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Transformation History Dependence of Shape Memory Effects

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Abstract. Calorimetric and thermomechanical experiments with single crystals and polycrystals of CuAlZnMn shape memory alloy show how the reverse martensitic transformation - shape memory effect - is affected by the forward transformation history, in particular by the: i) transformation path from austenite to martensite, ii) deformation in martensite, iii) annealing in martensite under stress. It is suggested that a shape memory alloy is able to partially keep information about the forward transformation history encoded in the complex martensite variant microstructure. Effects of the transformation history appear, particularly, if the reverse martensitic transformation proceeds under bias external stress.

1. INTRODUCTION

The shape memory effect/SME/ - recovery of the original shape of a deformed specimen upon heating - remains the most exotic property of shape memory alloys/SMA/ and has already found lots of engineering applications [1]. SMA element is transformed from the parent to martensite phase by cooling below the martensite start M_s temperature, without any accompanying shape change, then deformed to a new low temperature shape and heated. Upon heating, the reverse martensitic transformation/MT/ starts at the austenite start A_s temperature and completes at the austenite finish, A_f, temperature. The original shape of the specimen is restored regardless of the strains (combinations of strains) applied in the martensite phase provided they were brought about by mobile martensitic interfaces. Transformation temperatures M_s, A_f, together with the maximum achievable transformation strain and recovery force, are considered to be main material characteristics of SMA's as regards the SME applications. If an external bias stress is applied upon heating, the A_f temperature may be significantly raised due to the effect of the stress on MT.

This is the simplest view on the SME but, in reality, many SMA elements used in practical applications often do not follow this pattern. The strain response of the deformed shape memory alloy upon heating may unexpectedly become quite curious when more complex thermomechanical loads [2] are used to induce and/or deform the martensite phase. Some Cu-based alloys may exhibit wide transformation hysteresis/WTH/ effects following a severe deformation in the martensite phase [3]. Also, time dependent processes may start in the martensite phase kept for prolonged time at ambient temperature by the external stress and thus somehow stabilize the martensite phase [4]. Though the reverse MT leads ultimately to the restoration of the original shape (strain state) in all cases mentioned above, the characteristics of the SME reversion (A_s, A_f, recovery force, strain response upon heating etc.), are sensitive to the forward transformation history - i.e. depend on the way the martensite phase was created, deformed or annealed. This is, however, of extreme importance for engineering applications of SMA requiring strictly reliable performance of used elements. In this paper, the effects of the transformation history on the reverse martensitic transformation were investigated on oriented single crystals and polycrystals of CuAlZnMn SMA.

2. EXPERIMENTAL PROCEDURE

[001] oriented single crystal and polycrystals of an average grain size $d = 120\mu$m were prepared from a Cu-10Al-5Zn-5Mn [*wt.*%] shape memory alloy obtained from the Furukawa Electric Co. Calorimetric measurements were performed on small prism specimens in a Shimadzu DSC calorimeter. Compressive deformation along the [001] crystal axis of the prism specimen was applied in a special purpose built apparatus.

Cylindrical specimens, 50mm long, 4mm in diameter, were machined and their central parts, 12 mm long, were electrolytically thinned to a diameter of 3.3 mm. The specimens were given a standard thermal treatment by annealing at 700 °C for 2 hours in an argon atmosphere and quenching in ice water. Tension/compression stress-strain tests, as well as thermal cycling tests at constant applied load, were performed in an INSTRON 1362 testing machine equipped with a heating/cooling chamber. Torsion experiments were performed on thin wall tubular specimens machined from the polycrystal (gauge length l=35mm, diameters d_{ext}=8mm, d_{int}=5mm) using a Shimadzu AG-10TC combined load tester equipped with a heating/cooling chamber.

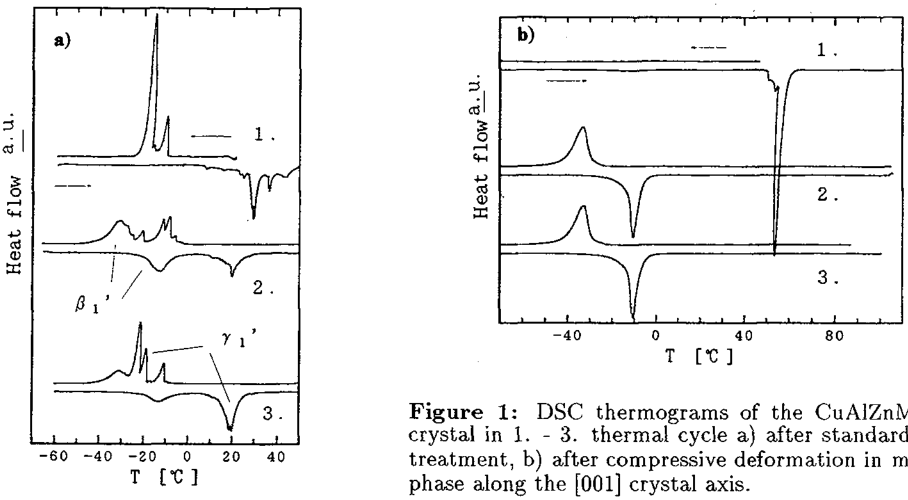


Figure 1: DSC thermograms of the CuAlZnMn single crystal in 1. - 3. thermal cycle a) after standard thermal treatment, b) after compressive deformation in martensite phase along the [001] crystal axis.

3. RESULTS AND DISCUSSION

3.1 SME - stress free recovery

3.1.1 *The effect of deformation in martensite*

CuAlZnMn SMA tends to transform into a mixture of β_1' and γ_1' martensitic phases upon stress-free cooling [5, 6]. DSC thermograms (figure 1a) recorded upon thermal cycles with CuAlZnMn single crystal clearly support this. The sharp peaks associated with a wide hysteresis correspond to the $\beta_1 \leftrightarrow \gamma_1'$ transformation, while shallow peaks with a narrow hysteresis to the $\beta_1 \leftrightarrow \beta_1'$ transformation. The shapes of the recorded thermograms varied significantly in the first few cycles suggesting that fractions of the volume of the single crystal transforming into β_1' and γ_1' phases are rather free. After three or four cycles, the microscopic transformation path quickly stabilizes (curve 3 in figure 1a).

However, we have never observed such a double peak DSC thermogram on the prism cut from a specimen previously used in a thermomechanical test. Therefore, a simple experiment was performed to check, whether the deformation in the martensite affects the subsequent thermal cycling behavior. The as-quenched prism was cooled and deformed in liquid N_2 by compression along the [001] crystal axis prior the DSC measurement (figure 1b). Indeed, the shape of the DSC thermogram changed as a result. The reverse transformation temperatures in the first thermal cycle (A_s=50 °C, A_f=58 °C) increased compared to the as quenched specimen and the transition proceeded in a single DSC peak only. This is sometimes called first cycle effect in the literature and it used to be associated with plastic accommodation of martensite variants or variant crossection effects [3]. Though well reproducible single peak DSC spectra were observed in subsequent thermal cycles, the transformation still proceeded into the mixture of martensitic phases, as was found by supplemental optical observations. The reverse transformation, however, finished at even lower temperature (A_f=-5 °C) compared to the virgin specimen (A_f=20 °C), which is a permanent effect of the deformation on the course of the MT. Single peak transformations were also observed on polycrystalline samples with characteristic temperatures M_s=-30 °C, M_f=-58 °C, A_s=-30 °C, A_f=-15 °C.

The effect of the deformation in martensite on the reverse MT was then studied in detail in thermomechanical tension/compression tests with [001] CuAlZnMn single crystals (see also [5] for basic thermal and mechanical experiments). It appeared [5] that single crystals tend to transform into the highly reversible β_1' martensite phase under tensile stress while the $\beta_1 \rightarrow \gamma_1'$ transformation proceeds under compressive stress. Mixture of both phases formed upon stress-free cooling (see the $\sigma - T$ diagrams in [5]). In this work, the results of more complex thermomechanical tests relevant for the shape memory effects are discussed.

Strain response of the single crystal deformed at low temperature in the martensite state (mixture of the β_1' and γ_1') in tension and/or compression (figure 2a) and heated back to the parent phase (figure 2b) was studied first. The imposed stress-temperature paths 1-3 are schematically suggested as paths in the non-equilibrium $\sigma - T$ diagram [5] in figure 2c. The specimen deformed in compression (curve 2) transforms back to the parent phase at evidently higher A_f temperature compared to the specimen deformed up to the same amount of strain in tension (curve 1). If the single crystal was deformed just above the M_s temperature to stress-induce the martensite phase from the parent phase (figure 3), the effect was even stronger. While the reversion of the tensile stress-induced β_1' martensite (curve 1) completes around $A_f \approx 10\,^\circ$C - even below the $A_f \approx 20\,^\circ$C temperature recorded in the thermal DSC cycle (figure 1a), the compression stress-induced γ_1' martensite recovers at temperatures as high as $A_f \approx 70\,^\circ$C (curve 2). Reloading of the tensile stress-induced β_1' martensite into compression (curve 3) results in the $\beta_1' \rightarrow \gamma_1'$ transformation and, consequently, in the upward shift of the A_f temperature upon subsequent heating ($A_f \approx 65\,^\circ$C). Clearly, the magnitude and sense of the stress applied during or after the formation of the martensite phase affects its reverse transformation back to the parent phase. The origin of the upward shift of the A_f temperature with deformation in the martensite (first cycle effect) can thus be associated with the martensite formation anisotropy (different martensite phases induced by the tensile and compressive stress states [5]) and no plastic accommodation or variant crossection phenomena [3] are required to explain it.

However, the magnitude of the induced strains in the martensite also plays an important role, particularly, as regards the γ_1' phase in compression (compare curves 2 and 3 in figure 2a,b). The large upward shift of the A_f temperature with increasing compressive strains applied to the γ_1' phase has a direct consequence for CuAlZnMn polycrystals - a wide hysteresis effect can be achieved by large deformation in compression but not that easily in tension (see [7] for more details).

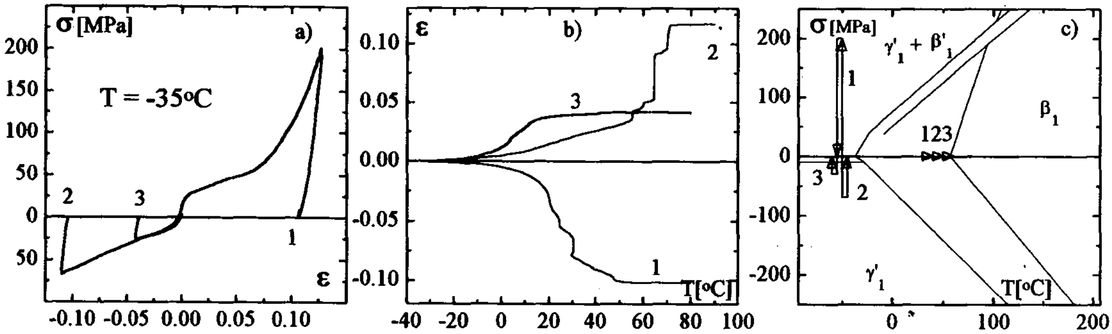


Figure 2: Three thermomechanical tests with the [001] single crystal; recovery of strains-(b) induced by deformation in the martensite phase-(a), c) imposed stress-temperature paths 1-3 in $\sigma - T$ diagram

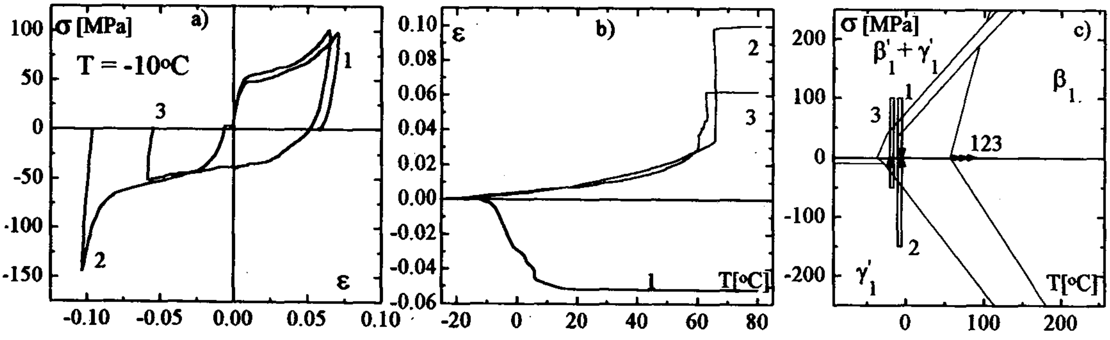


Figure 3: Three thermomechanical tests with the [001] single crystal; recovery of strains-(b) due to the reverse transformation of martensites stress-induced above the M_s temperature-(a), c) imposed stress-temperature paths 1-3 in $\sigma - T$ diagram

3.1.2 *The effect of transformation path to martensite*

Considering the applied stress and temperature as independent variables which control what kind of martensite phase will be formed in the CuAlZnMn single crystal, we find out that stress-free cooling is just one among various possible transformation paths to the martensite. To study the effect of the transformation path to the martensite on its reverse transformation, four thermomechanical tests were performed. The specimen was cooled under various applied stresses, as the bold lines 1-4 with arrows in figure 4a show. Reverse transformation paths were identical in all four cases. Strain response upon heating (figure 4b) is mainly of interest. The recorded A_f temperatures of martensites induced by various transformation paths 1-4 spread as much as 60K. The differences again likely originate from the martensite formation anisotropy since the martensite at low temperatures contains low (paths 3,4), medium (path 1) or high (path 2) fractions of the highly reversible β_1' phase in the mixture of martensitic phases undergoing the reverse MT.

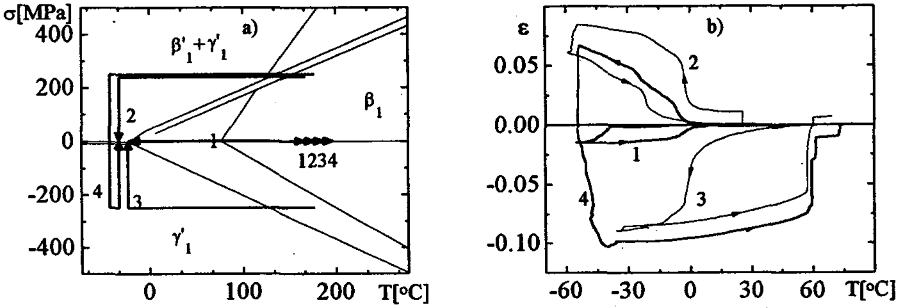
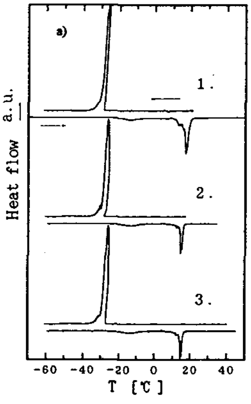


Figure 4: Four thermomechanical cycles with the [001] single crystal; a) imposed stress-temperature paths 1-4 in the $\sigma - T$ diagram, b) strain responses.

3.1.3 *The effect of annealing in martensite*

Time dependent processes taking place in the martensite phase under applied stress [4] could be just another source of history dependence of the SME. Diffusion processes over short distance, configuration changes or other thermally activated processes in the martensite phase are likely to be accelerated if the martensite structure is kept for a longer time at ambient temperature by an external stress. It was, therefore, interesting to find out whether the A_f temperature of the SME recovery depends on the time and temperature of the annealing in the martensite phase.

First, the single crystal was annealed in the parent phase at 150 °C for two hours in addition to the standard thermal treatment. As a result, the $\beta_1 \rightarrow \beta_1'$ transformation in the thermal cycle was almost eliminated (figure 5a) . The specimen transformed completely to the γ_1' phase and the DSC pattern did not vary in the subsequent cycles. The equilibrium $T_0 = (M_s + A_f)/2$ temperature of the $\beta_1 \rightarrow \gamma_1'$ transformation did not change due to the annealing - compare figures 1a and 5a. In spite of this, one may easily get relatively big variations of macroscopically measured transformation temperatures (e.g., the A_s temperature in this case), just as a result of the suppression or promotion of the one of the $\beta_1 \leftrightarrow \beta_1'$, $\beta_1 \leftrightarrow \gamma_1'$ transformations, when both martensite phases can coexist.



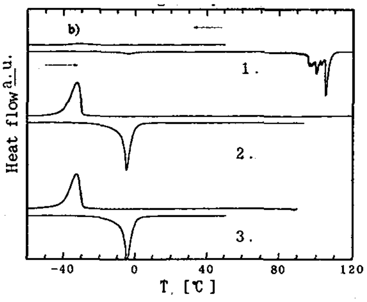


Figure 5: DSC thermograms of the single crystal in 1.-3. thermal cycle: a) annealed at 150 °C/2 hours in the parent phase, b) annealed at 150 °C/2hours in the martensite phase under stress.

Secondly, the specimen was annealed again at T=150 °C for two hours, but in this case in the martensite phase under compressive stress. As a result, the reverse transformation temperatures in the first subsequent thermal cycle (A_s=95 °C, A_f=110 °C) increased even more compared to the increase due to the effect of deformation in the martensite at low temperature (compare figures 5b and 1b). In the subsequent thermal cycles, single peak transformations (A_f=0 °C) were again observed. In conclusion, the annealing in the martensite phase under stress was found to bring about a temporary stabilization of the martensite (first cycle effect) even higher compared to the effect of simple deformation in the martensite at low temperature.

3.2. SME - recovery under bias stress

Recovery force of the shape memory effect developed by most of SMA upon heating can be extremely high and can do work. This is an excellent property of the SMA's that allows to design applications incorporatable in micromechanical systems as actuators. If the SME does work, however, the reverse martensitic transformation is forced to proceed under external bias stress. The bias stress results in a shift of the reverse transformation temperatures in accordance with the Clausius-Clapeyron equation. But not only that. It has been shown recently by experiments with combined tension/torsion loads with SMA tubes [2] that the transformation history effects interfere and influence the recovery path of the SME taking place under bias stress. Let us have a look at two sets of experiments on CuAlZnMn single crystal and polycrystal designed to elucidate the origin of such history dependence.

3.2.1 *Single crystal*

A single crystal was deformed in compression-tension (figure 6a) at room temperature. The loading was stopped in $[\sigma, \epsilon]$ points 1-10 and the specimen was heated under constant bias stresses marked as 1-10. The strain response (figure 6b) clearly shows how the bias stress affects the reverse transformation temperatures. The recorded A_f^{γ} temperatures are shifted up or down, depending not only on the magnitude (compare 1 vs. 3) and sense (compare 1 vs. 6) of the bias stress, but also depending on the deformation history (compare 6 vs. 7). Two reverse transformation lines corresponding to two tension and compression variants of the stress induced γ_1' martensite phase can be drawn in the non-equilibrium $\sigma - T$ diagram (figure 6c). Both lines cross the $\sigma = 0$ axis and, consequently, the reverse MT upon heating under bias external stress takes place on the one of the lines depending on the transformation history (on the γ_1' variant actually undergoing the reverse MT).

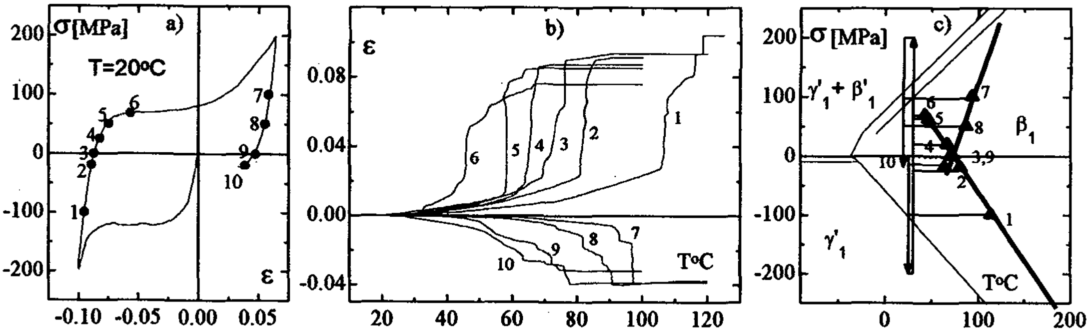


Figure 6: Ten thermomechanical cycles with the [001] single crystal; - recovery of strains induced by deformation at room temperature upon heating under applied bias stresses 1-10 (a,b), c) reverse transformation finish lines (thick lines) in the $\tau - T$ diagram.

3.2.2 *Polycrystal*

The shifts of the A_f temperature of the single crystal due to the bias stress are enormous (over 100 °C). Mainly 2 variants of the γ_1' martensite phase, however, were active in the transforming single crystal. How is it with a polycrystal transforming always into a large amount of misorientated martensite variant particles? 12 torsion thermomechanical tests (figure 7) were performed to get the answer. The CuAlZnMn polycrystal tube was deformed below the M_s temperature in the torsion right-left cycle and heated under applied stresses marked as 1-12. Strain response of the tube upon heating (figure 7b) was quite curious in some cases. Note the evolution of the strains during the reverse MT in cases 5,6,7,8. Upon heating under bias (-) stress, the tube twists (curve 7) at first almost 2% of the shear strain further in left torsion (-) , and only after that, untwists back to the original shape, as is natural for the SME.

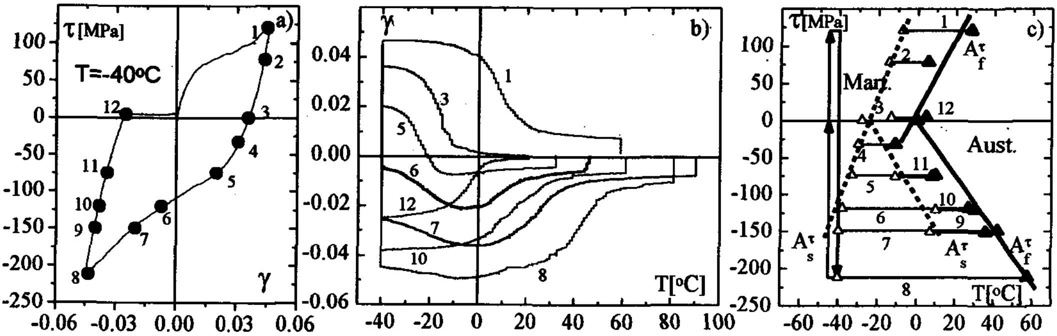


Figure 7: Twelve thermomechanical cycles with a polycrystal in the torsion test; - recovery of strains induced by deformation in martensite upon heating under applied stresses 1-12 (a,b), c) reverse transformation lines A^τ_s, A^τ_f in the $\tau - T$ diagram.

Both A_s and A_f temperatures are plotted in the torsion $\tau - T$ diagram of the polycrystal (figure 7c). The reverse transformation lines A^τ_s, A^τ_f are drawn through the experimental data points. Different lines apply, however, for different deformation histories. Comparing the A_s and A_f temperatures in tests 3 or 12 with the thermal DSC cycle data (A_f=-15 °C), one finds out that the reverse transformation intervals are evidently shifted upwards following the deformation in martensite. The history effects are, however, even more pronounced when the SME recovery proceeds under bias stress (compare cases 6 and 10). The reverse transformation interval widens with increasing magnitude of the bias stress (compare 4 and 8). The higher induced strain in the torsion right halfcycle, the larger the effect that can be expected upon heating under torsion left bias stress.

The complex response of the tube heated under bias stress can be qualitatively understood on the basis of the interaction of individual martensite variant particles with the bias stress (figure 6). Suppose that martensite particles are not completely reoriented upon torsion reloading at low temperature, but, instead, new particles are created while the original ones still partially keep their identity. Upon heating under bias stress, the reversing martensite particles are not equal thermodynamically (temperature and resolved shear stress as state variables). Depending on the orientations of the martensite variants with respect to the bias stress, the A_s and A_f temperatures are shifted up or down. Since variously oriented martensite particles thus recover at various temperatures, the measured transformation interval significantly widens and the strain response of the heated tubes may become apparently "curious" at suitable bias stress. The alloy is thus able to keep partially an information about the forward transformation history encoded in the complex martensite variant microstructure.

Acknowledgments

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