THE THERMAL AGING AND TWO WAY MEMORY EFFECT (TWME) IN Cu-Al-Be SHAPE MEMORY ALLOY

H. FLORES ZUNIGA*(1), S. BELKAHLA*(2) and G. GUÉNIN*
*Groupe d’Etudes de Métallurgie Physique et Physique des Matériaux, INSA de Lyon, Av. Albert Einstein, F-69621 Villeurbanne cedex, France

Abstract: In this study T.T.P. (Temperature, Time, Precipitation) curves of β-Cu-Al-Be have been determined by Differential Scanning Calorimetry technique. This alloy have been found to shows a remarkable thermal stability. The training experiments and the obtained two way memory effect (TWME) have shown that this alloy exhibits a good ability to memory properties comparable to the ones obtained on Cu-Zn-Al and Cu-Al-Ni. The aging kinetics of TWME have been drawn for several temperatures. This work has confirmed the hypothesis already advanced concerning Cu-Zn-Al and Cu-Al-Ni alloys, namely that the TWME aging is mainly due to the dislocation recovery, and in this case is independent of the precipitation phenomenon.

Introduction:
The Cu-Al-Be alloy is a good candidate as low temperature transforming alloy and resisting to the high temperatures agings [1,2,3,4,5]. The aim of this paper is first to precise the ability of a typical Cu-Al-Be alloy to resist at high temperature. The thermal aging is therefore investigated for several temperatures from 175°C to 500°C by using the Differential Scanning Calorimetry (DSC) technique to control the changes of the martensitic transformation. The second object is to explore the capacity of the same alloy to exhibit the two way memory effect (TWME) and to check its stability as a function of aging. Training experiments (which give the TWME) are therefore made followed by agings at temperatures between 150°C and 300°C.

Experimental:
The alloy of chemical composition: Cu-11.9wt%Al-0.5wt%Be has been supplied by TREFIMETAUX Society as a plate shape ribbon of thickness 3 mm. The measured $M_s$ temperature is -42°C for 10% martensitic transformation, in good agreement with the formula reported by Belkalha [1,5] which gives $M_s = -46°C$ for the given composition. Parallelepipedic samples of 100 mg are cutted from the plate for DSC measurements. The samples used for the TWME measurements are plate shape 30x3x1 mm$^3$ suitable for flexion experiments. According to metallurgical study [1,5] the samples are homogeneized 15 min at 650°C in the

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(2) On leave of absence from: Université d’Annaba, Institut de Physique, BP 12, Annaba, Algeria.
single β phase region, water quenched at 100°C and left 5 min at this temperature. The treatment has been proved to give a $M_s$ temperature stable in time[5]. The aging treatments are carried out in salt baths from 200°C to 500°C and in oil baths from 150°C to 200°C. After each aging treatment the samples are quenched at 100°C and left 5 min at this temperature before being tested. The martensitic transformation behaviour is studied by DSC technique using a DSC 30 Mettler Calorimeter. The transformation temperatures $M_s$ and $A_f$ are taken at 10% martensitic fraction respectively on cooling and heating, and the temperatures $M_f$ and $A_s$ are taken at 90% martensitic fraction respectively on cooling and heating. The martensite fraction is deduced from the transformation enthalpy peak integration, with the supposition that the transformed martensite is proportional to the integrated released heat. Typical DSC curves after different agings at 250°C are shown on Figure 1. The training process as well as the TWME measurements are made on a specific bending apparatus (Figure 2) already described elsewhere [6]. The training consists of a thermal cycling between two temperatures respectively higher than $A_f$ and lower than $M_f$ with a constant applied flexion force (constant weight).

Results and Discussion:

1. The β thermal aging.

The time of beginning of precipitation at each temperature is determined by the occurrence of some significant change in the DSC curve. For example Figure 1 displays curves corresponding to aging at 250°C. It can be seen that in this case a shift in $M_s$ temperature begins to appear between 100 and 150 h aging in correlation to a slight enlargement of the heat peak. The kind of change in the DSC curve depends in the temperature domain (Figure 3) and is probably associated to different precipitates. The results are collected on the Figure 4-a as a T.T.P. (Temperature Time Precipitation) curves where several temperature domains can be seen. On this curve the remarkable stability of the β phase of Cu-Al-Be is shown since, until 300°C no noticeable precipitation is seen below 100 h. Moreover, even when the precipitation takes place the alloy always transforms almost completely but with changes of temperature and hysteresis. The $M_s$ evolutions can be seen on Figure 4-b where it can be noticed again different behaviours depending on temperature according to the precipitate type produced.

2. The TWME Study.

The training treatment is made on the plate shape samples mounted on the flexion apparatus (Figure 2). The sample is sunk in a pentane bath that can be cooled to -120°C and heated to 30°C for thermal cycles. During these cycles the sample is permanently submitted to a constant flexion force. The stresses and strains are calculated from conventional elasticity laws which are a large approximation but which provide elements of comparison. The Figure 5 shows how the training strain and TWME strain increase with the number of training cycles. The Figure 6 displays how the previous strains, after 30 training cycles, changes with the applied stress until 80 MPa.
After a training of 100 cycles at 80 MPa the samples are cycled without any stress (TWME) Figure 7. As can be seen a fast decrease of TWME of about 20% occurs in the first 10-20 cycles, then a slow decrease leads to a final value of 70% (after 200 cycles) of the initial value.

3. Thermal Aging of T.W.M.E.

In order to study the degradation of the TWME strain, several agings are made on samples trained 100 cycles, and stabilised 30 cycles in TWME. The Figure 8 displays the TWME degradation as a function of time for 150°C, 175°C, 220°C and 250°C agings. The first thing to be noticed is that the TWME decreases well before any precipitation process in detected by DSC technique. Indeed at 220°C a significant decrease of TWME is observed after about 5h, whereas no precipitation process is detected before 100 h (Figure 4-a). It is therefore clear that the TWME degradation is not due to precipitation but rather to the annealing of the dislocations created during the training and responsible for the TWME, this hypothesis has already been given by Contardo[7] for Cu-Zn-Al, but in that case the annealing of dislocations and precipitation were simultaneous. More experiments are in progress to confirm these interpretations.

From curves of Figure 8 an apparent activation energy can be calculated, supposing that for the same strain decrease fraction at each temperature, corresponds the same internal state. Figure 9 displays the Arrhenius plots for decreases of 10, 20, 30 and 40%. The corresponding activation energy changes from 1.4 eV (10%) to 1.2 eV (40%).

Conclusion:

The Cu-Al-Be alloy seems to be a good alloy for industrial applications. The T.T.P. curves drawn in this work show a good ability of this alloy to resist at high temperature (more than 100 h at 350°C). The aptitude to take the TWME is proved. The stability of this TWME is good but is not so high than the β phase stability itself. This proves that the annealing of the defects responsible for the TWME occurs previously to the precipitation.

References:

Figure 1: DSC curves for different times of aging at 250°C

Figure 2: Bending apparatus. The sample is trained by a constant flexion stress during the thermal cycling.

Figure 3: Peak Changes of DSC curves for different agings
Figure 4-a: T.T.P. curve of β-Cu-Al-Be. Obtained from DCS curves.

Figure 4-b: Ms evolution for different aging temperatures

Figure 5: The training under constant stress and TWME as a function of number of cycles. The Maximal strain is measured between the martensite and austenite states.

Figure 6: The training and TWME maximal strains for several flexion stress, after 30cycles of training.
Figure 7: Thermal cycling in TWME ($\sigma = 0$), the strain fraction is measured between the strains in martensitic and austenitic states.

Figure 8: Thermal degradation of TWME in aging time

Figure 9: Arrhenius plots for different decreases of TWME strain fractions (Obtained from Figure 8)