

The Two Way Memory Effect in relation to the nucleation and growth of martensite.

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Introduction

The shape memory properties observed in some alloys are due to a structural transformation of martensitic type which occurs quasi reversibly in a narrow temperature range. The high and low temperature phases will be called austenite and martensite respectively regardless of their structures which can change from one alloy to the other.

The one way memory effect can be described as follow : a sample of a given shape in the austenitic state, cooled in the martensitic state does not change its macroscopic shape. At this temperature, it can be apparently plastically strained by an applied stress; a reheating in the austenite state regenerates the initial shape. This cycle can be repeated, the sample can be strained in martensite in the opposite direction, it will recover again its initial shape by heating.

After some special thermomechanical treatment, on cooling, in the way austenite to martensite, a spontaneous macroscopic strain of the sample appears, which vanishes on heating in the austenitic state due to the simple memory. Therefore, without any external applied stress, a spontaneous change occurs between two different shapes respectively in the austenitic and the martensitic states. This phenomenon is called the Two Way Memory Effect (TWME).

In the alloys which exhibit a thermoelastic martensitic transformation, the one way memory effect is always effective, it is inherent to the martensitic transformation.

The TWME must be induced by some thermomechanical treatment : it is an acquired property.

This paper will first shortly describe the relation between the martensitic transformation and the one way memory effect, then the TWME. Afterwards the thermomechanical treatment inducing the TWME which is called "Training" will be detailed. Finally, the possible origins of the TWME will be reviewed.

The One Way and the Two Memory Effects related to the martensitic transformation.

As defined in 1979 (1) the martensitic transformation is a displacive structural transformation, first order, without diffusion and which involves essentially an homogeneous lattice shear strain. The direct

transformation (austenite to martensite) occurs by nucleation and growth. Between M_s and M_f temperatures, the two phases coexist and have clearly distinct structures which do not change significantly. The reverse transformation occurs between A_s and A_f temperatures with a slight hysteresis in the case of shape memory alloys. The transformation strain of the lattice, in addition with a lattice invariant shear strain induces a macroscopic homogeneous shear strain. This shear strain is parallel to the habit plane, interface between the austenite and the martensite. The habit plane and the shear strain direction have no high symmetry character in relation to the austenite or the martensite. An austenite single crystal may therefore transform into any of several equivalent variants of martensite. These variants of identical structure differ only by their orientation and their habit plane in relation to the austenite. Very often the austenite is cubic and 24 variants occur for a single crystal of austenite.

When a single crystal of austenite is cooled down, all the variants are equally probable, the shear strains of the individual variants compensate and therefore no or very little macroscopic shape change is observed during this cooling. The variants induce new interfaces between them, these interfaces and the habit planes are coherent and mobile (conservative movement).

Two important facts are to be noticed :

a) The martensite appears by heterogeneous nucleation and growth; there is first creation of habit planes and interfaces, then they move in such a way that the whole space is invaded by the martensite variants. The reverse transformation, martensite to austenite occurs by the reverse movement of the interfaces and habit planes giving rise to the initial single crystal.

b) In the purely martensitic state, it is possible, by the application of a stress to exchange the variants one for the other by the movement of the interfaces. This exchange leads to a larger volume of variant(s) favoured by the stress and involves a macroscopic shape change.

The one way shape memory effect can therefore be explained from these features : the cooling of a single crystal of austenite induces all the martensite variants with the same probability for each of them. Applying a stress gives rise to the interfaces movements which lead to a macroscopic permanent strain. The heating towards the austenitic state regenerates the initial single crystal and therefore the initial shape. This is the one way memory effect. In the case of a polycrystal the same phenomena occur in each single crystal, however the strain is limited due to the strain compatibility at the grain boundaries.

The equipartition which occurs in a virgin sample by simple cooling below M_f can be destroyed when the martensitic transformation is driven with a stress. Indeed, a single martensite variant induces a macroscopic shear strain. Reciprocally, if a shear stress is applied, it will

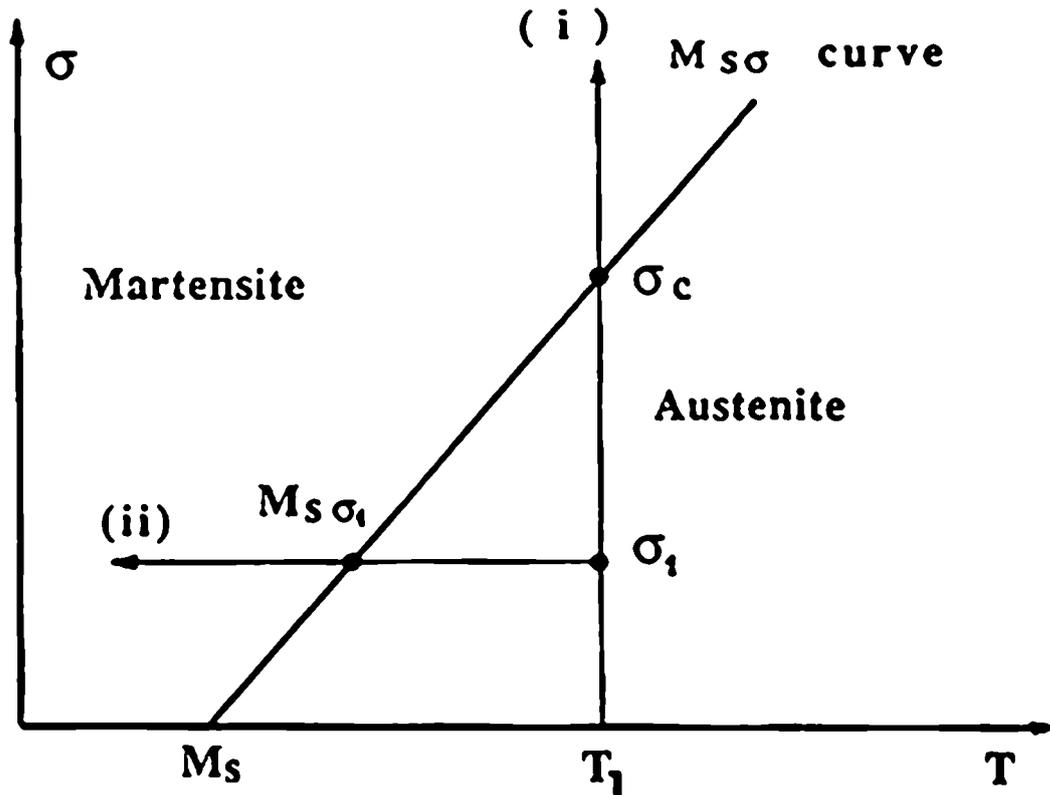


Fig. 1: Schematic phase diagram as a function of temperature and uniaxial stress (austenite \rightarrow martensite).

(i) induction of the transformation by increasing stress at constant temperature T_1 .

(ii) induction of the transformation by decreasing temperature at constant stress σ_1 .

rise the transformation temperature for the variant which strain occurs in the same direction as the applied stress, whereas for the other variants the transformation temperature will be less affected or even lowered. This phenomenon can be described by a modified Clausius-Clapeyron equation where the pressure is replaced by the applied stress and the volume change at the transformation by the shape change. (2) (3).

$$\frac{d\sigma_a}{dM_{s\sigma}} = \frac{\rho \Delta H_{a \rightarrow m}}{\epsilon_{a \rightarrow m} M_{s\sigma}}$$

$\Delta H_{a \rightarrow m}$ is the mass enthalpy of the transformation

ρ is the density

$\epsilon_{a \rightarrow m}$ is the transformation strain in the direction of the applied tensile stress σ_a

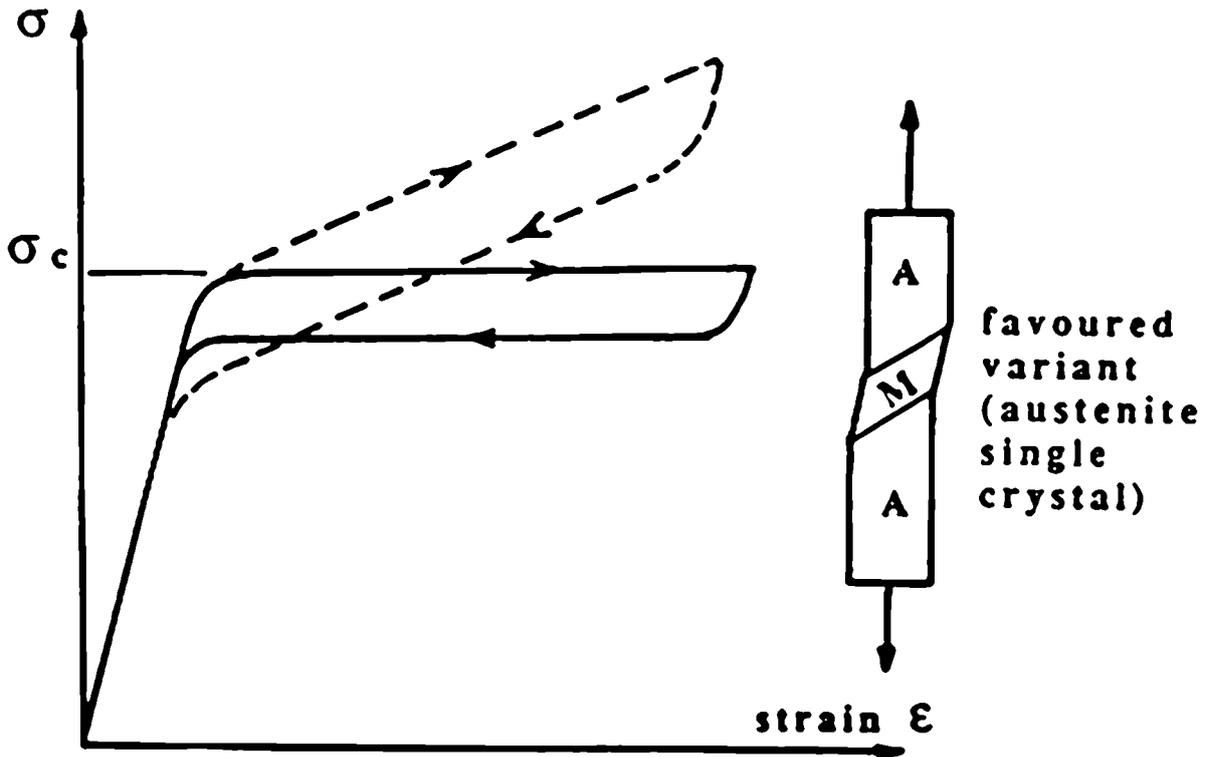


Fig. 2: The superelastic effect (schematic) corresponding to (i) in Fig. 1.

— single crystal
 --- polycrystal

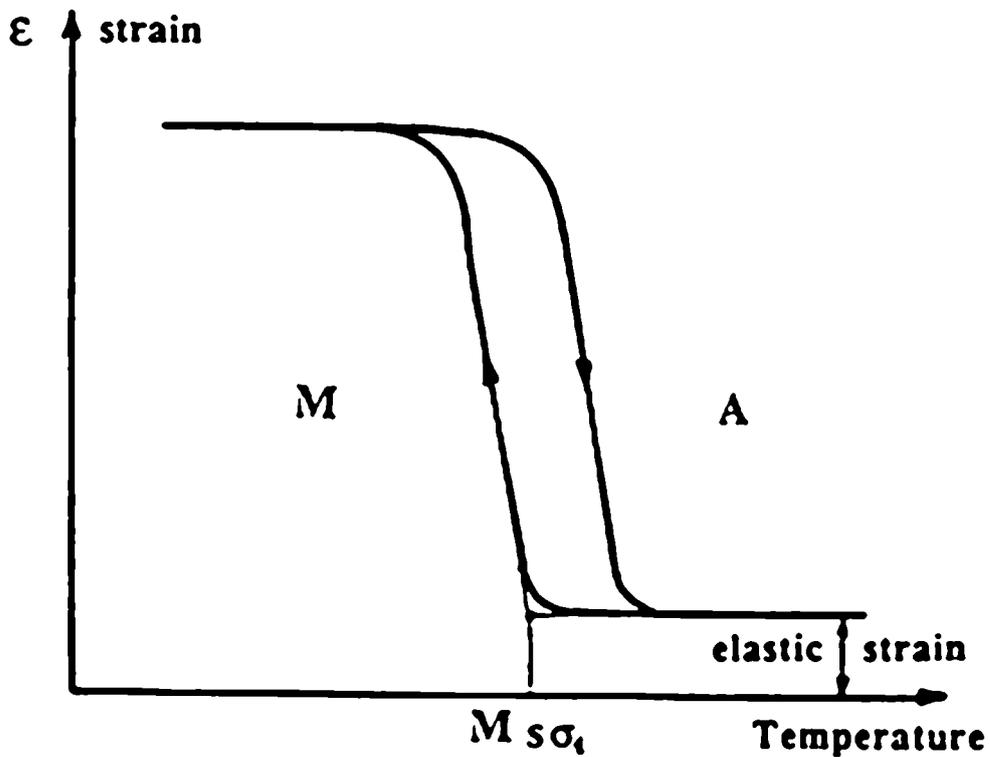


Fig. 3: Strain-Temperature behaviour obtained with a constant stress σ_1 , corresponding to (ii) in Fig. 1.

$M_{s\sigma}$ is the M_s temperature modified by the stress.
The curve of the Fig. 1. translates this equation.

This feature can be experimentally verified by two ways :

(i) At constant temperature above A_f , when the applied stress reaches the critical value σ_c one variant is induced giving rise to a large strain, which disappears at decreasing stress.

This is the so called superelastic effect (Fig. 2).

(ii) A constant stress σ_1 is applied, which is insufficient to induce the martensite at a temperature $T > A_f$; during the cooling, the $M_{s\sigma_1}$ is attained for one particular variant, also giving rise to a large strain, which disappears at increasing temperature (one way memory effect) (figure 3).

What happens when the Two Way Memory Effect is active, is the behaviour described just above (Fig. 3) but without any stress application. Therefore the TWME involves, during the cooling, the nucleation and growth of one particular variant of martensite (or a limited number of variants) whereas the other variants do not appear. During the heating the normal one way memory occurs, which is the come back to the initial austenite crystal. As said in the introduction this feature is not inherent to the martensitic transformation but occurs after particular thermomechanical treatments which will now be described.

The training processes and the Two Way Memory Effect obtained

Two classes of thermomechanical treatments can be distinguished for the training, one class involves some diffusion process, the other which is more universal is not concerned with any diffusion.

A - Trainings with diffusion process

In Cu-Zn-Al alloy with M_s slightly lower than room temperature it is possible to induce some TWME by the following treatment (4) (5) : the sample in the austenite state is straight at room temperature (Fig. 4). It is bended around a cylinder such as the maximum strain is about 1.5 %, therefore the sample becomes partially martensitic. The sample, compelled to be bent, is then heated to about 373K then cooled down to room temperature and leaved free from this moment. It remains therefore slightly bent and exhibits a TWME by further cooling and reheating to room temperature (Fig. 4). This occurs in polycrystal (4) and single crystal as well (5) and not only for bending stresses. For uniaxial stress on a single crystal, a single variant is induced and can be

partially stabilized by the upper treatment. It has been shown in this case that the TWME occurs by the further growth during cooling of the stabilized stress induced martensite variant which is reverted by heating to room temperature (5). It is supposed that the same mechanism occurs when the stress is not simple (several variants) and for polycrystals.

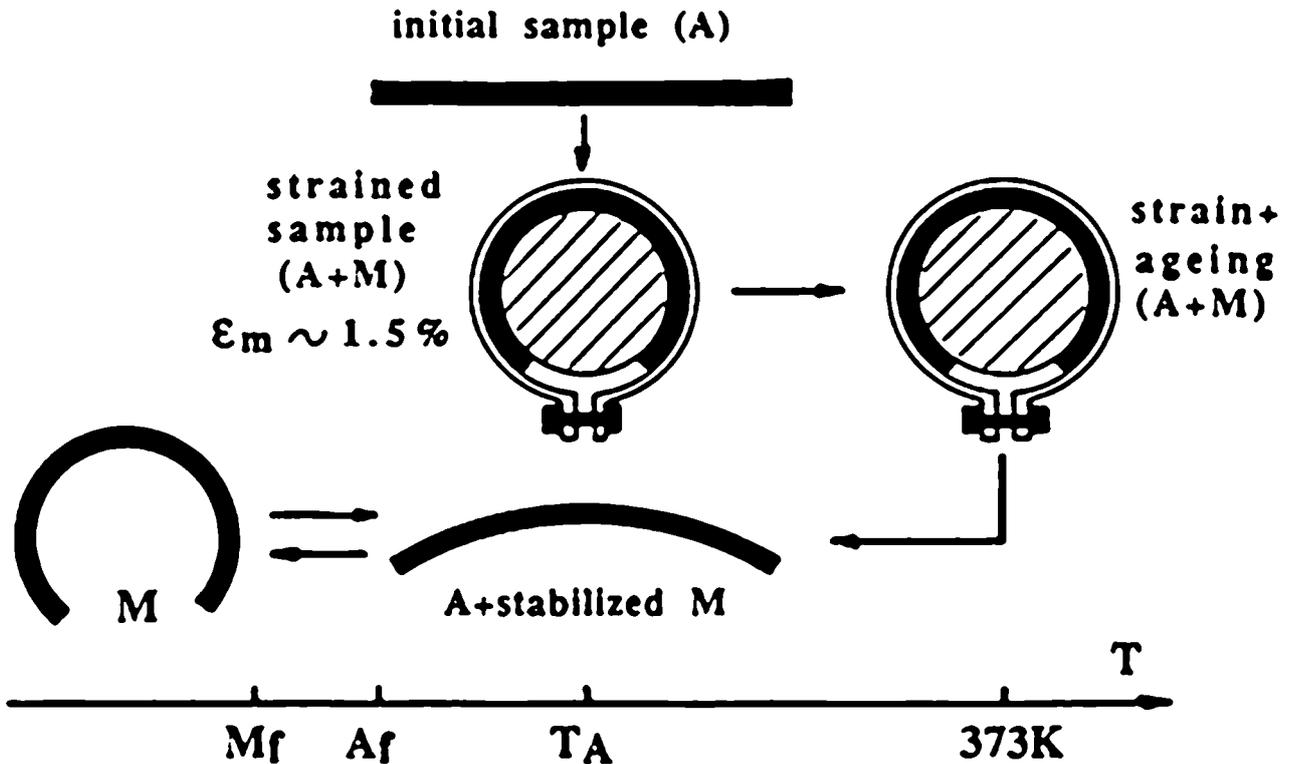


Fig. 4: Thermomechanical treatment leading to TWME in Cu-Zn-Al. This treatment involves a diffusion process which induces stabilized martensite above the conventional A_f (4,5).

Another way to obtain the TWME by diffusion controlled process has been found by Nishida and Honma (6) in Ni rich Ti-Ni alloy. The sample is submitted to constrained ageing during which a second phase precipitates. This second phase induces internal stresses which in turn are at the origin of a TWME when the martensitic transformation occurs (7) (8). The Fig. 5 summarises the behaviour : the sample has initially a straight ribbon shape after the solution treatment at high temperature, it is then constrained in a stainless steel tube and heated at moderate temperature (673 K to 773 K). During this thermomechanical treatment, some precipitation occurs which has been identified as $Ti_{11}Ni_{14}$. After cooling at $T > M'_s$, the sample is released and is partially curved in the way imposed by the tube. On further cooling, between 300 and 200 K a spontaneous shape change, opposite to the one imposed during the ageing, is observed due to the premartensitic (M'_s) and the martensitic

(M_s) transformations. This shape change strongly over-reach the initial straight shape. On heating above 300K ($T > A'_f$) the after ageing shape is recovered and the TWME cycle can be repeated. This behaviour can be understood as follow (Fig. 6) : the involved precipitate is coherent and plate shape; the lattice space is smaller along the direction perpendicular to the plate. When the sample is submitted to a tension stress the precipitation occurs in such a way that the normal to the plate is perpendicular to the tension axis. The external tension stress is suppressed but around the precipitates an internal local tension remains which is perpendicular to the initial external one. The martensite variants which will occur will therefore give an extension in this way and consequently a contraction in the direction of the initial tension stress. This effect has been called All Round Shape Memory Effect and is spectacular when shown with flexion thin samples. It must however be noticed that the strain involed in the total TWME does not exceed 2 %. Another common problem to the diffusion controled training processes is the fact that the high and low temperature shapes seem to be very hard to define in advance.

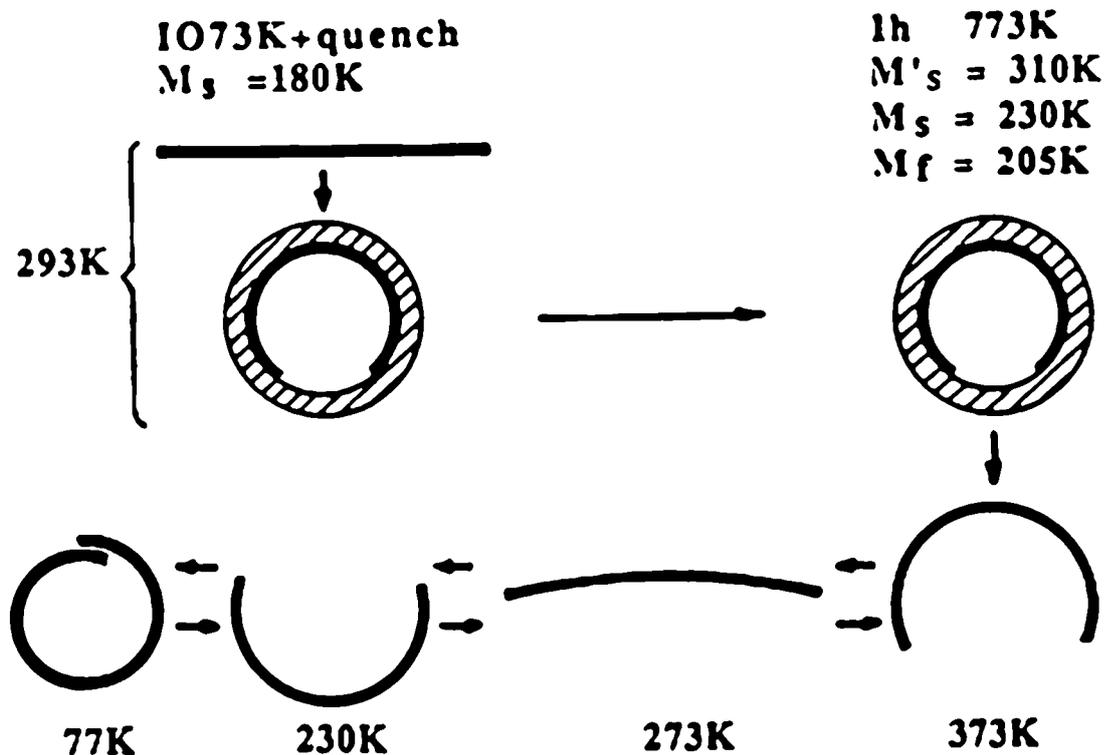


Fig. 5: Thermomechanical treatment leading to the All Round Effect in Ni rich Ti-Ni alloy (6,7,8).

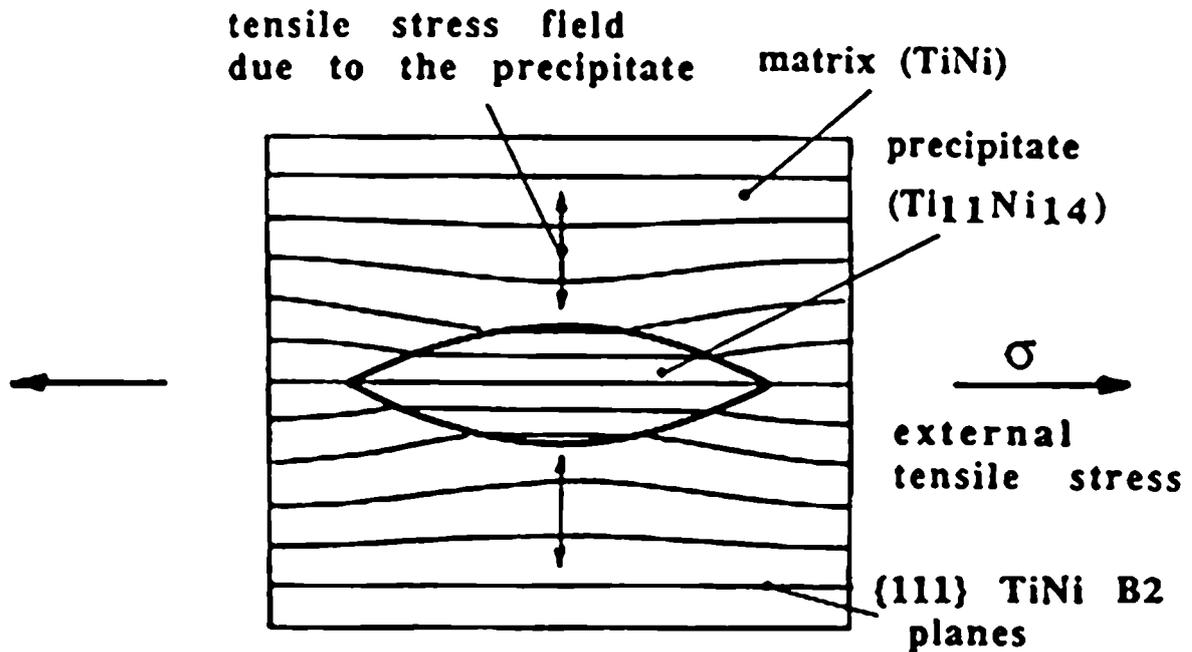


Fig. 6: Schematic illustration of the precipitation of $\text{Ti}_{11}\text{Ni}_{14}$ orientated by the external tensile stress and providing an internal perpendicular tensile stress field.

B - Diffusionless training processes.

Several training methods have been used which involve repeated cycles combining temperature, stress and strain variations :

* Thermal cycling with a constant stress :

When thermal cycles like those described in Fig. 3 are repeated a number of times (typically $N > 10$), it is consequently observed that, without any external applied stress, a spontaneous strain occurs in the same direction as with the stress and which amplitude depends on the number of cycles and on the applied stress during the training. The following results have been obtained on a polycrystalline Cu-Zn-Al, plate shape submitted to a torsion torque and free to deform (9, 10) : Fig. 7 exhibits the changes of the first strain-temperature cycles, the sample being submitted to a constant torsion torque. A noticeable change is observed during the first cycles, then a stabilization of the hysteresis loop occurs after 5-10 cycles. Following this training, a TWME is observed as seen on Fig. 8 : γ_p is the austenite permanent strain due to the training and γ_r is the TWME amplitude. γ_r increases linearly with the

applied stress then saturates at approximately 8 %, γ_p also increases linearly with the stress but without any saturation.

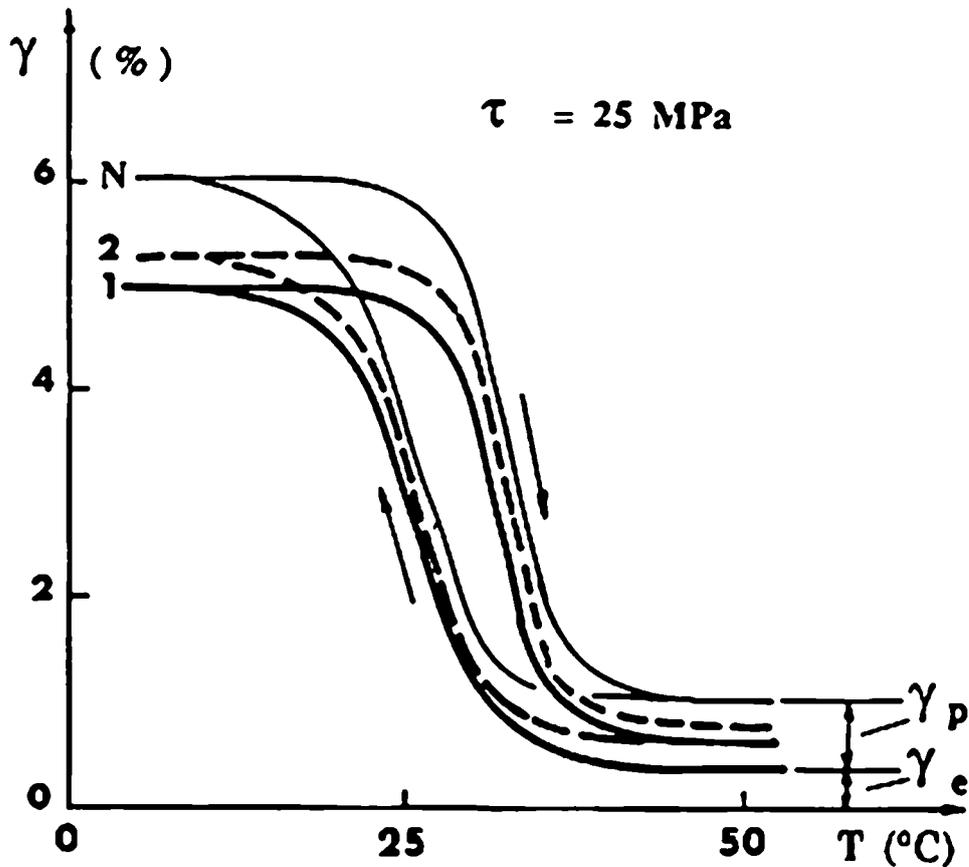


Fig. 7: Successive Transformation-Strain cycles in Cu-Zn-Al alloy (torsion)(10). For $N > 10$ the cycles are quasi closed and change very little. τ and γ are respectively the stress and the strain of the external fiber of the sample (the most strained in torsion stress). γ_e is the elastic strain induced by the constant stress τ in the austenitic state. γ_p is the plastic strain induced by the training.

* Transformation above A_f by superelasticity :

Another cycling can be applied to the sample like the one shown in Fig. 2 at a constant temperature above A_f . For the example of a polycrystalline Cu-Zn-Al sample submitted to a torsion torque, the behaviour during the first cycles is given in Fig. 9. As in the first method, some permanent strain γ_p is observed. By cooling and heating without stress the same TWME behaviour as the one shown in Fig. 8 is observed. The obtained γ_r is related to the maximum value of the stress attained during the training cycle but the relation is not linear and depends on the training temperature (10). The values of the TWME (γ_r) are generally smaller than in the previous case.

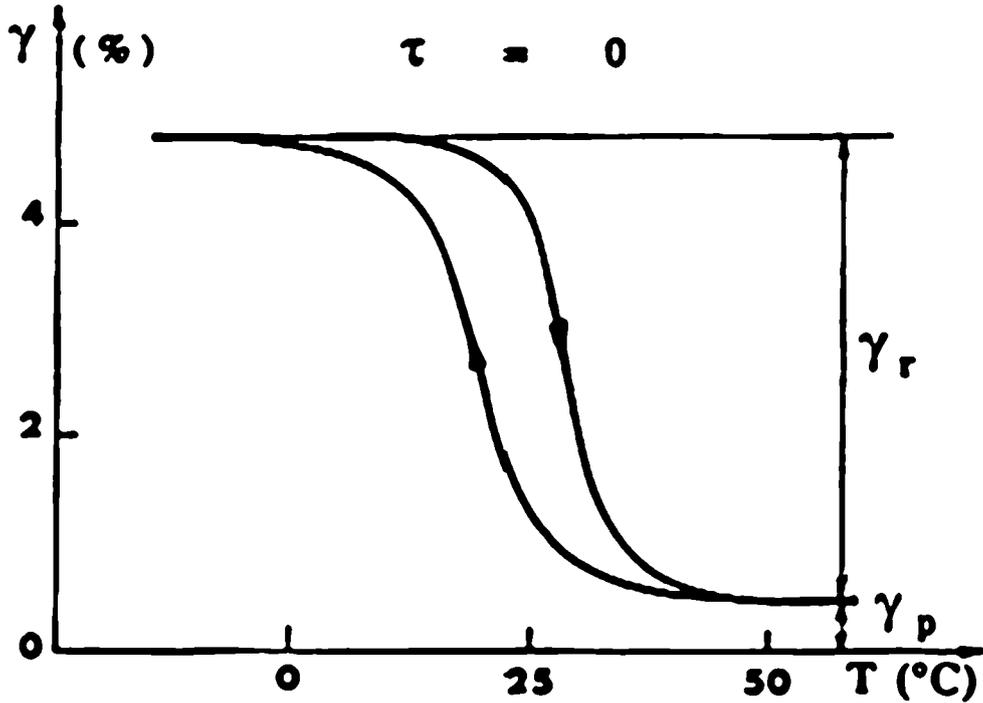


Fig. 8: Strain-Temperature cycle with zero stress after training with a constant stress of 25 MPa. γ_r is the reversible part of the strain and is the amplitude of the TWME.

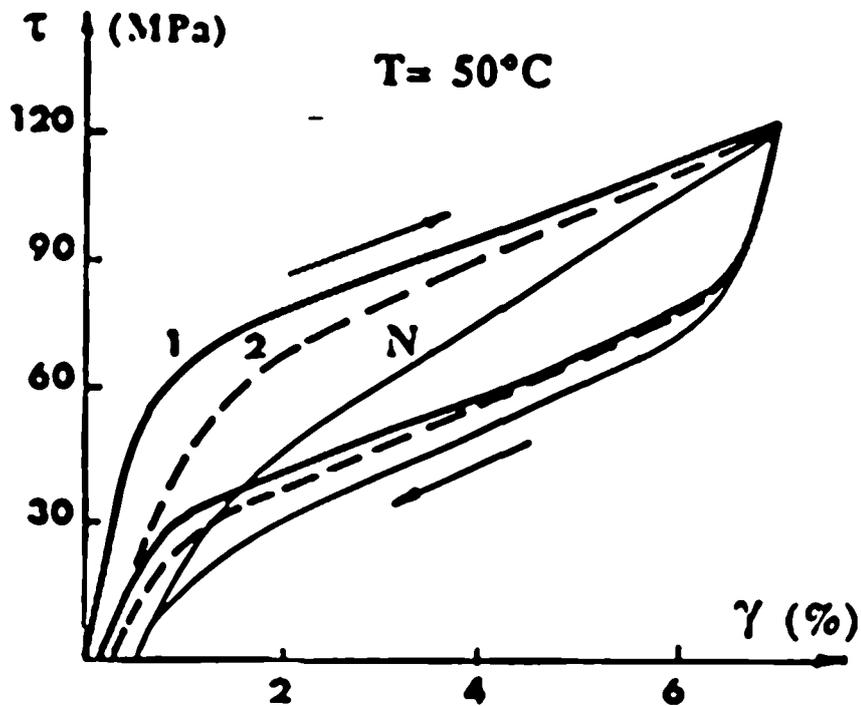


Fig. 9: Superelastic training cycles leading to the TWME in Cu-Zn-Al alloy with $M_s = 24^{\circ}\text{C}$ (torsion test) (10).

* Thermal cycling with imposed strain :

The sample in the austenite state is submitted to an elastic strain in such a way that the corresponding elastic stress is not enough to generate the martensite or the dislocation plasticity. By cooling the stress induces the favoured variants; this relaxes the stress itself because the strain remains constant. It is seen that the sample strain even overhapp the imposed one which proves that the favoured variants, once created, carry on to increase even with a zero stress during the cooling (Fig. 10). By heating, the sample recovers its initial shape and stress (in first approximation). Such a cycle, repeated a number of times also leads to the TWME but with less efficiency than in the previous cases.

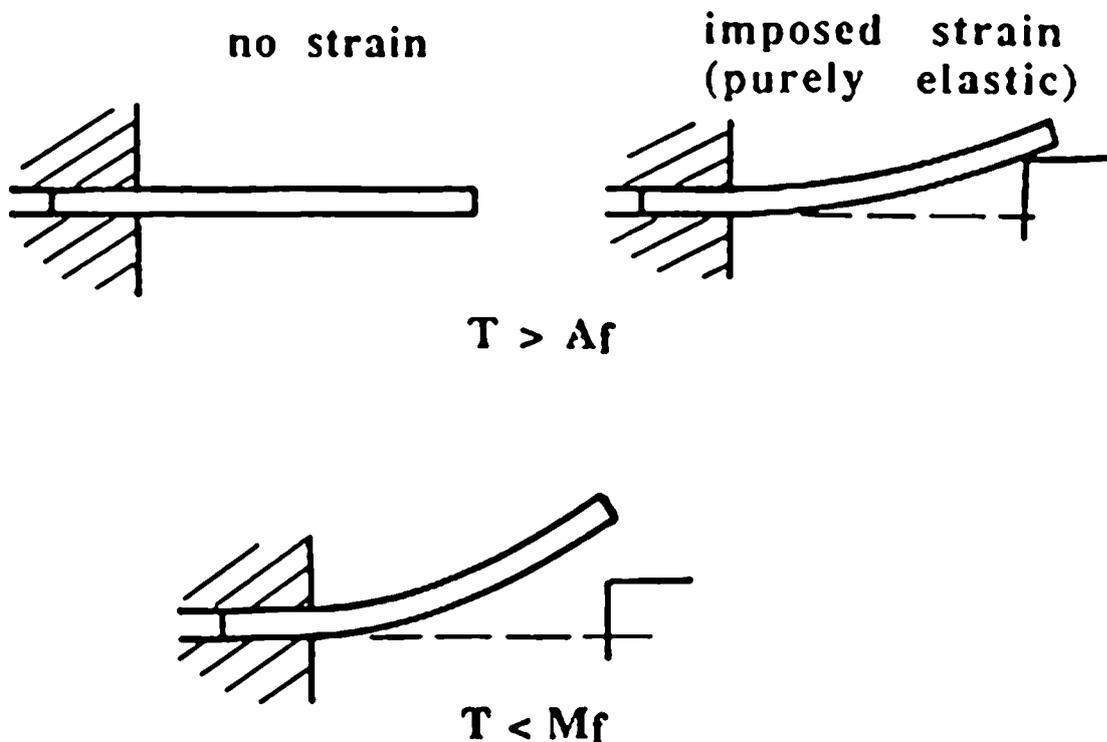


Fig. 10: Training process with imposed strain. A purely elastic strain is imposed in the austenitic state. This induces an elastic stress. By cooling the stress is relaxed by the orientated martensitic transformation. The strain over-reaches the imposed strain. By heating, the sample recovers its initial shape and is again submitted to the initial stress (in first approximation).

* Mixed training processes (11) (12).

At $T > A_f$ a strain can be applied in such a way that a partial martensitic transformation occurs. Then the temperature can be decreased inducing a new strain. During the heating the strain can be imposed or not. These processes are in fact the consequence of hard tensile test machines which are not well adapted for this kind of thermomechanical treatment.

The origin of the Two Way Memory Effect (diffusionless training process)

The TWME is due to the nucleation and growth of some given favoured martensite variant(s) and must be generated by some asymmetry in the austenite. Two main hypothesis have been proposed : Residual martensite "debris" subsisting above the conventional A_f which could increase by cooling; and orientated structural defects such as dislocations which could act on the nucleation and/or the growth of particular variant(s) of martensite. It has been observed that in trained samples M_s and A_f points increase with the number of cycles. This is confirmed by electron microscopy observation(11) which reveal the presence of martensite "debris" some ten degrees above the initial A_f . However the TWME remains even after heatings as high as 100 °C above A_f and in these conditions no martensite is observed (13).

The second assumption is more likely and has numerous experimental confirmations (11) (13) (14). It must be first noticed that, even without any external stress applied, the thermal cycling in shape memory alloys like Cu-Zn-Al generates dislocations in the austenite which initially contains very few defects (14) (15) (16). The generation mechanism of these dislocations is not the usual conventional plastic deformation but involves the participation of particular stacking faults produced in the martensitic structure during the transformation. Some models have been proposed (13) (17) which are still discussed.

The case of a Cu-Zn-Al single crystal training has been studied in details by Rios-Jara (13). The single crystal of austenite has been trained in traction by superelasticity above A_f , a single variant of martensite is then induced. Afterwards when the sample is cooled down without any stress, several regions are observed : two regions with two variants and one with a single variant. The whole sample, in the austenitic state, has only one kind of dislocations with Burgers vectors $\vec{b} = \pm [001]$ and line vector $\vec{u} = [111]$ or $[\bar{1}\bar{1}\bar{1}]$ whereas numerous other combinations of the same kind could be found with $\vec{b} = \langle 100 \rangle$ and $\vec{u} = \langle 111 \rangle$ type. Moreover, the single variant is observed in the region where the dislocation density is much higher than in the other regions. Therefore, the single variant is closely related with the presence of a high density of orientated dislocations. In the case of polycrystal training, large dislocation densities have also been observed but no close correlation with the produced variants have been shown until now.

Several mechanisms can be considered to explain the role of the dislocations in the nucleation and growth of the particular variants of martensite which lead to the TWME :

- * The direct participation of the dislocations in the nucleation

mechanism of the martensite by dissociation for exemple. This seems to be little probable in the shape memory alloys because, once created, the dislocations are particularly stable and do not move in the austenite after successive cycles. Moreover the dislocations of the parent phase seem to stay at the same place without large changes when the sample is invaded by the martensite. At last, as seen before, the TWME can also be induced by some other defects like precipitates which are not able to prefigure the new phase.

- The stress field of the dislocations can influence on the nucleation of particular variants. It has indeed been established (19) that a stress field can deeply modify the elastic properties of the austenite. In particular in the case of Cu-Zn-Al, the elastic constant $C' = 1/2 (C_{11} - C_{12})$ can locally be zero in a given direction which constitutes a mechanical instability, leading to the nucleation of a particular martensite variant. The stress field can also influence on the growth of a particular variant in providing the relaxation of the elastic strain energy induced by the growth of this particular variant in the austenite. This can be understood as the application of the Clausius-Clapeyron law, when the external stress is replaced by the local internal stress.

- Energetic considerations on the Burgers vectors of the dislocations have also been proposed to explain the TWME (20). As seen before in trained single crystals, the dislocations have particular Burgers vectors and directions. Depending if the austenite crystal transforms into one variant or the other, it has been shown that the Burgers vector length increases, stays identical or decreases. In first approximation (the elastic constant values have also some influence) the more favoured variant(s) will be the one(s) which gives the smaller Burgers vector.

Conclusion :

The TWME can be induced by various training schemes. Some of them involve diffusion processes, others the use of thermomechanical cycling. The most efficient is the thermal cycling with a constant stress which can lead to 70-80 % of the strain induced by the stress during the training (maximum $\gamma \simeq 8$ % torsion shear strain in the case of polycrystalline Cu-Zn-Al). This kind of training also allows to predict with a good accuracy the high and the low temperature shapes.

From the different results shown in this paper, the scheme of the TWME could be the following :

First occurs the nucleation and the beginning of the growth of some particular variant(s) induced by the internal stresses which origin can be either orientated dislocations, orientated precipitates or other

complex defects at the grain boundaries for example. In a second stage, the existing variant(s) increase without any assistance : indeed the internal stresses (elastic) are fastly released by the large shear strain of the transformation ($\sim 20\%$ shear) and therefore their action is limited. This stage is experimentally proved by the behaviour of a sample submitted to an elastic constant strain (Fig. 10) which deforms away from the initial imposed strain when no external stress is applied. In the case of the training by stress induced stabilized martensite, this should be the single stage observed.

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