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METASTABLE EFFECTS ON MARTENSITIC TRANSFORMATION IN SMA (I)

Recoverable effects by the action of thermodynamic forces in parent phase

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The applicability of SMA requires a matching of the properties with the technological needs. The metastability effects and the phase coexistence can produce, via atomic diffusion, some changes in the expected properties against time. The careful analysis of the external thermodynamic forces (stress) on the parent phase of a Cu–Al–Zn single crystal alloy establishes a proportional minor change in critical transformation stress (near 1 per cent of the external stress). Via the Clausius-Clapeyron coefficient, the stress effects show a similar behaviour but faster than the room temperature effects on the transformation temperature M_S. In parent phase, the effect of the thermodynamic force regarded as an M_S shift lies between 10 to 15 percent of temperature change.

Keywords: *atomic order, austenite phase, metastable effects, recoverable effects, Shape Memory Alloys, SMA, thermodynamic forces*

Introduction

The technological applications of Shape Memory Alloys (SMA) which is based on a martensitic transformation, i.e. a phase transition between metastable phases, depend on the confidence in the alloy properties and their long time lasting. The design imposes well specified conditions (working temperatures, amount and rate of deformation, number of cycles, expected lifetime, etc.), which the SMA device should tolerate and react accordingly. These aspects have been studied separately, as for instance the working life of the materials (i.e. fatigue and fracture), the coupling between stress and temperature (Clausius-Clapeyron equation), the thermal effects related to the release and absorption of latent heat and the self-heating by frictional contributions. In particular, when long time requirements are needed (as in civil engineering applications), a careful analysis of the behaviour of the alloy with time, either in parent or in martensite phase, is necessary. Obviously, the applications require that the changes are not relevant or that they remain well determined.

The parent phase of Cu–Zn–Al alloys has a cubic structure with atomic order [1]. The high temperature bcc structure orders at around 800 K into a CsCl arrangement (B2 type). On further cooling and at a temperature strongly depending on composition, the order increases to second neighbour atoms. The room temperature structure is then of the Heusler type (or $L2_1$). The martensitic transformation, which is normally below ambient temperature in civil engineering applications, depends markedly on the degree of order. Consequently, the changes induced by atomic diffusion can produce unexpected effects during the ageing for times as long as 20 years.

The degree of $L2_1$ order can be altered by quenching, whereas complete B2 ordering cannot be avoided. The resulting change in M_S, the martensitic transformation temperature, is up to 40 K [2]. It was also determined that these M_S shifts disappear after a three-day ageing at ambient temperature, obtaining a single value independent of the previous thermal treatment and characteristic of the alloy composition. In the actual working scales, the available resolution suggests that larger times are necessary (see, for instance [3, 4]).

The changes of atomic order, eventually induced by vacancies, is a subject of permanent interest in materials [5, 6], but in SMA produces changes that requires appropriate characterization and experimental tools [7, 8].

Experimental analysis performed in Cu–Zn–Al single crystal alloys shows some complex evolution in the phase coexistence domain. At constant load a spontaneous increase of the available martensite is noticed (see dcf in Fig. 1 and, for instance, references [4, 9]. When the cycle is completed the stress-strain curve re-

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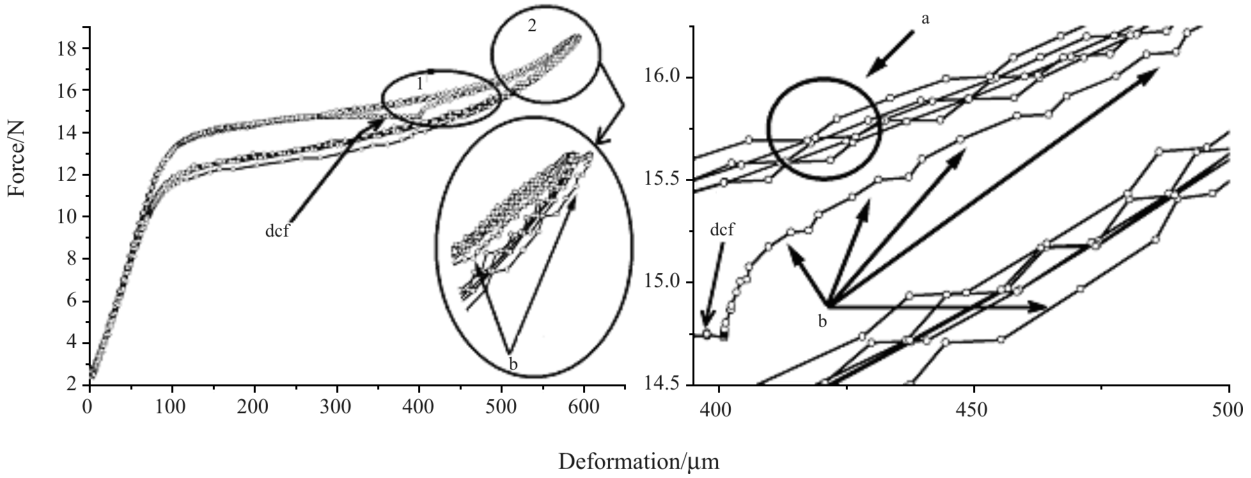

Fig. 1 Hysteretic behavior in force *vs*. lengthening. Particular evolution (b lines) at lower stress on loading (and unloading) after 7 days at constant force (see in Fig. 2 the outline of the force *vs*. time). Left: 1 and 2: expanded zones; dcf: deformation at constant force. Right: the a circle includes the loading process associated to cycles 1, 2, 3 and 5 and 6 in Fig. 2. The arrows b shows the particular evolution (at lower stress) after 7 days at constant force. The arrow dcf shows the last part of the deformation at constant force

mains under the standard cycles (the former three and the later two). See, for instance, the b curve in Figs 1 and 2 (sample length near 20 mm and cross section close to 0.5 mm^2). In fact, seven days at constant stress induces a complex pattern: first a drift to increasing deformation and, second, a lowering of the force for the force-deformation curve (close to the cycle peak of the difference approaches the experimental uncertainty). In all the previous analyses (i.e. in references [4, 9]) the first effect is related to a local increase of the transformation temperature and the martensite stabilization accounts for the second one (mainly for the retransformation part). Only recently [11] the changes on the critical transformation stress by applying constant stresses at the parent phase, has been investigated.

It is also observed that the M_S values are related with the ambient temperature [3, 4]. In fact, M_S 'tracks' the changes of the external temperature acting on the austenite phase. For instance, the yearly change (summer to winter) induces a reduced or damped M_S shift with a peak to peak amplitude close to 5 K.

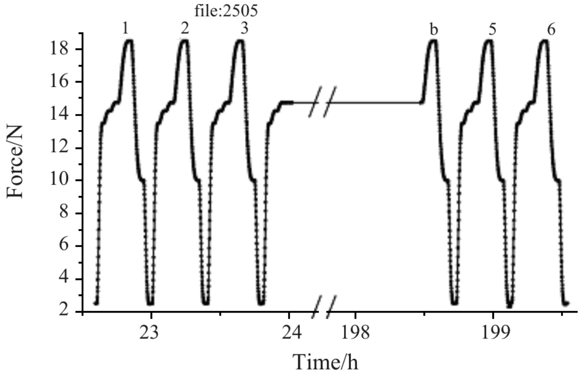

Fig. 2 Outline of the force against time in Fig. 1 left for a A1 for a Cu–Al–Zn single crystal alloy

In the present work, an attempt was done to visualize that the M_S changes induced by the temperature or by applying stresses to the austenite can be considered as equivalent actions induced by external thermodynamic forces (i.e. the mechanical force or stress and the temperature). As a working hypothesis, the thermodynamic forces act on the atomic order of the parent phase, which additionally alter M_S. The two effects were studied. First, the temperature effects (summer-winter) are outlined. Second, the changes on the transformation due to an aging of the parent phase under an external stress was analyzed. The study centers on the effects in Cu–Zn–Al alloys, but similar results could be also present in other of practical use. For instance, the temperature analysis of Cu–Al–Be single and polycrystalline samples requires further study [10] and remains beyond this work.

Experimental

The alloys were prepared with the appropriate compositions to obtain the transformation temperatures slightly below 273 K and with an electron concentration of 1.48, at which the maximum stability of the parent phase is found [1]. The 99.99% pure elements were melted in sealed quartz tubes under an Ar atmosphere. Single crystals of a diameter of around 5 mm and a length of around 14 cm were grown by the Bridgman method, also in quartz tubes and in Ar.

The consequences of temperature fluctuations on the long time behaviour were analyzed measuring the electrical resistivity with a high resolution resistance-temperature-time device described elsewhere [3, 4]. It uses the four wire methods and provides a resolution of nearly four to five significant figures for resistances exceeding 1 mΩ. The device uses Peltier plates for either cooling or heating, and the system is fully computerized. It also permits the appropriate cooling for the determination of the transformation temperatures. The samples were about 20 mm length and had a square cross section close to 0.5 mm^2. The sample was homogenized at 1123 K for 300 s and then was quenched into water at room temperature. The experiments were performed one year after the heat treatment.

The study of the changes of the critical transformation stress was performed on an Instron 5567 machine, as described elsewhere [11]. The orientation of the tensile axis was determined using the X-ray Laue technique. The sample was also homogenized at 1123 K for 900 s, air cooled to ambient temperature and aged at this value for a month. In this way the diffusion is expected to be reduced to a minimum. The experiments were performed at 318 K. The martensitic transformation was stress induced after ageing the parent phase under a constant load. Between each two such experiments, the reference state (the transformation after ageing at zero load) was controlled.

Results

The long time measurements with the appropriate resolution permitted to deduce that the transformation temperature M_S keeps track of the temperature (T_A) at which the parent phase was aged. This ageing include the room temperature variation from winter to summer. M_S was measured by carrying out ‘isolated’ cooling-heating cycles, on the hypothesis that these short time temperature variations do not modify the state of the sample. The observations allow to establish that M_S (in fact, the internal state of the sample) is influenced by the ageing temperature with a certain delay. In Fig. 3 an example is given, where the aging temperature (A) and the resulting M_S evolution (C) are shown. The representation starts after the sample has been kept at 353 K for one week. The transformation temperature value is then a complicated function of the time that the sample has spent in the parent phase, as also of the previous thermal story.

In Cu–Zn–Al, the transformation temperature changes are opposite to the changes of the sample temperature. A careful examination of the long time records suggests the presence of two contributions (labeled with superscripts $^{(1)}$ and $^{(2)}$) with different time constants, which depend on the ageing temperature. The value of $M_S(t)$ can be determined from the addition of two activated processes

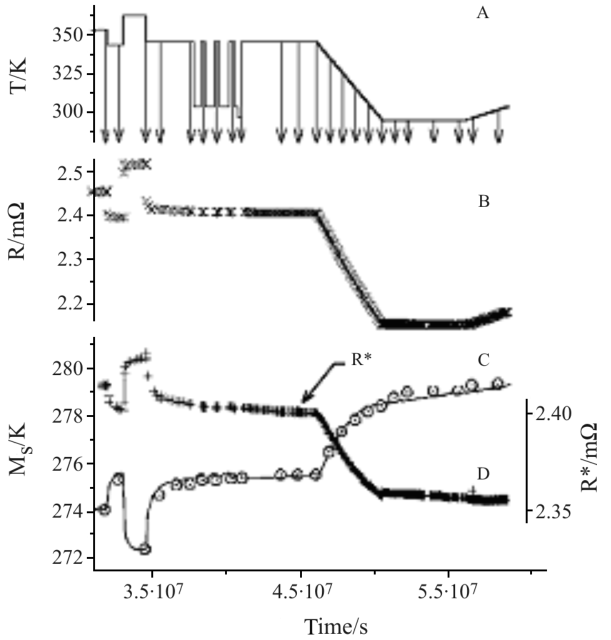

Fig. 3 Time and temperature effects on M_S. A – time evolution of the external ‘room temperature’ T_A. The arrows represent the ‘fast’ cooling and heating for determining the M_S temperature. B – electrical resistance R. C – measured M_S (dots); the continuous line is the calculated M_S value using the differential system of equations. D – reduced resistance R^* obtained by subtracting the classical phonon-temperature contribution

$$M_S(t)=M_S(T_A^I)-a^{(1)}[T^{(1)}(t)-T_A^I]-a^{(2)}[T^{(2)}(t)-T_A^I] \qquad (1)$$

T_A^I represents the initial reference temperature, where the steady state is represented by the M_S value denoted as $M_S(T_A^I)$. $T^{(1)}(t)$ and $T^{(2)}(t)$ are two virtual temperatures that track the variations of the ageing temperature from the original to the final value T_A^F. From the experimental measurements, the values of $a^{(1)}$ and $a^{(2)}$ can be estimated. The sum $a^{(1)}+a^{(2)}$ is close to 0.16 for the studied alloys, i.e. the global long time fluctuation of M_S is roughly 16% of the external temperature change. The virtual temperatures $T^{(1)}(t)$ and $T^{(2)}(t)$ can be evaluated by means of the following differential equations (i=1, 2)

$$\frac{\mathrm{d}T^{(i)}(t)}{\mathrm{d}t}=-\frac{T^{(i)}(t)-T_A^F}{\tau^{(i)}} \qquad (2)$$

The time constants ($\tau^{(1)}$ and $\tau^{(2)}$) are determined from the time evolution of the internal state of the sample when a Heaviside step in the temperature is imposed [12, 13]. Their values, determined for a Cu-14.6 at.% Zn-16.2 at.% Al, are

$$\tau^{(1)}[\mathrm{s}]=1.18\cdot10^{-13}\exp\left(\frac{13630}{T[\mathrm{K}]}\right)$$

$$\tau^{(2)}[\mathrm{s}] = 4.43\cdot 10^{-8}\exp\left(\frac{10330}{T[\mathrm{K}]}\right) \tag{3}$$

The time constants are larger near room temperature. At 300 K, $\tau^{(1)}$ is near 2.5 months, and $\tau^{(2)}$ is greater than 15 months, while at 373 K their values reduce to 870 s and to 0.55 days respectively. Being $\tau^{(2)}$ much greater than $\tau^{(1)}$, it is possible to estimate the $a^{(1)}$ value as close to 0.11. For 'short' times and moderate temperatures the contribution of $\tau^{(2)}$ can always be neglected.

The behaviour of the electrical resistance R *vs.* the temperature is similar to that of M_S (Fig. 3 A, B and C). In particular, subtracting the linear relation of R as a function of the temperature (Fig. 3 D), the phonon effects are roughly suppressed and the reduced resistance $R^*(t)=R(t)[1-\alpha(T-T_A^1)]$ behaves opposite but very close to $M_S(t)$.

Additionally, changes in transformation temperature can appear if a tensile load is applied during a time interval at parent phase, before stress inducing the martensite. It was found that the transformation critical stress decreases by an amount ($\Delta\sigma$), which is a function of the stresses applied to the austenite and the time held at this stresses. The value ($\Delta\sigma$) can be converted into a change in the M_S temperature through the Clausius-Clapeyron coefficient $(\mathrm{d}\sigma/\mathrm{d}T)_{CC}$ applying $\Delta M_S=(\mathrm{d}\sigma/\mathrm{d}T)_{CC}\Delta\sigma$. As was already observed [11], the transformation temperature increases when the parent phase is aged under load. The phenomenon was found to be recoverable and the maximum reported M_S shift was around 0.9 K for the greatest applicable load. It corresponds (using an approximate value of 1 MPa/K for the Clausius-Clapeyron coefficient) to a stress of a few MPa below that necessary for the transformation. The increase in M_S is reflected in a decrease of the critical transformation stress in tensile experiments. In Fig. 4 an almost linear increase of M_S as a function of the applied load can be observed (similar behavior that shows Eq. (1) for the steady state). The circles correspond to an ageing for an hour at each load value, whereas the squares resulted from one day ageings. The lines are a guide to the eye. It has to be remembered that between pairs of load values, the reference state at zero stress was recorded by ageing for a similar time. The sequence of load values was at random. The squares correspond to the maximum obtainable shift for the given load. In the time scale used, it represents the saturation value.

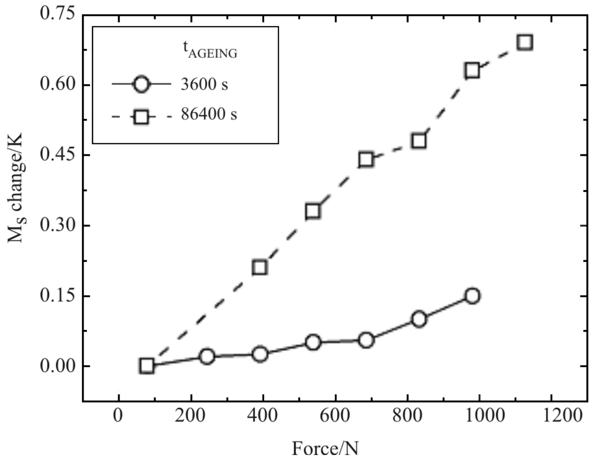

Fig. 4 Stress effects in a Cu–Zn–Al single crystal alloy. M_S dependence of the load under which the parent phase was aged. Values calculated from the measurements on the changes in the critical transformation stress. The used value of Clausius-Clapeyron coefficient is 1 MPa/K

Within experimental scatter, the present data points and the changes from the circle dots to square dots in Fig. 4 can be interpreted as an exponential evolution of the transformation temperature

$$\Delta M_S = \Delta M_S^{\infty}\left[1-\exp\left(-\frac{t}{\tau}\right)\right] \tag{4}$$

In this context, the τ values decrease with increasing load (from $2.8\cdot 10^4$ s to $1.3\cdot 10^4$ s). For practical purposes it has a mean value of $2\cdot 10^4$ s. The experimental process seems to go faster at higher loads when, relatively, the atomic barriers are reduced, permitting an increased diffusion or a faster transfer of the atoms.

Discussion and conclusions

It is straightforward to express the transformation shift, in the case of the tensile load, as a percentage of an intrinsic variable. The applied load activates the transformation to a single martensite variant for which the resolved stress is the relevant value. For the alloy under study, the measured 0.9 MPa (equivalent to the 0.9 K) is to be related with 68.1 MPa of operating resolved stress. In this manner the shift corresponds to only a 1.3%.

In both cases, during a temperature change or by the application of a load, the parent phase changes its internal state, i.e. its atom distribution. The evaluation of the time constants of Eq. (3) for the ageing temperature of the tensile experiments, T=318 K, results $\tau^{(1)}\approx 4.86\cdot 10^5$ s and $\tau^{(2)}\approx 5.68\cdot 10^6$ s. Therefore, the application of a load seems to induce faster changes but of a lower magnitude. This can be rationalized by thinking that a change of temperature alters the population of the lattice sites mainly due to the entropy contribution [1], whereas the applied load facilitates the accomodation of atoms in certain positions (changing the energy barriers for the jumps). This is similar to the statistical contributions (mechanical and thermal) to the internal energy.

The summer to winter ambient temperature variation (i.e. around 40 K) induces the classical change of the pseudoelastic cycle, described by the Clausius-Clapeyron equation. Additionally, it is now clear from the measurements that the additional effects of the thermodynamic forces on the atomic order of the parent phase of Cu–Zn–Al alloys cannot be avoided. They induce a M_S variation of around 4 to 6 K (peak to peak) from summer to winter, which is a supplementary shift due to tracking of the variation of atomic order.

Independently, if the tensile state is also modified (up to 70 MPa in the present work), a change of up to 1 K is obtained. Generally, such subtle changes in atomic order are extremely difficult to be observed, but this is the great advantage of the martensitic transition. The transformation temperature as also the critical transformation stress are highly sensitive to the atomic interchanges.

At the present state of the art a more detailed analysis is necessary to evaluate the possible actions of the crystallographic orientation (tensile axis *vs*. crystallographic axis). It is also of interest to search for the present behaviour in other shape memory alloy systems, either for the practical applications in polycrystalline samples (Ni–Ti or Cu–Al–Be) as, also, for the basic knowledge. Also, the similar behavior of thermodynamic forces (related with force and temperature) on the transformation temperature i.e., the proportionality in steady states, suggests that the particular evolution of SMA seems related with the rules of Non-Equilibrium Thermodynamics [14].

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