Stability and ageing of the Two Way Shape Memory Effect in a Cu-Zn-Al alloy

L. Contardo, Trefimétaux, Research Center, Serifontaine, France, now at Souriau, Research Center, Boulogne Bill, France
P. Naudot, Trefimétaux, Research Center, Serifontaine, France
G. Guénin, Institut National des Sciences Appliquées, Villeurbanne, France

Introduction

Among the thermomechanical properties of the shape memory alloys, the Two Way Memory Effect (TWME) corresponds to the memorization of two shapes : a low temperature one in the martensitic state and a high temperature shape in the austenitic state. the change from one shape to the other is only driven by the temperature change excluding the application of any mechanical stress. This property is obtained after special thermomechanical treatments called "training".

Several training processes can be used which involve true plastic deformation of austenite or martensite (Perkins (1), Nagasawa (2)) ; ageing under stress of austensite (Takesawa et al (5), Rapacioli et al (6) ; transformation cycling by stress application at fixed temperature above Af or by temperature cycling with stress application (Schroeder et al (7), Morin et al (8), Todoroki et al (9), Perkins et al (10) Reyhani et al (11).

Two kinds of training processes have been used by the present authors for a Cu-Zn-Al alloy. The influence of different training parameters on the TWME obtained have been quantitatively measured (12).

In spite of the technological interest for the use of such alloys, the ageing stability of the TWME has not yet been studied. The aim of this work is therefore to provide informations on the stability of the TWME of a room temperature transforming Cu-Zn-Al alloy and on the kinetics of its degradation above 100°C.

Experimental details

A polycrystaline industrial alloy, elaborated by TREFIMETAUX has been used. The composition is Cu-26.13 wt%- Zn 4.00 wt% Al. Before training, the thermal treatments are the following : β phase homogenization 200 s at 825°C, then a quench at 100°C followed by a stay of 55 ks at 50°C. This last thermal treatment is effecitive to avoid any stabilization problem of the martensite (13) and to obtain well defined transformation temperatures. These temperatures are $M_s = 24°C$, $M_f = 10°C$, $A_s = 23°C$, $A_f = 30°C$.

The training process has been realized on a torsion apparatus built especially for this aim and which has been described elsewhere (14). The samples are small plates of size e = 1mm, b = 4 to 5mm, L = 20 to 30mm.

Article available at http://www.esomat.org or http://dx.doi.org/10.1051/esomat/198903005

Two training processes have been used (14) :

1) Temperature cycling from above to below the transformation temperature with an applied constant stress : the sample is free to deform when the martensitic transformation occurs.

2) Stress cycling at constant temperature above Af leading to the superelastic effect (induction of the orientated martensitic transformation by the stress). A typical Strain - Temperature curve for the obtained TWME is given in figure 1.

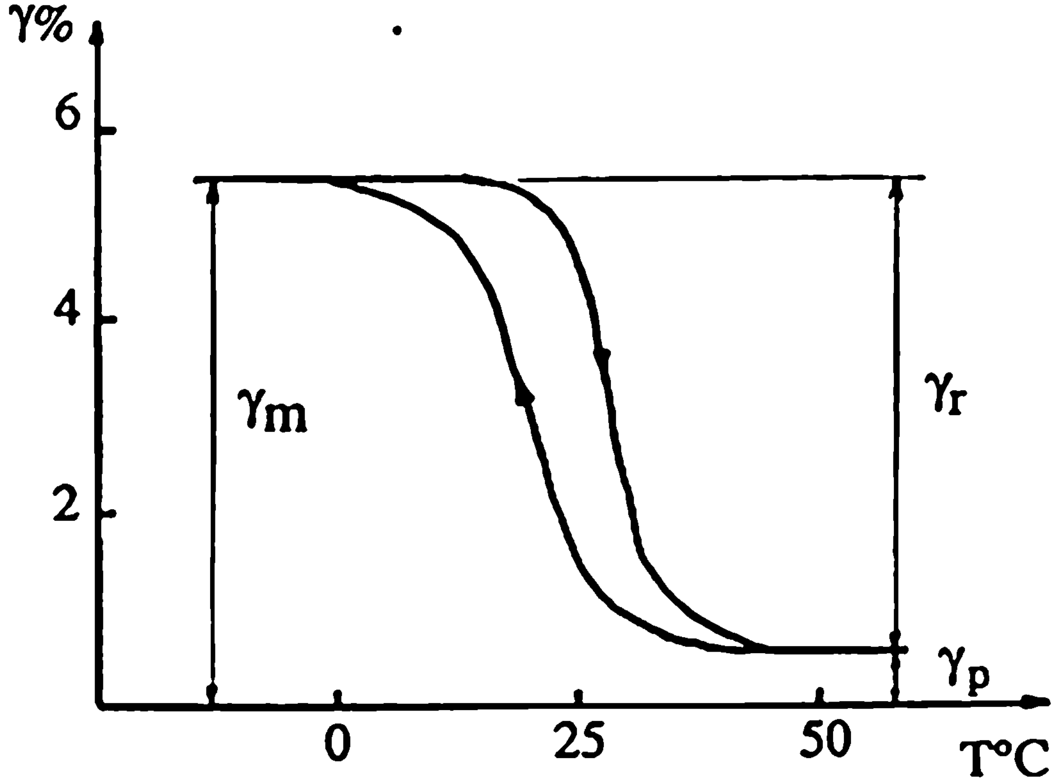

Fig. 1: Strain-Temperature curve obtained with a sample which exhibits the Two Way Memory Effect.

$\gamma = \Theta e/L$; γ is the maximum shear strain in the sample, Θ is the torsion angle, e is the thickness of the sample and L is its length.

The strains are referred to the initial shape of the sample above Af before any training : γ_p is the plastic strain induced by the training process, γ_m corresponds to the memorized low temperature shape and γ_r is the amplitude of the TWME ($\gamma_r=\gamma_m-\gamma_p$).

The stability of the TWME or the ageing kinetics have been studied without any enternal mechanical stress and without thermal cycling (except those necessary to check the TWME). This is the most unfavourable case, indeed, the ageing behaviour is improved when an external stress is applied in the same way as the TWME or when transformation cycles are done.

Experimental results

The maximum temperature of the sample during the training was usually 50 to 60 °C. Although this temperature is above A_f (A_f=30°C) some residual martensite is retained at 50°C after the training, so the samples have been heated to 100°C to suppress this retained martensite (14). This heating leads to the complete reversion of the martensite corresponding to a substantial decrease of γ_p which threfore is only due to true plastic strain.

The annealing at 100°C also induces a decay of the TWME amplitude, this decay proceeds with the ageing time as will be seen later. If a flash heating to 100°C is done, the decrease is small and only depends on the training process : the decrease is smaller if the training cycles number is larger. Above a defined cycling number, the decrease no longer depends on cycling. For example, when the training consists in transformation cycles with constant stress, the decrease of the TWME amplitude by flash heating at 100°C is 24% for 13 training cycles and becomes 8 % above 40 cycles. For training by superelastic effect, the decrease of the TWME is 16 % above 200 cycles.

Following the flash heating at 100°C, a decrease of γ_p is observed at 50°C during the first days of ageing. This value is then stable for times as long as 300 days at 50°C. The stable value is 16 % below the value obtained after the flash heating (figure 2).

It must be noticed that

1) the relative decrease is the same whatever is the amplitude of the TWME,

2) this decrease does not depend on the training process,

3) the stable value is not affected by a second flash heating at 100°C.

During the isothermal ageing at T>100°C a continuous decrease of the TWME is observed. The ageing kinetics have been studied for four temperatures : 100°C, 118°C, 130°C, and 140°C.

In this case all the samples have been trained by temperature transformation cycling with constant stress; 50 training cycles have been done and the strain γ_r after the flash heating was the same for all the samples (γ_r=3 %) except for the sample aged at 140°C for which γ_r=6.8 %.

$\gamma_r(t)$ is the TWME amplitude after the annealing time t. The variation of $\gamma_r(t)/\gamma_r(t=o)$ as function of time is drawn on figure 3.

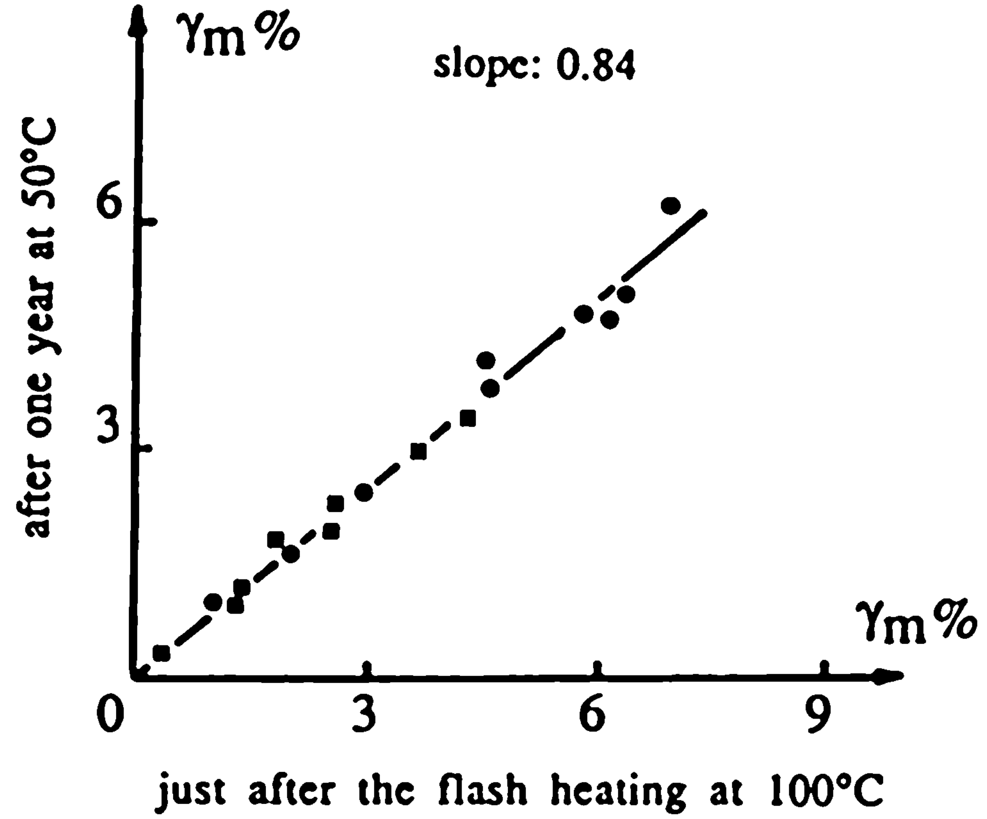

Fig. 2: Martensite strain γ_m for the TWME obtained after 50°C ageing as a function of the same value obtained just after the flash heating at 100°C.
● Values obtained by temperature cycling with a constant applied stress
■ Values obtained by stress cycling at constant temperature above Af

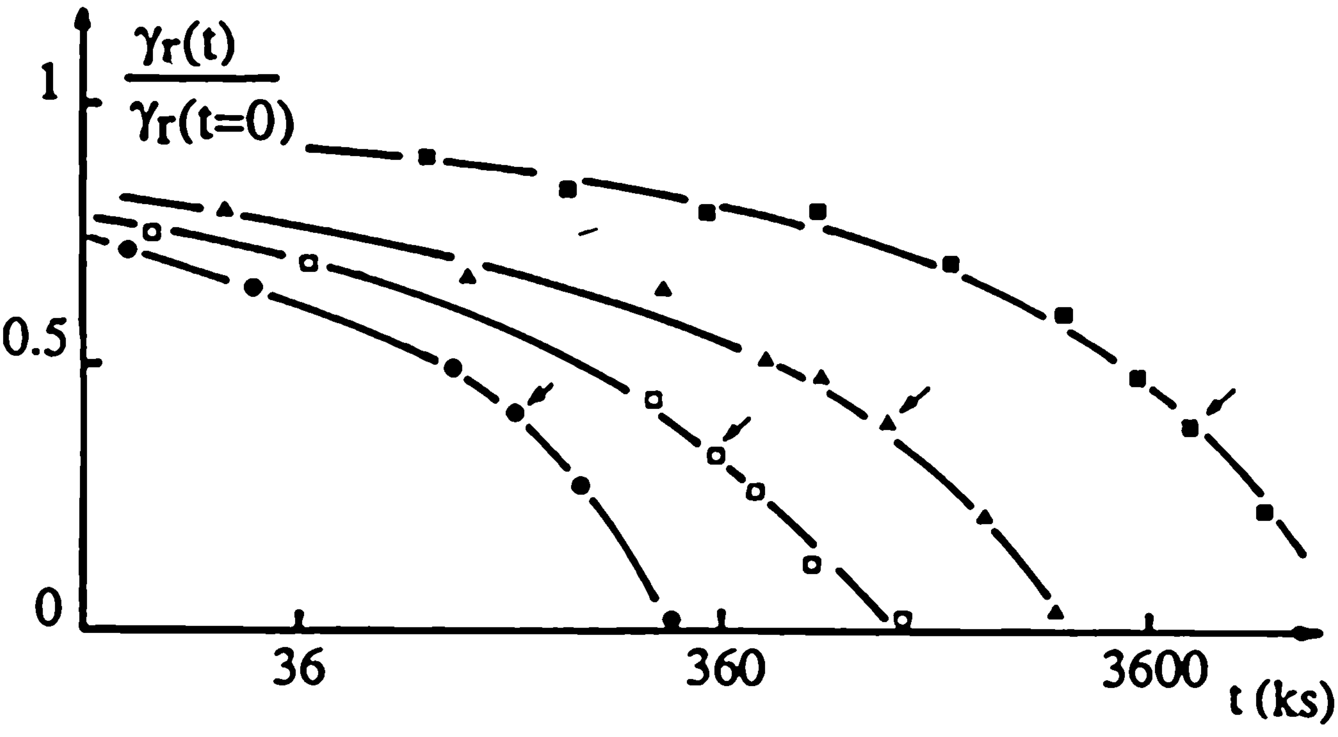

Fig. 3: Changes of the TWME amplitude as a function of the ageing time for several ageing temperatures: ■ 100°C, ▲ 118°C, □ 130°C and ● 140°C. The arrows indicate the times from which the transformation temperatures begin to decrease (precipitation).

During the ageing a precipitation of second phase is involved (essentially a α type phase). This one can be detected with a good sensitivity by the change of the transformation temperatures. This actually accurs, but after a substantial decrease of the TWME (at least 50 %). The arrows drawn on figure 3 indicate the time at which the transformation temperatures begin to decrease, indicating a precipitation. Although the ageing is done without any extermal stress, the precipitation also produces a strong change in the value γ_p corresponding to the high temperature shape : for example, this value changes from o.4 % to 1.5 % for 100 ks and 500 ks ageings at 140 °C respectively. This strain occurs probably because the precipitation has a bainitic character and is orientated by the intermal stresses, the same which are responsible for the TWME. This have been observed by transmission electron microscopy (figure 4).

Fig. 4: T. E. M. micrography showing the bainite in a sample aged 500 ks at 140°C.

The precipitation occurs when the TWME has decreased by 60% almost independantly of the ageing temperature.
This decrease does not involve any change of the transformation temperatures or change in γ_p.(figure 5)
This means that this decrease is probably due to a restauration or elimination of the structural defects responsible for the TWME. Dislocations are introduced in the sample by the training process as can be observed by transmission electron microscopy and they are responsible for the residual γ_p. During the ageing these dislocations are allowed to climb, rearrange and possibly dissappear. This leads to a decrease of the internal

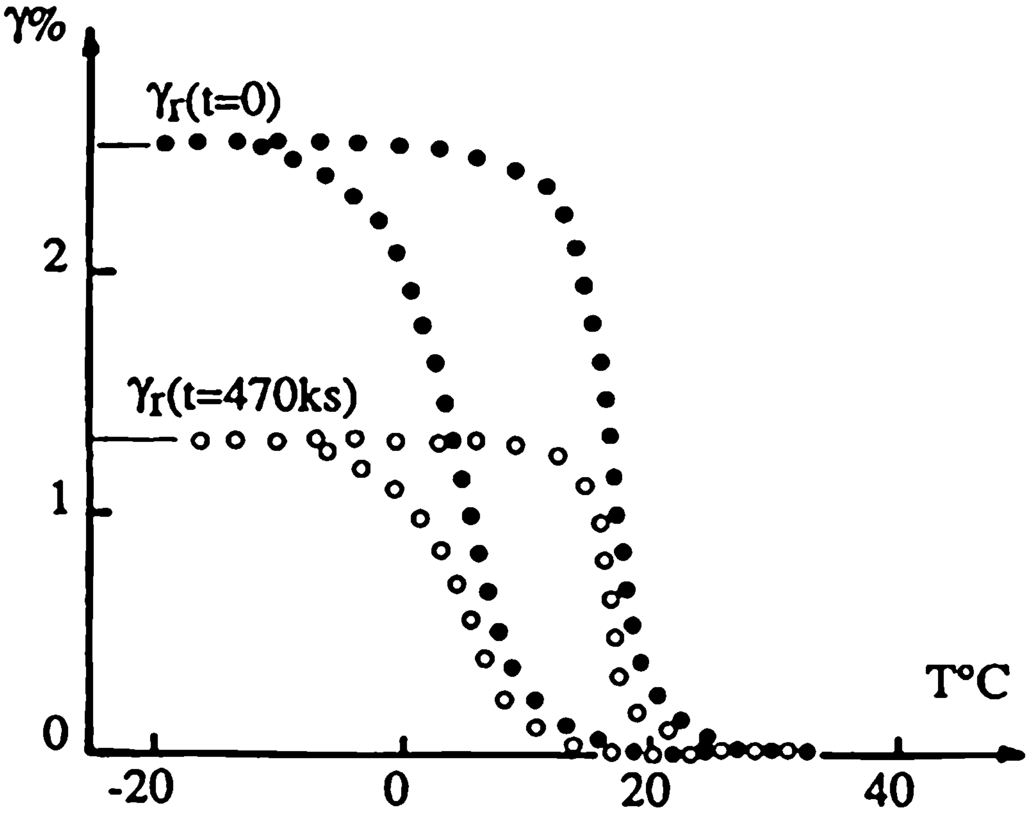

Fig. 5: TWME for a sample aged at 118°C:
● just after heating at 118°C
o after 470 ks at 118°C

stresses which are supposed to be important for the TWME. The climb mechanism involves a thermally activated process. An apparent activation energy can be calculated with the times corresponding to a 50 % decrease of the TWME amplitude according to:

$$t_{50\,\%} = \text{cste.} \exp(E_a / kT)$$

These times are given in the following table

ageing temperature (°C)	100	118	130	140
$t_{50\,\%}$ (ks)	3100	470	180	80

The points of the curve $\ln(t_{50\,\%}) = f(1/T)$ are actually on a straight line (figure 6) including the one corresponding to the 140 °C ageing where the initial amplitude was different.Therefore it seems to that the ageing kinetics does not depend on the amplitude of the TWME.
The apparent activation energy is $E_a = 1.20 \pm 0.03$ eV.

An extrapolation for 80°C gives $t_{50\,\%}$ = 300 days and for 50°C $t_{50\,\%}$ = 33 years. Therefore the apparent stability observed at 50°C is coherent with this activation energy.

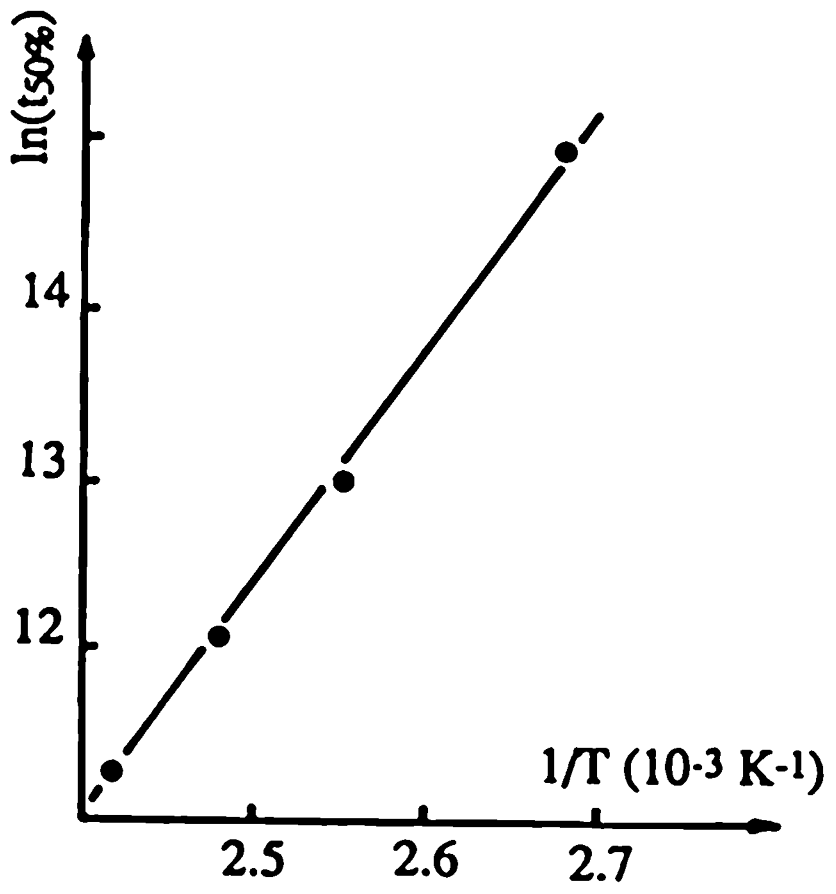

Fig. 6: Curve ln $t_{50\%}$ as a function of 1/T

Conclusion :

The ageing behaviour of the TWME of a Cu-Zn-Al alloy transforming around room temperature has been studied.

The training process induces a plastic strain in the high temperature state; this strain is partly suppressed by a flash heating at 100°C which eliminates the retained martensite and little affects the TWME amplitude.

At 50°C the TWME amplitude first slightly decreases during several days and then remains stable for times as long as 300 days. The TWME is not modified by a second flash heating at 100°C.

Two physical phenomena are at the origin of the TWME decrease above 50°C :

1) A restauration or eliminiation of the defects (dislocations) introduced in the sample during the training process and which are responsible for the TWME.

2) A precipitation of equilibrium or metastable second phases with a bainitic character. This precipitation can be detected by the martensitic transformation temperatures changes and by a one way deformation at high temperature.

In a first stage only the first phenomenon is effective.

It is thermally activated and the study of the kinetics for temperatures above 100°C gives an apparent activation energy of 1.20 eV. From these results the TWME is expected to be stable over years for a use below 50°C.

References

(1) J. Perkins: Scripta Met. 8(1974) 1469

(2) A. Nagasawa, K. Enami, Y. Ishino, Y. Abe, J. Nenno: Scripta Met. 8(1974) 1055

(3) T.W. Duerig, J. Albrecht, G. H; Gessinger: Journal of metals (1982) 14

(4) T. Honma: Proc.ICOMAT 86, J. I. M. (1987) 709

(5) K. Takesawa, S. Sato: Trans. J. I. M Supl. 17 (1976) 223

(6) R. Rapacioli, V; Torra, E. Cesari, J. M. Guilemany, J. R Miguel: Scripta Met. 22 (1988) 261

(7) T. A. Schroeder, C. M. Wayman: Scripta Met. 11(1977) 225

(8) M. Morin, G. Guénin, P. F. Gobin: Journal de physique C5 (1981)1013

(9) T. Todoroki, H. Tamura, Y. Suzuki: Proc. ICOMAT 86, JIM (1987) 748

(10) J. Perkins, R. O. Sponholtz: Met. Trans. 15A (1984) 313

(11) M. M. Reyhani, P G. Mac Cormic : Proc. ICOMAT 86, J. I. M. (1987) 896

(12) L. Contardo, G. Guénin : to be published

(13) M. Mantel: Thesis, Lyon 1985

(14) L. Contardo: Thesis, Lyon 1988