Thermal and thermomechanical stability of Cu-Al-Ni shape memory effect
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Introduction
The Cu-Al-Ni is well known for its ability to work at elevated temperature as a shape memory alloy. For applications which involve mechanical and thermal cycling, the evolution of the shape memory effect must not reduce the capacity of a device to satisfactorily operate. Until now, no study exists on both thermal and mechanical ageing effects. In this work, a new concept of fatigue adapted to shape memory alloys is developed by two kinds of thermomechanical cycling. In a parallel direction, another study details the changes which occur during heat-treatments between 423 K and 633 K. It allows to analyze phenomena that interfere in the fatigue life of Cu-Al-Ni alloy.

Experimental conditions:
The copper-based alloy with nominal composition Cu-13wt%Al-4wt%Ni, has been industrially prepared by TREFIMETAUX society. After a standard treatment (further precised), the following transformation temperatures have been found: Mₐ=424 K, Mₛ=452 K, Aₛ=444 K, Aₐ=461 K. Thermal ageing study was made on 50 to 100 mg weight samples, taken from an extruded rod. After homogenization at 1123 K during five minutes, followed by a water quench at room temperature, a range of heat-treatments between 423 K and 633 K were carried out in oil or salt bath. Calorimetric measurements were made on a DSC 30 Mettler which allowed to define transformation temperatures and enthalpy as a function of ageing time.

Part -1- β -phase ageing (473 K - 633 K)
From figure (1), which exhibits a range of isothermal curves and figure (2) that shows the evolution of transformation temperatures and enthalpy during heat-treatment at 513 K, three stages of ageing kinetics can be described:
1- A slight decrease of the transformation temperatures with respect to the ones of the quenched state. This stage seems to be completely inhibited by the following stage above 573 K.
2- A regular increase of Aₛ as function of ageing time.
3- A change of the calorimetric thermograms which appears by an increase of the hysteresis and a spreading of the reverse and direct transformations. In addition, the transformation enthalpy, ΔH representative of the amount of transformed martensite, is significantly reduced.
The Cu-13Al-4Ni alloy, close to the stochiometric composition (Cu,Ni)₃Al displays a high thermal stability compared with Cu-Zn-Al alloy. The microstructural interpretation of β-phase ageing is still controverted; the first and the second stages could be attributed to two short range phenomena (DO₃ ordering process (1,2), ω-like precipitation (3), beginning of spinodal
decomposition (4)). During the third stage, equilibrium phases precipitation phenomenon occurs which affects the transformation and finally inhibits it. It is not excluded that the second stage should also be due to the very beginning of precipitation process ($\gamma_2$ precipitation), taking into account the sensitivity of the alloy to small composition changes.

Fig. 1: Isothermal curves of $\beta$-phase ageing

Fig. 2: $A_s, A_f, M_s, M_f, \Delta H$ evolution during ageing at 513 K.
Part -2- Martensite stabilization

The term of stabilization refers to the effect observed after a rapid quenching and/or a heat-treatment more or less prolonged below $A_f$. The stabilisation effect appears here by a simple shift of the first reverse transformation towards high temperatures and a large spreading in the case of quenching without annealing. The kinetics of the phenomenon depends on three parameters (fig. 3) : (i) thermal history of the alloy, (ii) transformation temperatures, (iii) ageing temperature. The evolution is faster when the ageing temperature is more elevated and close to the $A_s$ temperature.

![Fig. 3: As evolution with martensite stabilization](image)

1- ageing temperature $T_a=453$ K, water quenched $T_q=293$ K
2- $T_a=453$ K, water quenched $T_q=373$ K
3- $T_a=453$ K, standard treatment, $A_s=444$ K
4- $T_a=423$ K, standard treatment, $A_s=444$ K
5- $T_a=453$ K, standard treatment + annealing, $A_s=503$ K

During stabilization treatment, an ordering process in martensite occurs. This order is different from DO$_3$ order inherited from $\beta$-phase. Structural changes in martensite by short range diffusion phenomena, modify the difference between free energy of martensite and $\beta$-phase (5,6,7). By reversion to the $\beta$-phase, DO$_3$ order is fastly recovered and destroys the stabilization effect in martensite. Near the reverse transformation, the efficiency of the stabilization treatment is higher; the mechanical instability of the lattice at the proximity of $A_s$ temperature could favour the vacancy migration.

The spreading of the first reverse transformation after quenching is attributed to the mechanical pinning of the interfaces by quenching defects or by accumulation of this defects (6,7,10). Short time annealing at 423K after quenching is therefore justified to obtain reproducible transformations with low spreading and hysteresis.
Part -3- Thermomechanical behavior

The shape memory effect has been evaluated by testing the alloy in a specific bending apparatus driven by a computer. The plate shape sample (25x3x1 mm³), immersed in a thermostated bath, is submitted to a constant flexion stress and is free to deform. The computer controls the thermal cycling and the acquisition of the data (temperature, position). In fig. 4, the specific parameters of the shape memory effect are defined. The heat-treatment before testing includes an homogeneization at 1123 K (5 mn), a water quenching and a annealing at 423 K (10 mn).

\[ \varepsilon_m \]

\[ \text{Fig. 4: shape memory effect cycle} \]

Cu-Al-Ni training treatment: the sample is thermally cycled under a constant flexion stress between \( T<M_f \) and \( T>A_f \). Consequently, two shapes are memorized, related to the high temperature state (close to the initial shape) and the lower temperature state. Results (fig. 5): the transformation strain obtained after twenty-five training cycles increases linearly with the stress. A saturation effect is observed above 60 MPa. The obtained spontaneous strain is also linear with the training stress for the same number of training cycles. The efficiency (\( \varepsilon_m \) of the first cycle in Two Way Memory Effect divided by \( \varepsilon_m \) of the last training cycle) is about 67%.

\[ \text{Fig. 5: evolution of the strain with training stress and cycling} \]
Thermal cycling under a constant stress: transformation strain in martensite ($\varepsilon_m$) raises rapidly during the first stage so-called "transient" (fig. 6). The increase of $\varepsilon_m$ during this transient stage is intensified when the applied stress is stronger (fig. 5). The residual austenite strain ($\varepsilon_a$) also increases with cycling. After the transient stage, the evolution of $\varepsilon_a$ follows $\varepsilon_m$.

Fig. 6: cycling under a constant stress

Thermal cycling in Two Way Memory Effect: after training (fifty thermal cycles with a rate of 10K/mn between $T_{\text{max}} = 473$ K and $T_{\text{min}} = 423$ K, and under stress of 60 MPa), the samples are cycled in T.W.M.E. ($\sigma=0$). The spontaneous strain in martensite decreases during the first two hundred cycles and stabilizes at 88% of its initial value. The residual austenite strain raises linearly with the number of cycles (fig. 7).

Fig. 7: cycling in T.W.M.E.
Thermal degradation of the T.W.M.E.: during isothermal ageing at 473 K or 493 K of trained sample (fig. 8), $\varepsilon_m$ decreases regularly with the time of heat-treatment down to a minimum value and $\varepsilon_a$ decreases of 60% from its initial strain during a simple rise of temperature up to 493 K, but remains stable later on. At last, another phenomenon occurs and involves the evolution of $\varepsilon_m$ and $\varepsilon_a$ in the same direction as the memorized strain.Simultaneously with this, the increase of transformation temperatures and hysteresis is observed.

**fig. 8:** evolution of T.W.M.E. with thermal ageing time

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**Part -4- General discussion:**

Transformation strain in martensite: the transformation strain is explained by the preferential nucleation and growth of some martensite variants under the effect of the stress. The linearity between stress and transformation strain has been also observed in another alloy like Cu-Zn-Al and for different kinds of solicitations (9,10). Patoor & al. (8) have shown that a maximum strain is obtained in a single crystal for different stresses even low ones. During transformation, the strain incompatibilities near grain boundaries create internal stresses that are opposed to the effect of the applied stress until they cancel it. That is why the final strain is limited and depends on the applied stress. Following the same argument, it is generally understood that the saturation of $\varepsilon_m$ in a polycrystal is lower than the strain obtained on a well-orientated single crystal. During cycling under stress, evolution of $\varepsilon_m$ can be explained by Transmission Electronic Microscopy observations made by Ritter & al. (11) and Nakata & al. (12). Orientated dislocations are created during each martensitic
transformation; the density of defects increases strongly at the beginning. It is supposed that these dislocations involve internal stresses, so they allow an additional efficiency of the applied stress on $\epsilon_m$ during each new cycle.

Residual strain in austenite: during the heating, the reversion of the initial austenitic shape is incomplete. A slight strain is observed in austenite which increases more or less intensively according to the kind of cycling. This residual strain is constituted of two components; the one, the largest, due to stabilized martensite. This can be shown by calorimetric measurement during further heating. The other component is true plastic strain that would be responsible for the T.W.M.E. (9).

The stabilization of martensite during cycling can be explained by two phenomena:

(i) Evolution of the martensite structure by thermal cycling below $A_f$ (Part 2). The parameters of the thermal cycles like heating and cooling rate and the difference between maximum temperature and $A_f$, influence the evolution of $\epsilon_a$.

(ii) "Mechanical" stabilization: the defects created by cycling, could prevent the reversion of martensite plates. The dislocations density depends on the number of cycles, the applied stress and the maximum strain obtained. This stabilization effect could be similar to that one observed in the case of quenched sample.

T.W.M.E.: the defects created during the training would be responsible for the T.W.M.E. The dislocations could induce an internal stresses field in the same direction as the one of the external stress (9). The decrease of the T.W.M.E. as well by the thermal cycling as by the pure thermal ageing at 473 K or 493 K, could be due to annihilation of less stable dislocations. During the cycling, the defects annihilation could be compensated by the creation of other ones (self-training observed elsewhere).

During $\beta$-phase ageing at 473 K or 493 K, a third phenomenon occurs in the last stage: an increase of austenitic and martensitic strains in the same way as the memorized strain is observed. This effect can be explained by an orientated precipitation process due to the internal stresses related to the training. This effect appears with the same kinetics as in the simple thermal ageing discussed in part 1.

Conclusion:
The different phenomena responsible for the ageing process of the shape memory effect by thermal cycling either under constant stress or without stress after training (T.W.M.E.), have been analyzed.

From the results of simple ageing process and considering the possible origin of the T.W.M.E., the thermomechanical fatigue behavior have been explained in terms of:

- Stabilization of martensite
- Annihilation of dislocations created during the training
- Orientated precipitation.
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