Diffusion Effects on Transformation and Deformation Behavior in Copper-Based Shape Memory Alloys

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Experimental mesoscopic observations of the parent phase in Cu-based shape memory alloys, the associated martensitic transformation and the corresponding hysteresis cycle, are carried out. The coexistence effects between martensite and parent phase and the evolution of the transformation temperature (Ms), due to yearly effect on the parent phase, are determined. Several years of continuous measurements, mainly using Cu–Zn–Al alloys, establish: (A) The evolution of the transformation temperature with time and temperature in parent phase (amplitude close to 15% of the ambient temperature change). (B) The changes related with the coexistence among the phases (close to 5 K). (C) The existence of remnant after quench effects are also partially visualized via neutron diffraction. A model based on the experimental results describes the hysteresis cycle and the internal loops. The diffusion effects can be included in the model and the time evolution of Ms and of the hysteretic behavior can be well established. The simulated results allow predicting the damping performance of the material for long-term actions.

Received August 27, 2001; Accepted November 12, 2001

Keywords: diffusion, shape memory alloys, guaranteed behavior, copper-based alloys, phase coexistence, long time analysis

1. Introduction

The thermoelastic martensitic transformation is the origin of the peculiar properties of the shape memory alloys (SMA). One of the potential uses consists on taking advantage of their hysteresis cycle to smooth oscillations, for instance oscillations induced by wind or by earthquakes in buildings. In Cu-based alloys, particularly in Cu–Zn–Al single crystals, the microscopic characteristics, as dislocation concentration and the existence of hard precipitates, determine the hysteresis width. Diffusion effects taking place at room temperature and also local diffusion induced by the phase coexistence and interfaces movement produce changes in the microscopic states. For instance, in the atomic order, which in turn produces fluctuations on the long-term behavior of the material, and that can be predicted by appropriate models.

Recently, several smart or active devices have been developed to smooth the effects of the mechanical oscillations. For instance, gondola systems for skiing facilities use mechanical compensation via appropriate feedback of auxiliary mass movements. In particular, the electro-rehologic or magnetorehologic fluids allow to design efficient dampers with variable viscosity via the appropriate feedback of high voltage or intensity current. In general and at very long term, these fluid devices require some periodic attention and, also, an easy accessibility to assure a correct repair and revision. To some extent, these requirements are partially inappropriate in civil engineering applications. Usually it is expected a very long term guaranteed operation without continuous attention and with reduced accessibility of integrated devices in the built system. When an effective softening of scarce events separated by long intervals of time is required, the very long term guaranteed behavior of SMA could be advantageous via elements partially integrated in the structure.

In this work, we analyze the necessary basic characteristics of the alloys to assure the long time operation of a SMA damper. The after quench effects that include minor structural changes (observed via neutron diffraction), the effects on the parent phase of the seasonal temperature variations and the actions produced by the coexistence between parent and martensite phases are all experimentally studied. Using an elementary one-dimensional model the short and long time effects, related to diffusion actions, are visualized as changes in the hysteretic behavior. The simulated results allow a guaranteed prediction for the long-term behavior of the material.

2. Experimental

The observations that are presented here correspond to several samples prepared from single crystals of Cu–Zn–Al and Cu–Al–Be alloys. The very long-term analysis has been carried out determining the electrical resistance of prismatic samples (resistance R near 1 mΩ, resolution close to 0.1 mΩ) with the help of a fully computer-controlled system. The study of coexistence among the phases has been carried out taking into account the resistance measurements and, using flat dog bone shaped samples, the stress-strain-temperature and time observations were performed in devices fully computerized. The single crystals were prepared from pure metals via Bridgmann method. The samples are cut to the appropriate shape using a low speed diamond saw and adapted via fine blades and, when necessary, carefully polished via mechanic grinding and chemical or electrochemical polishing. In general, the copper–zinc–aluminum samples have been homogenized at 1123 K during 10 min and subsequently water quenched at room temperature (293 K). The samples used in neutron diffraction observations have a cubic shape of 2×2×2 mm³ and these experiments were realized eight months after quench.

Special Issue on Smart Materials—Fundamentals and Applications
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3. Experimental Results

The experimental results are classified in three groups. In the first place, resistance measurement against time is used, and the action of the room temperature changes on the austenite phase and on the transformation temperature \( Ms \) is studied. To determine \( Ms \), the automatic controlled device changes the temperature until a transformation-retransformation cycle is accomplished. In the second place, the phase coexistence effects are partially analyzed: Several series of transformation-retransformation cycles induced by temperature or by mechanical stresses are performed. The measurements establish an increase of the transformation temperature that disappears with time once the sample recovers the austenite phase. In the third place, the residual effects after quench and their laborious disappearance via a long aging at moderate temperatures are clearly visualized.

3.1 Time and temperature in parent phase

The behavior of Cu–Zn–Al samples over one year after quench and, also, after some hundreds of transformation-retransformation cycles is analyzed. The \( Ms \) value is a time function including the previous history of temperature and time \( (T \text{ or } T_{RT}(t)) \) that the sample has spent in austenite phase. Carrying out “isolated” cycles of cooling-heating the transformation temperature \( (Ms) \) is measured. The long time observations establish that \( Ms \) (and the internal state of the sample) is influenced by the room temperature with a certain delay. See, for instance, in Fig. 1, the temperature (A) and the experimental \( Ms \) points in (D), and also the resistance and the reduced resistance, (B) and (C). The representation starts after the sample had been kept at 353 K for one week. The transformation temperature changes are opposite to the changes of the sample temperature, and careful examination of the long time records suggests the introduction of two components of dependence (labeled with superscripts \(^{(1)}\) and \(^{(2)}\)), with different delays. The value of \( Ms(t) \) can be determined from,

\[
Ms(t) = Ms(T_{RT}^0) + a^{(1)}(T^{(1)}(t) - T_{RT}^0) + a^{(2)}(T^{(2)}(t) - T_{RT}^0)
\]

The \( T^{(1)}(t) \) and \( T^{(2)}(t) \) are two virtual temperatures that track the daily or seasonal room temperature \( T_{RT}(t) \). The \( T_{RT}^0 \) represents a reference room temperature value when the steady state is achieved. In this situation the \( Ms \) value is denoted by \( Ms(T_{RT}^0) \). From the experimental measurements the values of \( a^{(1)} \) and \( a^{(2)} \) are estimated. The \( a^{(1)} + a^{(2)} \) values for the studied alloys range between 0.15 to 0.20, i.e. the long time fluctuation of \( Ms \) value is roughly the 15% of the external temperature change. The virtual temperatures tracking the sample temperature \( T_{RT}(t) \) are evaluated via two differential equations:

\[
\frac{dT^{(1)}}{dt} = -\frac{T^{(1)} - T_{RT}}{\tau^{(1)}}, \quad \frac{dT^{(2)}}{dt} = -\frac{T^{(2)} - T_{RT}}{\tau^{(2)}}
\]

The time constants \( \tau^{(1)} \) and \( \tau^{(2)} \) are determined from the time evolution of the internal state of the sample (the evolution of the \( Ms \) temperature, or the electrical resistance value) when it is carried out in a Heaviside step in the room temperature.\(^5,7\) Their behavior relates activated phenomena. The experimental values \( (\tau^{(1)} \text{ and } \tau^{(2)} \text{ in s when the temperature } T \text{ is in K}) \) determined for a Cu–69.2 at%, Zn–14.6 at%, Al–16.2 at% single crystal (electronic concentration 1.48 e/\( a \)) are:

\[
\tau^{(1)} = 1.18 \times 10^{-13} \exp \left( \frac{13630}{T} \right) \\
\tau^{(2)} = 4.43 \times 10^{-8} \exp \left( \frac{10330}{T} \right)
\]

The time constants are large near room temperature: at 300 K, \( \tau^{(1)} \) is near 2.5 months, and \( \tau^{(2)} \) is greater than 15 months.

The \( Ms \) behavior is similar to that of the electrical resistance. In particular, subtracting a straight line to the resistance \( R \), as \( R^*(t) = R(t)\left(1 - \alpha(T - T_{RT}^0)\right) \), the phonon effects are roughly suppressed and the reduced resistance \( R^*(t) \) is obtained with very similar behavior to the \( Ms(t) \). The Fig. 1 shows the good agreement of the transformation temperature \( Ms(t) \) against time (average better than \( \pm 0.15 \) K in 15 million seconds, between experimental and calculated values), from the room temperature \( (T \text{ or } T_{RT}(t)) \) acting on the sample and the parameters given.

3.2 Coexistence effects

The coexistence effects in single martensite plate are reported in the literature.\(^2,7,8\) The phase coexistence and, also, the movement of the interfaces modify the local transformation temperature. The effects remain strong only when the observations are carried out in the immediate hours after the heat treatment. The experimental analysis establishes that this effect decreases with the time elapsed (some hours or days) after quench but is always observable long term after quench. The coexistence effects can be observed in temperature induced as in stress induced transformation. Also, according to
the temperature in parent phase, cycling induces accumula-
tive, apparently bounded changes in \( M_s \).

Changes on the hysteresis width and on the slope of the
hysteresis cycles were observed during the mechanical cy-
cling of Cu–Zn–Al single crystal of electronic concentration
1.48 \( e/\) in (Fig. 2). In the INSTRON testing machine fur-
nace, the sample is constantly kept at 329 K. The hysteresis
cycle (Fig. 2(A), curve (a)) evolves after carrying out 900
transformation-retransformation cycles (Fig. 2(A), curve (b)).
The evolution is not permanent and is practically recovered
after 21 h in austenite phase (Fig. 2(A), curve (c)). The pro-
cess is carried out progressively. The curve b in Fig. 2(B)
corresponds to an intermediate state (after 4.5 h). The obser-
vations suggest that a part of the hysteresis width is associated
to recoverable local effects induced by cycling. They can be
interpreted as local stabilization (close to 5 K in Fig. 2) par-
tially induced by the movement of the interfaces.2 The global
stabilization depends on the time the material spends in parent
and in martensite phase. Some evanescent part plus a perma-
nent increase of the hysteresis width related to permanent de-
fects (as dislocation arrays and/or martensite debris) was only
observed up to about 2000 cycles. Then, for higher number of
cycles, the slope of the cycle also gradually increases.9)

Similar effects are observed in temperature induced trans-
formations (Fig. 3). The \( M_s \) increases continually with cy-
cling with a tendency to an asymptotic value. Their value
mainly depends on the time and temperature (see the arrow in
Fig. 3) that the material remains in parent phase.

3.3 Residual after quench behavior

The usual preparation of the material requires a fast quench
to assure that the sample remains in the austenite phase. Car-
rying out continuous measures of resistance or other magni-
tudes (energy dissipation by means of conduction calorime-
ter, positron annihilation, etc.) it has been observed that after
one or two days the material practically reaches an asymptotic
value. In the resistance measures no appreciable changes are
observed during weeks. In fact if there is a further modifi-
cation of the internal state this changes take place with ex-
traordinary slowness. The constants of time introduced in the
Sec. 3.1 have very high values at 293 K: 0.92 and 2.80 years
respectively.7)

Usually, some aging treatment is carried out after quench-
ing, for example one or two hours at 373 K. The observations
shown in Fig. 4 show that performing continuous observa-
tions after a jump to higher temperatures, the residual after
quench effects are visualized and, eventually, might be sup-
pressed. After a jump to 390 K more than 6 days are required
so that the resistance takes a steady value. The material needs
several days to adopt the microscopic configuration associ-
ated to 390 K. If the remnant quench effects are to be sup-
pressed, some hours to 373 K seem insufficient to suppress
all the residual effects.

3.3.1 Crystallographic changes after a temperature step

The disappearance of the residual after quench effects be-
gins when an increase of the ambient temperature (usually
a Heaviside step) takes place. Once the new temperature
is reached the corresponding electrical resistance value of
the sample is, also, attained. After that, the resistance in-
creases slightly (an overshoot effect) and, later, it diminishes
with more slowness (Fig. 4). All the carried out observa-
tions suggest that if the resistance evolves also the transfor-
mation temperature is modified. In general, the microscopic
observations allow visualizing the structural changes only im-
Fig. 4 After quench behavior from high-resolution electrical resistance measurements. The remnant effects last much longer than the measure at room temperature suggests. Top: temperature against time $T(t)$. Bottom: resistance against time $R(t)$. (a) and (b), remnant after quench effects; (1) and (1') slow decay to 348 K; (c) and (c') fast recovery to 390 K.

Immediately after quench. In this initial time interval relevant changes are observed in the $M_s$ value. A tentative study of the residual after quench effects in beta phase, carried out by means of neutron diffraction, suggests the appearance of an anisotropy after the initial overshoot phase. This is related to progressive and asymmetric changes in the position of some diffraction peaks of several particular directions (Fig. 5, top). Figure 5, bottom, shows the extreme changes observed in the $(-1, 1, -1)$ peak in the available observation time (near 33 h). These diffraction peaks are indexed as corresponding to the DO$_3$ structure, with cubic cell parameter 0.586 nm, for a single crystal of composition Cu–68.4 at%, Zn–15.3 at%, Al–16.3 at%.

4. Hysteresis width and Simulation

The dampers based on SMA can be considered, in a simple configuration, acting only in one-dimension and built by single crystals of reduced section. The transformation-retransformation cycles and the internal loops are carried out by means of great number of parent and martensite domains with only one variant. A description of the hysteresis cycle needs two levels of treatment. In the first place, the thermo-mechanical characteristic of the material formed by thousands of martensite plates. In second place, the diverse effects of the diffusion need also to be considered.

The detailed observations of the behavior of the single variant martensite domain: thermoelasticity and intrinsic pseudoelasticity-, frictional effects (as nucleation, decoalescence or parent nucleation and interface displacement), the Clausius-Clapeyron equation, etc. is described in the literature. The hysteresis cycle is the result of the behavior of a set of $N$ similar elementary cycles, one for each martensite plate. Figure 6 outlines one elementary cycle. The path 1-A-B-5 and backward relates the reversible behavior of one plate. The path (1-2-3-4-5-6-7-8-9-1) corresponds to a complete cycle with nucleation of martensite (2-3), growth (3-4), coalescence (4-5), and nucleation of beta (6-7) or decoalescence of martensite (after the martensite plates coalesce with the neighboring plates), growth of beta (7-8), and complete disappearance of martensite (8-9). This path has the actual maximal hysteresis width $h_2$. The trajectory a-b-c-d-a represents an internal loop associated to only one interface with minimal hysteresis width $h_1$. The A point represents the Critical Stress of Reversible transformation (CSRT).

Starting from a group of $N$ similar elements it is possible to establish the behavior of the global hysteresis cycle and of the internal loops. The diffusive effects can be simulated starting from the experimental measurements, by means of the local (or collective in fast cycling) changes corresponding to the CSRT introducing the time evolutions of the equilibrium temperature $T_0$. In the considered model, the point A represents the CSRT at the actual room temperature for each martensite domain. Modifying its position the room temperature changes can be easily simulated. Also, minor changes in the CSRT can be associated to the complete set of diffusion effects. In the model the thermal effects of the latent heat are
not considered. They should be programmed separately as changes in the local ambient temperature $T$ (or in the CSRT) since the dissipated and absorbed latent heat changes the critical stress of transformation: the local temperature changes modify, via the Clausius-Clapeyron equation, the CSRT.

4.1 Damping simulation including the diffusive actions

To reduce the oscillations induced by scarce events the dampers can be designed with the help of groups of fine rods. By means of a system of two elements it is possible to use alternatively each element only in traction (see Fig. 7). In this preliminary description a "simple pendulum model", related to only one element in a 2-D flat structure is outlined (Fig. 8). The system is similar to a group of many plates of $20 \times 10^3$ m$^2$ with a slab of 300 kg m$^{-2}$ and supported by steel columns. In the Figs. 9 and 10 the one-dimensional damping effects are simulated in this simple system with a mass of 60000 kg. The recovering force ($10^6$ N/m) is associated to the bending of a 4 m steel column with inertia ($\int \int y^2 ds$) of $2.7 \times 10^{-5}$ m$^4$. Two examples are used. The first one (Fig. 9) relates an impulsive force of 3 MN as a positive half of sinusoidal signal with a period of 80 ms. The second one relates seismic input obtained from the accelerogram of the "Imperial Valley" earthquake, "El Centro" register in 1940. The cross section uses 50 cm$^2$ for each SMA damper. The following parameters are used in the model: An intrinsic thermoelasticity of 60 $\mu$m/K, a Clausius-Clapeyron slope of 1.5 MPa/K, a nucleation and de-coalescence of 4 MPa. The interface friction is considered symmetric around the reversible path that corresponds to a standard material with dislocations ($5 + 5$ K or 15 MPa). A coexistence action of 5 K for the fast coexistence effects is considered. For the diffusive effects maximum changes between the annual temperatures of 50 K are considered (yearly maximum change). The initial $Ms$ is close to 260 K.

In the Fig. 9 have been plotted the free oscillations induced by the impulsive force, the progressive reduction of the available energy against the time and the damping differences between winter and summer with SMA dampers. Also, the damping trajectories described by the SMA damper in the force and displacement coordinates are included. In the Fig. 10 the following processes have been located: (a) The initial 10 seconds of the acceleration described in. (b) The corresponding free movements without any damping. (c) The damped oscillations associated to winter ambient conditions (at 268 K). (d) The system response in summer conditions (at 318 K). The summer-winter cases include the time-temperature effects. (c′) and (d′) relate the hysteretic behavior for winter and summer respectively. At the used scale, the coexistence effects (close to 4 K) are practically unobservable in (c′). The energy lost for each cm of complete cycle described (mechanical converted to thermal energy) is close to 0.75 kJ in the approach considered. The thermal effect induces an increase of local temperature near 3 K modifying the transformation path.

5. Conclusions

Long-term experiments allow estimating the diffusive effects on the shape memory alloy samples. In the first place, using material sufficiently aged, time and temperature actions in austenite phase are predictable. At long term the changes on transformation temperature reach 15 percent of the ambient temperature change. In the second place there are the coexistence effects. Their action depends on the transformation rate and, in fast cycling they can reach 4 or 5 K.
the third place, the residual or remnant after quench effects. These effects disappear with extraordinary slowness and it is useful to carry out a long time aging at moderate temperature (i.e., 373 K) until the homogeneous situation of the material is reached. The reduction of the after quench effects produces structural changes that are translated in structural asymmetries during the evolution.

The peculiar properties of the SMA, in particular their hysteresis cycle, suggest the use of the material as a damper for scarce events. The detailed analysis of the behavior of the material establishes an appropriate representative model to include predictive and quantitatively the diffusive effects. An appropriate choice of transformation temperature for each region permits the uses in extreme summer-winter conditions without large loss of basic properties. It allows a predictive behavior in traction under different environmental conditions. The choice of $M_s$ also requires an evaluation of the parasitic effects associated to the phase coexistence to avoid relevant undesired effects.

**Acknowledgements**

The work is carried out in the frame of the existing convention between UPC and CAB-IB and the research program between the two groups centered on phase metastability and time evolution. The financial support between the two groups,
via the integrated action ACI99-6 (Generalitat of Catalonia), is gratefully acknowledged.

REFERENCES

12) S. T. De la Cruz (2001) adapted data corresponding to the seismic input in "Imperial Valley" earthquake, “El Centro” register (May 18, 1940, 270°).