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STUDY OF THERMOMECANICAL TREATMENTS USED FOR A CuZnAl INDUSTRIAL ALLOY

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Abstract : The use of CuZnAl industrial shape memory alloys requires to approach the questions of their stability and their transformation temperatures in the long run.
We have investigated the influences that have education and time periodes between the several processing phases for several annealing times at 100°C.
These three parameters have an effect not only on the alloy transformation temperatures but also on the evolution kinetic of these temperatures in the long run.
This fact requires an exact characterization of the alloy state in order to master the industrial reproduction of such processings.

Introduction :

We have developped a new industrial device, the Thermomarker, to detect overheating of products such as frozen food, vaccins or blood.
This device is driven by a shape memory spring made of a CuZnAlNi alloy.
It is well known that in this kind of alloy thermomechanical properties are primarily controlled by the chemical composition. The second order parameters to be considered are the thermal and thermomecanical treatments which have a great influence on the martensitic transformation, and also on the ageing of the alloy [1][2].
We introduce a new concept, the "mechanical hysteresis" to characterise the martensitic transformation of the alloy in a device.
As we need to have a high accuracy and stability of triggering for the thermomarker, we study the effect of the annealing and training treatments on the mechanical hysteresis and its evolution on the long run.
The treatments of homogeneization and quenching are discussed in another communication of this symposium [3].

I- Experimental Procedure :

I.1 - The Thermomarker :

The mechanism of the thermomarker is schematised on figure (1). One can see that the SMA spring is assembled on a piston with a counter-spring to bind the piston to the SMA spring.
The first triggering of the thermomarker happens during cooling when the SMA spring is transforming into martensite. At that time, the length of the spring diminishes and the displacement of the piston allows the four balls to move foreward. The first of these balls is green and appears in a magnifier.
We call the temperature at which the green ball appears into the magnifier the green ball triggering temperature and we note it **BV** (Bille Verte).

The second ball, a red one is now just before the piston.

If now the temperature increases the SMA spring recovers his original full size and thus pushes the red ball into a second magnifier.
The temperature at which the red ball appears is called red ball triggering temperature and we note it **BR** (Bille Rouge).

Three red balls are provided in the thermomarkers and allow the detection of three successive overheating.

I.2 - The alloy :

We used an industrial shape memory alloy (SMA) whose atomic composition is Cu 24,4%Zn 8,4%Al 1,1%Ni and minor additives such as Zr to prevent too large grain size.
We realized our samples in a 0,8 mm diameter wire, drawn from ingots. Initial state of that wire is $\alpha+\beta$, resulting from an annealing of one hour at 773 K.

The martensitic transformation temperatures measured by differential scanning calorimetry are obtained for a betatisation of 15 min at 1123 K, water quenching at 300 K and annealing at 373 K for one hour :

M10% = 252 K; M90% = 243 K; A10% = 253 K; A90% = 258 K

I.3 - Studied Treatments :

In this paper, we are concerned with the thermal and thermomecanical treatments used after the betatisation/quenching treatment whose parameters are held constant :

- Betatisation of 15 min at 1103 K.
- Quench into water at ambiant temperature.

After that thermal treatment, the samples are annealed and thermomecanically cycled.
The temperature of annealing is held constant and equal to 373 K. We studied the effect of the **annealing time** on the mecanical hysteresis.
The thermomecanical treatment (otherwise called training treatment) is a result of a 15 times repetition of the following cycle :

- The springs are strained at 288 K until their turns join each other.
- The strained spring is cooled until 213 K.
- The strain is relaxed and the temperature risen up to 288K.

In order to analyse the effect of these two treatments, we have inverted the use of annealing and training. This results in two types of treatments:

- the **direct treatment** : annealing then training
- the **inverse treatment** : training then annealing

The **isothermal holding time** following the quench and needed for sample manipulation is the third parameter to be considered.

We present in table (I) the values used for each of these three parameters.

I.4 - Investigation methods :

The mechanical hysteresis is characterised by the measurement of the **Thermomarker triggering temperatures (Ttt).**

This last method allowed us to estimate the behaviour of the samples whithout involving too much measurements.
The test machines are shown on figure (2), twelve thermomarker can be put inside.
The tested thermomarkers are placed on a radiator. The variations of temperature are obtained by a circulation of cold or hot alcohol flow through the radiator.
The mesurement of the triggering temperature are performed using numerical thermometers connected to a computer. A thermocouple is introduced in each thermomarker, near the SMA spring, figure (3).
When a thermomarker triggers, the triggering temperature (either BV or BR) is recorded.
The time-temperature profile used for the thermomarker test is annalysed in an other paper of this symposium [4].

We are looking for a good representativity of our results, so we use **sets of six SMA springs.**
The results presented afterwards are the mean values of the measurements for each spring of a set.
The reliability of the mean values is tested using the NF X 006 standard [5] relative to the statistical control.
The accuracy of the mesurements of the Ttt presented in this paper is about ±2 K.
If one considers both the dispersion of the results and the NF X006 standard, one can say that **two mean values are different if they are separated at least by 2K.**

II - Results : We resumed the results, for more informations see reference [1].

We follow the evolution of our samples on a period of at least two months. These evolutions show that the time of annealing at 373 K, the isothermal holding time and the inversion between annealing and training treatments haveinfluences both on the mechanical hysteresis and on its ageing.

The influence of the inversion between the treatments is the most important and interesting.
One can see on figures (4) that, for the same values of annealing time and isothermal holding time, the inverse
treatment results in a slower rise of the triggering temperatures of the thermomarker.
We observe this phenomenon for all the values of **annealing time between 0 to 60 min** and for all the **isothermal holding times between 15 min to 24h.**

The influence of the inversion is much more fundamental than the simple effect on the ageing :

II.1 - Direct treatment :

The figures (4a and b) show the evolutions of the Ttt for direct treatments with isothermal holding time of respectively 15 min and 24 h.
On can see that the **longer the annealing time** is, the **slower the kinetic of evolution** is. This is true not only for 15 min and 24 h of isothermal holding time, but also for all the values between 15 min and 24 h.

A look at the figures can give the feeling that a difference of Ttt between 2 min and 60 min for the annnealing time is still sensitive even after a long time of aging. But mesurements performed after 100 days of aging show that the Ttt are the same.
The influence of the isothermal annealing time can be seen when one compares figure (4a) and (4b). The longer the isothermal time is, the lower the Ttt are. A diference of 3 K is observed between 15 min and 24 h of isothermal holding.

The influence of the isothermal holding time seems to be additive to the annealing time one.

II.2 - Inverse treatment :

One can see on figure 4c and 4d that, as already observed for the direct treatment, the Ttt increase is slower if the annealing time is longer.
The influence of the annealing time on the Ttt aging kinetic is independent of the type of treatment.

Figure 4c (Isothermal holding times of 15 min) shows that after 100 days of aging, the Ttt of samples annealed for 2 min or 30 min are the same.
Figure 4d (Isothermal holding times of 24h) shows that after 100 days of aging, the Ttt of samples annealed for 2 min or 30 min are different.

The effect of an annealing time longer than 15min is different than the effect observed for an annealing time smaller than 15 min. This difference is also dependant on the isothermal holding time.

We added on figures 4c and 4d the aging curves for samples wich have not been annealed. The Ttt evolution kinetics have the same trend for 2 min annealed sample or unannealed ones.
But, the Ttt obtained for 2 min and no annealing are very different when the isothermal annealing time is greater than 15 min and smaller than 12 h.

If the annealing time is greater than 15 min, a critical isothermal holding time is observed. The Ttt are dependent of the isothermal holding time only if this one is lower than the mentionned critical value.
The critical isothermal holding time is an increasing function of the annealing time : for annealing time of 15 min, the critical isothermal time is between 3 and 6 hours; for annealing time of 30 and 60 min the critical value is between 6 and 12 hours.

III - Discussion :

The CuZnAl alloys are chemicaly ordered. The observed martensitic transformation temperature evolutions are certainly associated with variations of the degree of order.
We showed that the inversion between the annealing and the training treatments has a great influence on the mechanical hysteresis of our alloy.
This influence depends on the isothermal holding time and on the annealing time.
The physical mechanisms involved in the training and the annealing treatments but also during the isothermal holding time seems to irreversibly alterate the microstructure of the alloy (the effect is sensitive even after a long time).
The modifications of the microstructure are certainly thermally activated.
We present other results of transmission electronic microscopy and differential scanning calorimetry in a second paper of this symposium [7]. An answer to the questions resulting of our observations is given.

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