tracking the external or room temperature $T(t)$ via two independent differential equations, as:

$$\begin{aligned}\frac{\mathrm{d}T^{(1)}}{\mathrm{d}t}&=-\frac{T^{(1)}(t)-T(t)}{\tau^{(1)}}\\ \frac{\mathrm{d}T^{(2)}}{\mathrm{d}t}&=-\frac{T^{(2)}(t)-T(t)}{\tau^{(2)}}\end{aligned} \tag{3}$$

The calculated time dependent *Ms* values are deduced from $T^{(1)}(t)$ and $T^{(2)}(t)$ (the hidden order temperatures) usually starting in a steady state at external temperature T^0 by:

$$Ms(t)=Ms(T^0)+a_1(T^{(1)}(t)-T^0)+a_2(T^{(2)}(t)-T^0) \tag{4}$$

The a_1 and a_2 parameters are determined from experimental *Ms* values (for the sample in Fig. 2 they are -0.105 and -0.067 respectively). Using classical Runge–Kutta algorithm and starting in a more or less well known state the differential equations can be solved. The continuous line in Fig. 2 shows the excellent coherence (near ±0.15 K) between experimental and calculated values (elapsed time in Fig. 2 near four months) [14, 16]. Parallel observations in other samples suggest the appropriateness of the representative model for a *Ms* prediction extended to several years. The guaranteed behavior of SMA for several years can be used in scarce dampers. For instance, in structural damping, to smooth the earthquake waves.

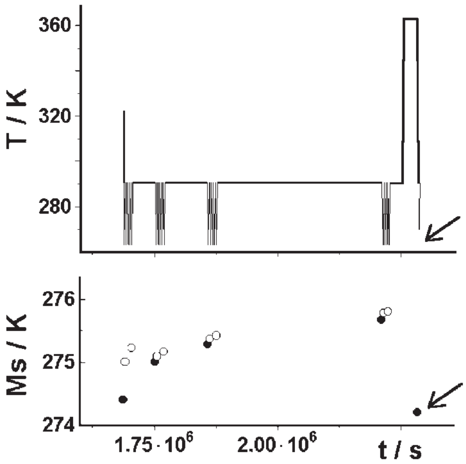

Fig. 3 Cycling effect on *Ms* in temperature induced transformation. Temperature profile *vs.* time for a long time analysis (top). Four series of five cycles of transformation are indicated. Measured *Ms* values in first (full dots), second and fifth cycle (bottom). The arrow shows the effect on *Ms* of the time spent at 363.15 K

Cycling and *Ms* value

Thermomechanical cycling (TMC), producing transformation and retransformation cycles modifies *Ms* value. TMC is a complex phenomenon. The creation and annihilation of dislocations, the interface movements and time and temperature effects are involved. Carrying out continuous cycles (in temperature induced and in stress induced), a progressive evolution of the *Ms* value and of the hysteresis cycle can be observed. Figure 3 shows the evolution of the *Ms* with series of 5 cycles. In parent phase, *Ms* evolution diminishes or 'disappears'. The disappearance needs a relative higher temperature in parent phase (see the arrow in Fig. 3). *Ms* evolution can be interpreted via the time that the material remains in each phase. This process can be described by the combined action of the martensite stabilization and of the parent phase recovery. Each cycle, the time in martensite accumulates stabilization and the time in austenite partially blurs the previous action [2, 9, 17–18].

Stress induced and temperature induced produce similar effects. In particular, the stress rate induces some 'hardening' on the samples. *Ms* evolution with cycling can be also interpreted via successive actions of martensite stabilization and β-recovery. The evolution takes place by the two phases coexistence. It induces several effects: the micromemory, the martensite creep (at constant load) or the stress decreases (at constant elongation) [2, 17]. The long time *Ms* value (mainly from parent phase) relates two concomitant effects. The first one, the long time and temperature

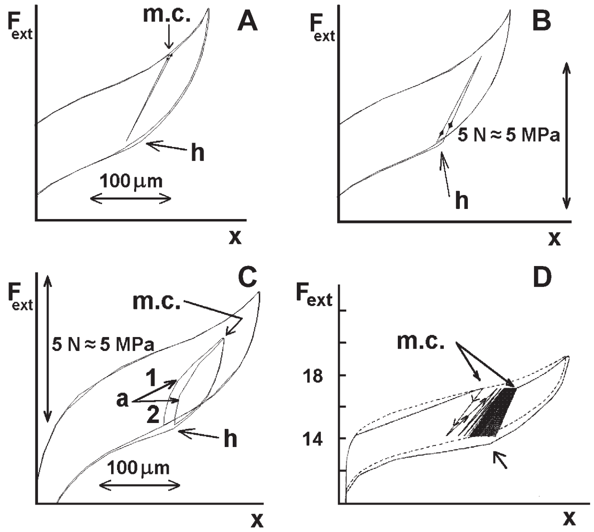

Fig. 4 Stress-strain effects on cycling. m.c.: martensite creep; h: change of hysteretic behavior. A: Partial unload-load in loading (only the extreme points are considered). B: partial load-unload in unloading. C: two internal loops (1 and 2) in unloading. D: Series of partial loops (as in A) produces relevant martensite creep and local hardening modifying (see the arrow), in a recoverable way, the hysteresis shape

effects in parent phase ‘without’ cycling actions. The second one, the additional actions related to the cycling effects. *Ms* changes are modified with temperature or stress rates. Figure 4 shows the effects of cycling in a high-resolution stress-strain-temperature and time equipment [19]. In the loading part of the hysteresis cycle, Fig. 4 A shows the effect of a local unloading-reloading: a minor martensite creep (m.c.) is observed. In B a similar effect is visualized in the unloading branch of the hysteresis cycle. Also in A and B a slightly change in local hysteresis (h) arises. In C, two partial and consecutive cycles increases the effect: a minor martensite creep (m.c.) and an apparent local widening of hysteresis. In D (Fig. 4) a series of internal loops (as in A and B only the extreme points are outlined) produces an intense creep of martensite (m.c.) and a hysteresis change (see, the arrow).

Long time after quenching, *Ms* evolution due to thermal cycles (or the critical stress in mechanical cycles) is relatively reduced and temperature and rate dependent. *Ms* changes, near 1 K at an extremely low stress rate (<10 kPa s^{-1}) [18] or near 2 K as in Fig. 3. In literature, using standard stress-strain equipment, 3 or 4 K can be noticed [9, 18, 20]. In fatigue analysis, after several thousands of mechanical cycles, the observed evolution in one- or two-day decreases with the increase in dislocation concentration [18]. This effect can be associated to a true decrease in amplitude or to a true increase of the time constant. In the same observation time, an apparent reduction of the amplitude can be obtained. At the present state of the art, the link between time constants and fatigue is not well understood.

Remarks

From high-resolution resistance measurements *vs.* time and temperature, the main evolution in SMA can be identified and predicted. This permits a choice of the expected changes and of the available temperature producing the expected time constants. The study can be used for eventual structural analysis [14–15].

Careful resistance measurements furnishes the time evolution of transformation temperatures (or the hysteresis cycle behavior). This experimental approach opens a way for SMA applications with several years of guaranteed behavior.

Conclusions

The disappearance of the after quench effects is a slow process activated by the temperature. The analysis indicates that the classical aging process (i.e. several h at 373 K) seems insufficient.

Experimental analysis establishes the rules to predict *Ms* values for a sample in parent phase. The analysis of the time behavior allows, in particular, to predict the aging effects associated to the room temperature fluctuations with time constants deduced from resistance measurements.

Ms tracks the external surroundings (or room) temperature. In steady state *Ms* changes approach 17 per cent of the external temperature change.

As time evolution and phase coexistence can be predicted, SMA can be useful material in damping without frequent controls and repairs as other classical dampers, i.e. using liquids inside a dashpot.

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