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METASTABLE EFFECTS ON MARTENSITIC TRANSFORMATION IN SMA
Part VI. The Clausius–Clapeyron relationship

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The Clausius–Clapeyron coefficient (CCC or α_{CC}) or relation of the stress to transform a thermoelastic SMA sample and temperature, is revisited for 1-dimensional stressed SMA when polycrystalline materials are used. The experimental method is discussed in the frame of equilibrium thermodynamics for polycrystalline materials. Suggestions for evaluation of the experimental value in polycrystalline NiTi and CuAlBe specimens are proposed. The analysis for NiTi wire gives a CCC of α_{CC}=6.3±0.3 MPa K^{-1}. On the other hand CuAlBe provides a value of α_{CC}=2.2±0.4 MPa K^{-1} for tensile stress.

Keywords: *CuAlBe, hysteresis, martensitic transformation, metastable phases, NiTi, shape memory alloys, thermoelastic phase transition*

Introduction

The technological applications of shape memory alloys (SMA) are based on their martensitic transformation, i.e., a thermoelastic phase transition between metastable phases [1, 2], with some particularities [3]. In applications, the design imposes well specified conditions (working temperatures, amount and rate of deformation, number of cycles, expected lifetime, etc.), that are to be fitted by the corresponding behavior of the SMA. In particular, their use as dampers in Civil Engineering requires some particular conditions i.e., that the yearly room temperature effects and, also, the self-heating actions produced on cycling (Fig. 1) have to be taken into account via an appropriate simulation of the damper inside the structure, at least for the extreme conditions. In fact when the transformation rate remains under 1 Hz and the strain does not overcome 3.5% (in a CuAlBe wire of 3.4 mm of diameter) the local temperature change induced by self-heating is close to 15 K [4]. A similar value is obtained for NiTi wire of smaller diameter (2.46 mm). Since the stress induced martensitic transformation follows the Clausius–Clapeyron equation, important changes in the transformation–retransformation stresses take place due to self-heating [4]. The particular conditions of SMA behaviour, and its relation to previous applied thermodynamic forces (temperature and stress), their microstructure, and some difficulties associated to the measurement of properties and establishment of rules of behavior and appropriate simulation for design purposes has been studied recently [5–8].

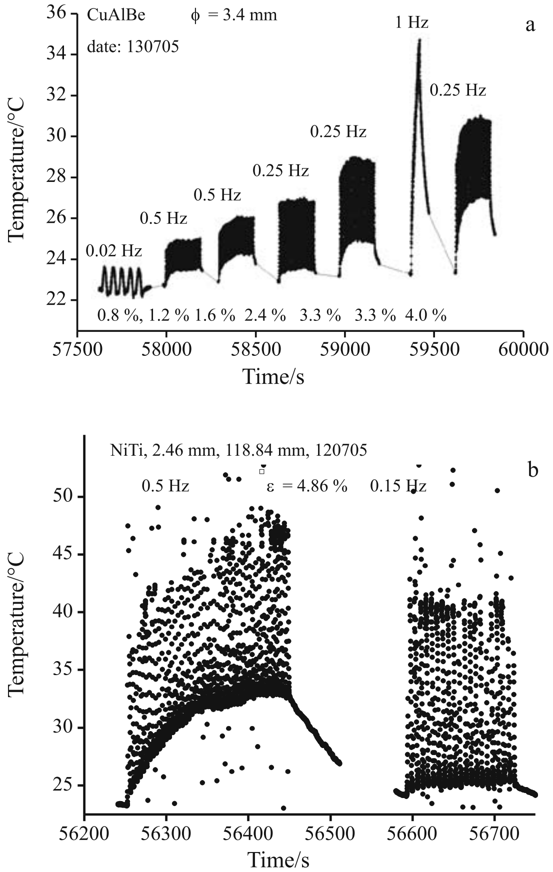

Fig. 1 Effects of cycle-rate and amplitude in self-heating associated to ‘fast’ cycling for a – CuAlBe and b – NiTi. The spread of the points is due to poor electrical contact induced by sample movement

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In the application domain, generally polycrystalline materials are used, interaction among grains is high, and a rough approach to the coefficient (i.e., 10%) is considered satisfactory. Also, the interaction between martensite and grain boundaries facilitates, in Cu-based alloys, the accumulation of parasitic permanent deformation via stabilized martensite and, also, plastic deformation. In fact, for damping at relative higher frequencies (i.e. up to 1 Hz) the self-heating, the fatigue, the accumulative permanent deformation (the 'SMA creep' [7]) and the eventual seasonal (summer–winter) effects modify the alloy behavior and cannot be avoided.

Also, it can be found a wide spread of the Clausius–Clapeyron coefficient (CCC or α_{CC}) for the case of NiTi alloys: The reported values range from 4 to 20 MPa K^{-1} [2, 9], indicating difficulties in correctly defining the thermodynamic magnitudes in polycrystalline materials. It can be stated that a too large span of the CCC values exist for NiTi alloys.

In this paper (paper VI in a series about metastable effects on martensitic transformation in SMA and in SMA properties influencing the applications possibilities), the formalism of the 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 are pointed out. Also, an experimental approach for CCC evaluation in CuAlBe and in NiTi is suggested.

CCC in solid to solid phase transition

The Clausius–Clapeyron relationship provides the basic link between external force or stress and temperature, along the equilibrium line of the martensitic transformation. The thermodynamics of pseudoelastic shape memory alloys has been treated in detail by several authors [10–13]. The main aspects of the thermodynamic formalisms are reviewed in the following to highlight the origin of some difficulties.

To determine the formal expression of the Clausius–Clapeyron relationship, a reversible thermoelastic martensitic transformation of a homogeneous part of a material, in only one dimension and at constant volume is considered. The nucleation and any other irreversible contributions are neglected. Using a rod of one mole (molar volume V_p in parent phase) with initial longitude x_p, appropriate cross section A_p ($V_p=A_px_p$) and operating close to the coexistence zone, it allows to perform a differential cycle (Fig. 2). The cycle is described in the neighbors of the phase transition, basically changing the length from x_p (rod in parent phase) to x_m with a deformation Δx $x_m=x_p+\Delta x$ (rod in martensite phase) in the frame of strictly '1-dimensional single variant transformation'.

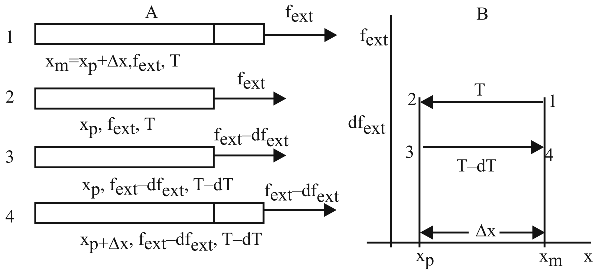

Fig. 2 SMA: an approach to Clausius–Clapeyron equation via an elementary and reversible cycle in the coexistence zone. A – outline of the cycle steps in external force (f_{ext}) *vs*. sample length (x). 1–2–3–4 equilibrium states: respectively martensite, parent, after an elementary adiabatic cooling and near martensite state at T–dT.
B – Working cycle in external force (f_{ext}) *vs*. length in the coexistence zone

The cycle described by the material (1–2–3–4–1), starts at the point 1 at temperature T and external force f_{ext}. Starting with the sample transformed in martensite (point 1), the four elementary paths are:

- 1→2: at constant force and temperature the complete retransformation (martensite to parent) is performed. The length of the sample rod changes from x_m to x_p. Using the latent heat at constant force ($\Delta h_{m\rightarrow p}$) in J m^{-3} the quantity of absorbed heat ($Q_{1\rightarrow 2}>0$) reads,

$$Q_{1\rightarrow 2}=V_p\Delta h_{m\rightarrow p} \tag{1}$$

- 2→3: an elementary adiabatic and reversible process is realized. The changes in the external coordinates are df_{ext} and dT with negative value and the changes in length are of second order (the transformation implies a finite change in length). The elementary process can be represented via one straight line.
- 3→4: at constant force the transformation is practically achieved. The length recovers the initial value x_m.
- 4→1: via an elementary adiabatic and reversible path (also one straight line) the sample recovers the initial state.

The elementary cycle is equivalent to an elementary Carnot cycle in, for instance, the liquid-gas equilibrium. In the coexistence zone the intrinsic pseudoelasticity is not considered and the lines at constant force also remain at constant temperature. The cycle is similar to a Carnot cycle with only two isotherms and two adiabatic paths. The work realized on the system in a general path (for instance the path 1→2) includes the hydrostatic and the SMA contributions,

$$\delta W_{1\rightarrow 2}=p_{ext}dV_{ext}+f_{ext}dx_{ext} \tag{2}$$

At constant volume the hydrostatic work is zero and the external work in the complete cycle is the cycle area outlined in Fig. 2B. The net work (δW_{cycle}), realized from the surroundings to the system in the elementary process $1\rightarrow2\rightarrow3\rightarrow4\rightarrow1$ reads,

$$\delta W_{\text{cycle}} = -\mathrm{d}f_{\text{ext}}\Delta x_{\text{ext}} \qquad (3)$$

The work released by the material ($\delta W'_{\text{cycle}}$) in these reversible process is,

$$\delta W'_{\text{cycle}} = -\delta W_{\text{cycle}} > 0 \qquad (4)$$

and the $Q_{1\rightarrow2}$ absorbed at 'high' temperature (T) can be related to the efficiency in the Carnot cycle. In the actual configuration reads,

$$\delta W'_{\text{cycle}}/Q_{1\rightarrow2} = \mathrm{d}T/T \qquad (5)$$

Using Eq. (3) in (5):

$$\delta W'_{\text{cycle}}/Q_{1\rightarrow2} = \mathrm{d}f_{\text{ext}}\Delta x\,/V_{\text{p}}\Delta h_{\text{m}\rightarrow\text{p}} = \mathrm{d}T/T \qquad (6)$$

The force *vs.* temperature dependence in the coexistence zone (CCC) reads:

$$(\mathrm{d}f_{\text{ext}}/\mathrm{d}T)_{\text{coex}} = (V_{\text{p}}\Delta h_{\text{m}\rightarrow\text{p}})/(T\Delta x\,) \qquad (7)$$

Defining the mechanical stress σ, the deformation ε, (as the classical engineering values) and the molar entropy $\Delta S^{\text{m}\rightarrow\text{p}}$ change from martensite to parent, respectively, by

$$\sigma = f_{\text{ext}}/A_{\text{p}}; \quad \varepsilon = \Delta x/x_{\text{p}}; \quad \Delta S^{\text{m}\rightarrow\text{p}} = V_{\text{p}}\Delta h_{\text{m}\rightarrow\text{p}}/T$$

The Clausius–Clapeyron coefficient $\alpha_{\text{CC}} = (\mathrm{d}\sigma/\mathrm{d}T)_{\text{coex}}$ is given by:

$$(\mathrm{d}\sigma/\mathrm{d}T)_{\text{coex}} = \Delta S^{\text{m}\rightarrow\text{p}}/(\varepsilon V_{\text{p}}) \qquad (8)$$

The Clausius–Clapeyron equation in terms of σ and ε is the appropriated formalism for single crystal representation in, for instance, CuZnAl single interface transformation. However the α_{CC} coefficient given by Eq. (8) depends on the crystallographic orientation of the single crystal, therefore it is more convenient to define a specific CCC in terms of the critical resolved shear stress to transform (τ) and the shear strain associated to the transformation (γ_{tr}):

$$(\mathrm{d}\tau/\mathrm{d}T)_{\text{coex}} = \Delta S^{\text{m}\rightarrow\text{p}}/(\gamma_{\text{tr}}V_{\text{p}}) \qquad (9)$$

In single crystals, $\varepsilon_{\text{tr}} = \mu\gamma_{\text{tr}}$ and $\tau = \mu\sigma$, where μ is the Schmid factor [12, 14].

In polycrystalline materials, the previous expression should be averaged over all the grain orientations of the transformed volume. Then, grain boundaries, grain size and the texture of the sample influences the obtained value for $(\mathrm{d}\sigma/\mathrm{d}T)_{\text{coex}}$. Moreover, polycrystalline shape memory materials exhibit a complex hystereticaI behavior in the pseudoelastic range, namely, large hysteresis, transformation stress depending on the amount of transformation (inclined stress-strain cycles), residual deformation and strong evolution of these parameters on cycling. In addition, the stress-strain curve depends on the cycling strain rate due to the self-heating. The latter depends on the latent heat (stress dependent) and on the coefficients of heat transfer to the surroundings. The occurrence of these irreversible processes makes more difficult to apply the formalism of equilibrium thermodynamic, particularly in assigning a CCC to the transformation stress–temperature curves. This is reflected in the wide spread of the CCC for the case of martensitic transformation in NiTi alloys (and the parasitic R-phase contribution): The reported α_{CC} have values ranging from 4 to 20 MPa K^{-1} [2, 9], indicating the difficulties in correctly defining the thermodynamic magnitudes.

From an experimental point of view in polycrystalline materials, an average value of $(\mathrm{d}\sigma/\mathrm{d}T)_{\text{coex}}$ can be established from series of cycles performed at different temperatures, measuring the stresses needed to achieve a given degree of transformation. This, in fact, expresses the knowledge of the material behavior needed to design a practical device which can work in a domain of temperatures and stresses. The evaluation of the $\mathrm{d}\sigma/\mathrm{d}T$ value need to be carried out very carefully, i.e., avoiding the parasitic deformation effects induced by thermal expansion and by Young modulus, as well as any permanent deformation and fatigue effects. The appropriate models would use the experimental approach to $\mathrm{d}\sigma/\mathrm{d}T$ but, now, their thermodynamic meaning (i.e. with the latent heat) may be not straightforward. In polycrystalline samples, no homogeneous situation is achieved by applying stresses, and, in fact, optical micrographs (Fig. 3) show the appearance of martensite localized at the grain boundaries. As the inhomogeneities change with stress and degree of transformation, some difficulties may arise on the thermodynamic significance of the α_{CC}.

Another important fact to be considered in the applications of shape memory materials is related to the latent heat associated to the martensitic transformation. In stress induced transformation the latent heat depends on the applied stress. Assuming that the heat capacities and the thermal expansion coefficients

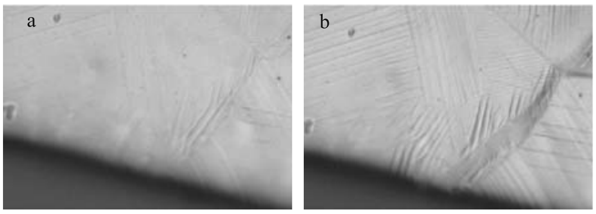

Fig. 3 Optical micrographs for a polycrystalline sample of CuAlBe under constant stress (40 MPa) on cooling: state at a – 261.8, b – 258 K. The height of the micrographs corresponds to 0.25 mm

are nearly equal for the parent and martensite phases, the heat per unit volume ($q^{\mathrm{p}\to\mathrm{m}}$) delivered by the specimen on transforming is given by [11, 12]

$$q^{\mathrm{p}\to\mathrm{m}}=\Delta h_{\mathrm{ch}}^{\mathrm{p}\to\mathrm{m}}-\sigma\varepsilon_{\mathrm{tr}} \qquad (10)$$

where $\Delta h_{\mathrm{ch}}^{\mathrm{p}\to\mathrm{m}}$ is the chemical enthalpy change for σ=0. Thus in a dynamical process, the self-heating of the specimen in the transformation path will depend on the applied stress among other factors, like the deformation ratio and the heat exchange with the surroundings.

Experimental

The analysis is centered on CuAlBe wire (composition Al 11.5 mass%, Be 0.5 mass%, Cu balance) provided by Trefimetaux (France) and in NiTi wire from Special Metals (USA). In CuAlBe, the polycrystalline samples are homogenized in beta phase at 1123 K at least for 30 min followed by a quench in water at 293 K. Subsequently the samples are aged at 373 and 323 K. This treatment produces, for the wires of 3.4 mm of diameter used, a beta phase with grains near 1 mm in size and an increased resistance to creep [7]. The Ti–50.7 at% Ni (Ti–55.8 mass% Ni) wires were furnished by Special Metals (USA) [15]. Wires of 2.46 mm were used, with a 'straight annealing' treatment done by the furnisher, in order to obtain pseudoelastic behavior. The wires were used in the 'as furnished' condition. Mechanical testing was performed in a universal electromechanical testing machine INSTRON 5567 equipped with a temperature chamber INSTRON 3119.

Results and discussion

The relationship between the transformation stress and the temperature in NiTi alloys

The pseudoelastic behavior of polycrystalline NiTi alloys depends strongly on the microstructure of the material. For example, for sufficiently low strain rate, a nearly horizontal plateau is observed for the first cycle of transformation and retransformation stresses in NiTi wires subjected to the so called 'straight annealing'. The shape of the force-elongation curves evolve strongly with cycling until a somewhat asymptotic value is obtained (Fig. 4a).

The following characteristics are to be emphasized from Fig. 4. The transformation stresses drop cycle after cycle, the decrease being rather more important during the first cycles, until an asymptotic hysteresis cycle is reached at about a hundred of cycles for a constant cycle rate. Together with the evolution of the transformation stresses a residual deformation is gradually built up in the specimen (SMA creep), also attaining an asymptotic value concomitantly with the transformation stress decrease. Conversely, the level of the reverse transformation stresses change very little, as a consequence the hysteresis width is drastically reduced on cycling. When increasing the temperature to 323.5 K, as in Fig. 4b, higher forces are needed to induce the transformation and the cycles evolve faster on cycling towards a rather more pronounced degradation than in Fig. 4a.

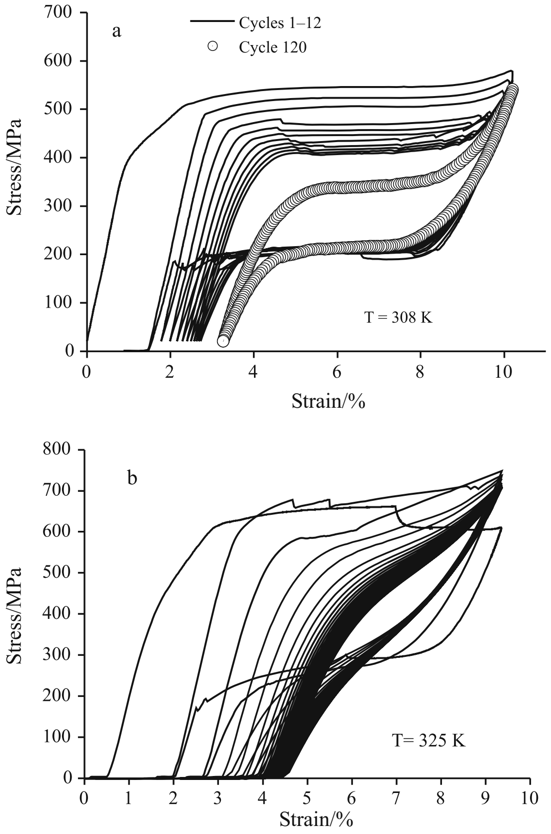

Fig. 4 Stress-strain cycles for a NiTi wire of 2.46 mm diameter. a – Temperature 308 K, specimen length between grips=93 mm, cross head speed=0.1 mm min^{-1}. The transformation forces drop on cycling and, in addition, a residual deformation remains after unloading. The retransformation stresses remain almost unchanged. b – Temperature 325 K, cross head speed=0.1 mm min^{-1}. The cycles evolve stronger than at lower temperature

Because of the very strong mechanical evolution, it is difficult to define a thermodynamic CCC coefficient to describe the transformation stress–temperature relationship when the SMA is at work. Instead, a more complex and complete description involving the plastic deformation and the evolution on cycling would be needed.

The most straight forward way to obtain the α_{CC} is by measuring the critical transformation stress of a fresh specimen for each temperature, or alternatively by taking advantage of the localised character of the stress induced transformation exhibited by the NiTi pseudoelastic material [16]. In that way, a first partial transformation is induced at 303 K and the temperature is then increased in steps of 3 K to a maximum of 333 K, at each temperature a larger strain is applied. Therefore, at each intermediate temperature level a fresh portion of the material is then transformed for the first time. The deformation rate has to be slow enough in order to reduce the self-heating as much as possible. The method proposed here is advantageous because it allows performing the temperature dependence evaluation at constant material microstructure (the initial one) and it is economical because only one specimen is necessary for the procedure. Figure 5a shows the increasing plateau levels obtained for the successive increasing temperatures while in Fig. 5b the temperature dependence of the partial plateaus for the forward transformation is represented. Arrows were included in Fig. 5a to help identify the plateau level for 303, 318 and 333 K.

Since the Clausius-Clapeyron equation was developed on the frame of equilibrium thermodynamic, one of the main difficulties in Fig. 5a is to find the equilibrium transformation line in the stress-strain curves. As a first approximation, it will be assumed that the equilibrium transformation stresses (σ_0) differ from the experimental transformation stress (σ) by a constant value ($\Delta\sigma=\sigma-\sigma_0$). $\Delta\sigma$ is mainly related to the nucleation and other irreversible processes contributing to the hysteresis. If the experimental hysteresis is nearly constants, it can be expected that $\Delta\sigma$ would also be constant. Since α_{CC} depends on the derivative of σ, it will be independent on $\Delta\sigma$.

The transformation stresses of portion of the first time transformed material, at different temperatures, are plotted in Fig. 5b. After a linear regression analysis of the data represented in Fig. 5b, a value of 6.6±0.2 MPa K^{-1} is obtained for the σ–T dependence. The total deformation associated to the transformation is estimated to be ε_{tr}=6.6±0.3%.

It is worth to mention here that the often employed method consisting in completely transforming a single specimen at successive increasing or decreasing temperatures would not provide in general a correct value for temperature dependence. For example, if such criteria is applied in Fig. 5a, to obtain the σ–T relation the form the successive cycles at increasing temperature, in the same area of the specimen, values ranging from 2 to 4 MPa may be obtained. The decreased value of the CCC is due to the interaction with the decrease of stress to transform in given conditions with the cycling.

On the other hand, when a similar experiment as in Fig. 5a is performed, but the σ–ε curve is recorded at temperatures higher than the cycling temperature (i.e., the temperature at which the cycling to obtain the asymptotic behavior was performed), the σ–T slope gives higher values (higher than 8 MPa K^{-1}) than those obtained from Figs 4 and 5. Increasing the temperature means increasing the transformation stresses to values higher than the threshold attained during cycling. The higher stresses produce further evolution of the cycles (some hardening), making difficult to assess a right value to the α_{CC}.

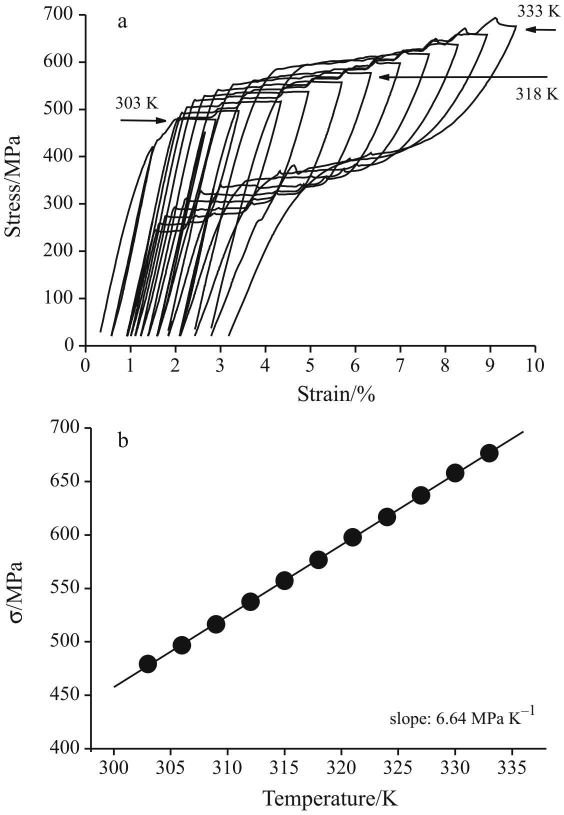

Fig. 5 Temperature dependence of the stress induced martensitic transformation in polycrystalline NiTi wire (diameter 2.46 mm). a – Progressive stress induced transformation cycles obtained at increasing temperatures in steps of 3 K (specimen length between grips=93 mm, cross head speed=0.1 mm min^{-1}, medium: air). b – Temperature dependence of the plateau stress level corresponding to the forward transformation

As mentioned above, when the material is subjected to cycling it evolves towards an asymptotic behavior. The evolution means that the microstructure of the material is changing and no σ–T slope at constant microstructure (or specimen state), i.e., in the frame of the Clausius–Clapeyron equation, can be assessed. Nevertheless, the α_{CC} coefficient could still be meaningful when a steady state behavior on cycling is achieved. This was done by using the specimen of Fig. 4b, after the asymptotic steady state was attainted at about 130 cycles. Two other cycles were performed at different lower temperatures. Since the force elongation curves show a sigmoidal shape, the stresses at the inflexion points were chosen as the representative value at each temperature (Fig. 6a). Figure 6b gives

Table 1 Values of the α_{CC} coefficient and the entropy change $\Delta s^{P\to M}$ for different specimens of NiTi, and different measuring methods (see the text)

Method	Specimen	CCC, α_{CC}/MPa K^{-1}	$\Delta s^{P\to M}\cdot 10^5$/J m^{-3} K^{-1}
Steps of partial transformation	1	6.6±0.1	4.3±0.2
	2	6.2±0.1	4.1±0.2
Inflexion points	1	5.9±0.4	3.9±0.3
	2	6.5±0.2	4.3±0.3
	3	6.5±0.3	4.3±0.3
Average		6.3±0.3	4.2±0.3

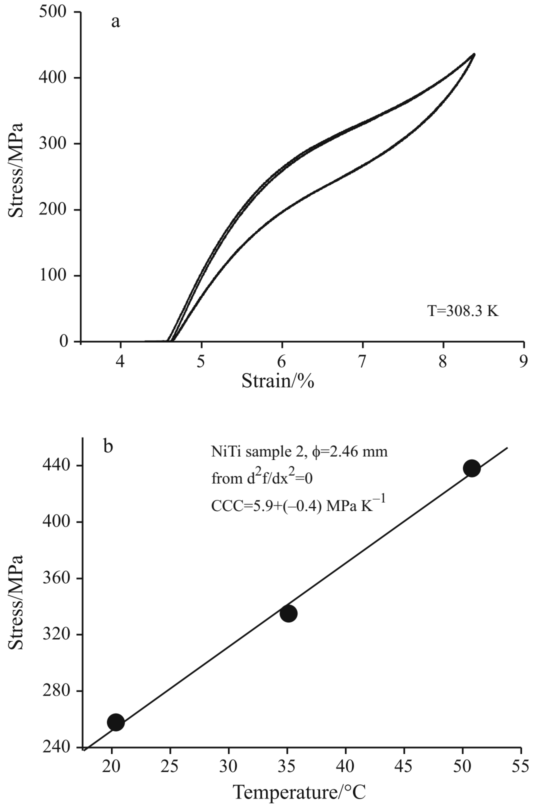

Fig. 6 CCC of a NiTi cycled specimen. a – The cycle number 131 showing a sigmoidal shape. b – The critical stress–*T* curve, on the base of the critical stresses determined using the inflexion point from cycle as Fig. 6a

the linear fit to the σ *vs.* *T* dependence. The measurements performed over several samples are given in Table 1. An average value of α_{CC} was obtained, which is in good agreement with the value obtained from Fig. 5. Figure 5a shows the residual deformation for a NiTi sample on cycling and the progressive accumulation of remnant deformation increasing the deformation percentage.

Determination of CCC in polycrystalline CuAlBe alloys

The α_{CC} in polycrystalline CuAlBe alloy can be determined following a similar method as the one outlined in Fig. 6. Cycling is performed with strains lower than 2.5–3.5% that is, avoiding SMA creep, then the transformation stresses at homologous point in the σ–*T* curve are obtained at different temperatures (Fig. 7). A value of α_{CC}=2.2±0.4 MPa K^{-1} was obtained.

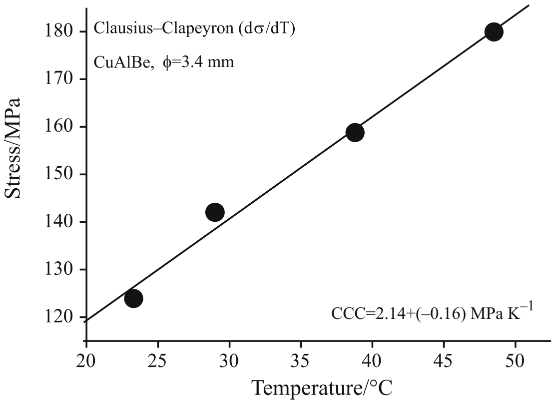

Fig. 7 Determination of the CCC in CuAlBe polycrystals. Transformation stress-temperature for homologous points in the stress-strain curves registered at different temperatures

Conclusions

Polycrystalline materials of NiTi and CuAlBe alloys show a strong evolution on cycling in the pseudoelastic range. A deep decrease of the transformation stresses takes place on cycling. The decrease is more important during the first cycles, until an asymptotic value is reached at about a hundred of cycles. Together with the evolution of the transformation stresses a residual deformation is gradually built up in the specimens, also attaining an asymptotic value concomitantly with the transformation stress decrease. For a given number of cycles the degradation increases with the temperature, because higher stresses are needed to induce the transformation.

The experimental evaluation of the CCC may be affected by any evolutive or cycling effects. Suggestions for evaluation of the experimental value of the CCC in NiTi and CuAlBe are proposed. The analysis for NiTi wire gives a CCC of α_{CC}=6.3±0.3 MPa K^{-1}, with an uncertainty close to 5%. On the other hand

Table 2 Thermodynamic values of the martensitic transformation in NiTi

Reference	$\Delta h^{P\rightarrow M}$/J kg^{-1}	$T^{P\rightarrow M}$/K	$T^{M\rightarrow P}$/K	T_0/K	$\Delta s^{P\rightarrow M}$/J kg^{-1} K^{-1}	$\Delta s^{P\rightarrow M}\cdot 10^5$/J m^{-3} K^{-1}
Liu–MacCormic [17]	18±0.2	301	331	316±15	57±2	3.7±0.2
Lahoz–Puértolas [18]	17.3±0.1	275	302	288±14	60±1	3.9±0.1
Average						3.8±0.2

CuAlBe wire provides a value of α_{CC}= 2.2±0.4 MPa K^{-1} for tensile stress.

The entropy change of the transformation can be obtained from the Clausius–Clapeyron equation given in Eq. (8). For the NiTi alloy, using the average value of the α_{CC} in Table 1 and the value of ε_{tr} given above (ε_{tr}=6.6±0.3%), the values for $\Delta s^{P\rightarrow M}$ were calculated, and they are given in Table 1. The average value reads

$$\Delta s^{P\rightarrow M}=4.2\pm0.3\cdot10^5\ \mathrm{J\ m^{-3}\ K^{-1}} \qquad (11)$$

On the other hand, Liu and MacCormick [17] have obtained the enthalpy change of the martensitic transformation in a Ti–50.2 at% Ni subjected to high annealing temperatures, to obtain a parent to martensite transformation avoiding the complications of R-phase transformation. The obtained average values are listed in Table 2. More recently Lahoz and Puértolas [18] have performed calorimetric measurement of a Ti–50 at% Ni, some of their results related to the transformation enthalpy are also given in Table 2.

From the data of Table 2, the entropy change of the transformation can be calculated as:

$$\Delta s^{P\Leftrightarrow M}=\frac{\Delta h^{P\Leftrightarrow M}}{T_0} \qquad (12)$$

where T_0 is the equilibrium temperature between the parent and the martensitic phases. The T_0 temperature may lie somewhere in between the $T^{P\rightarrow M}$ and $T^{M\rightarrow P}$ temperatures (the parent to martensite transformation temperature and the reverse, respectively). It is generally assumed that T_0=($T^{P\rightarrow M}$+$T^{M\rightarrow P}$)/2, we shall follow this convention but keeping in mind that an uncertainty of half the hysteresis width can be expected. The results of the entropy change obtained with expression (12) are also given in Table 2. The density of the alloy ρ=6.49·10^3 kg m^{-3} was used to obtained the values of the last column on the right in Table 2.

It can be observed that the value of the entropy change obtained from the Clausius–Clapeyron equation and given in Table 1 (or expression (8)) is in good agreement, within the experimental uncertainty, with the result obtained from the calorimetric data and given in Table 2.

It can be concluded that in spite of the large amount of irreversible process taking place in polycrystalline specimens, the Clausius–Clapeyron equation can still be applied if some cares are taken. The measurements of the transformation stresses at different temperatures must be performed in the material at the same state, i.e., same microstructure and defects density or in equivalent words using the same deformation percent, after reduction of the temperature dilatation effects only for materials without accumulated permanent deformation (or SMA creep) [7].

The difficulties remarked here have to be taken into account in any realistic simulation of SMA working conditions, which is needed to correctly design devices as, for instance, dampers in engineering. Besides initial state of the SMA, all the facts producing changes on the working point of the devices have to be considered: time spent before the activity, and temperature at which the sample is kept; applied stresses for long time; number of cycles, strain rate and self-heating; time and state in phase coexistence [19].

Finally, it should be remarked that the CCC of NiTi is about 3 times greater that the CCC of CuAlBe alloys. This means that the transformation stresses in NiTi alloys will change by a factor of 3 compared with the changes in CuAlBe alloys, for the same temperature change ΔT.

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