

**INFLUENCE OF BETATIZATION HEAT TREATMENT ON MARTENSITIC TRANSFORMATION TEMPERATURE OF INDUSTRIAL COPPER BASED SHAPE MEMORY ALLOYS**

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**Abstract :** The paper shows the effects of two types of long heat treatment at high temperature on copper based alloys with zinc or aluminium. The resulting increases of transformation temperatures seem to be governed both by loss processes and oxidation of the constitutive elements of the alloy. Different characterization techniques performed on heat treated samples demonstrate that the surface of the alloy plays an important role during betatization.

**Introduction**

The transformation temperatures of copper based shape memory alloys are very sensitive to the heat treatment undergone by the sample before training.

Several authors have shown the influence of parameters such as the step quenching, the quenching rate and thermal aging (1) (2) (3).

In this paper we have focussed on the study of the betatization treatment for Cu-Zn-Al and Cu-Al-Ni alloys. It will be shown that the holding time for betatization has a great influence on the transformation temperatures of the material and that surface phenomena are relevant to explain their evolution during the thermal treatment.

**I - Experimental Procedure :****I.1 - Samples :**

The chemical composition of the alloys (in weight %) is given hereafter:

70.0 Cu - 26.3 Zn - 3.7 Al

83.1 Cu - 12.9 Al - 4.0 Ni

Zr is added in both materials as a refining element, in order to prevent grain growth. The Cu-Zn-Al samples (2 mm diameter wires) and the Cu-Al-Ni ones (1.25mm diameter wires) exhibit an austenite start temperature (As) of 62°C and 158°C respectively. The transformation temperatures of shape

memory alloys are strongly dependent on the composition and can be obtained by empirical expressions (3), (4).

**1.2 - Thermal treatment :**

Two types of thermal treatment have been performed on Cu-Zn-Al and Cu-Al-Ni samples.

The first one is shown on figure1. After betatization at 850°C, the samples are quenched in water at 20°C and finally annealed in boiling water for 1 hour (CuZnAl) or in salt bath at 250°C for 10 mn (CuAlNi). Different holding times at 850°C have been investigated.

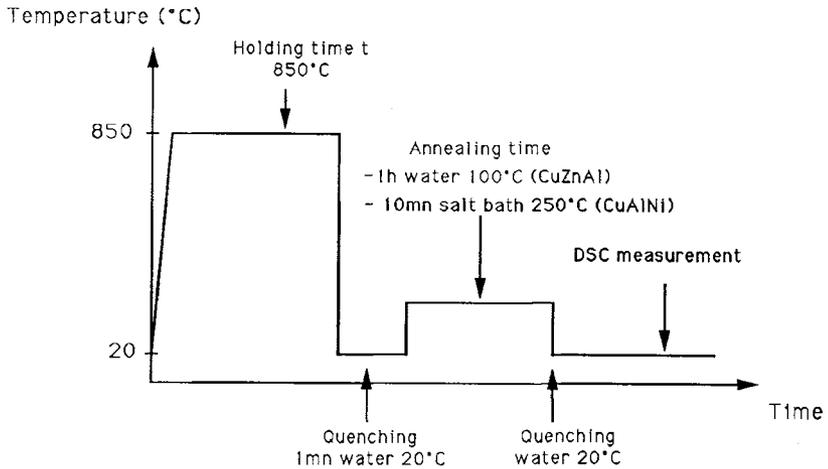


Figure 1 : type of thermal treatment used.

The second heat treatment performed on the samples is shown on figure 2. It is called **cumulative heat treatment** and will be described in detail in one of the following sections.

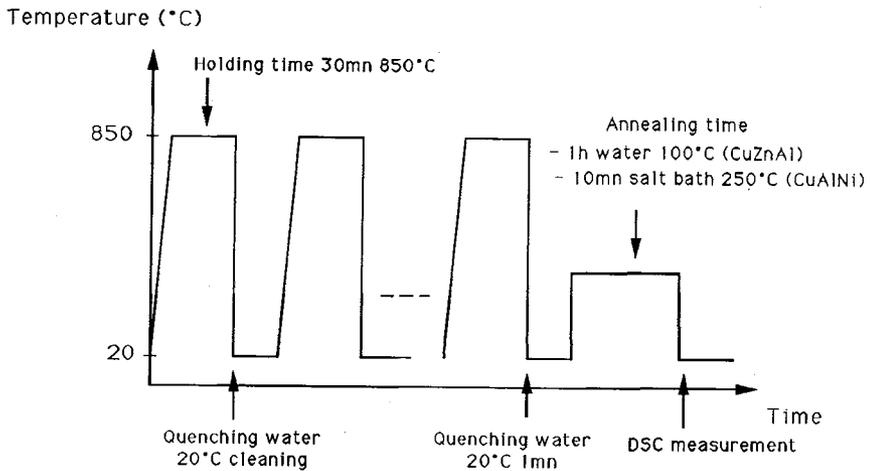


Figure 2 : "Cumulative heat treatment".

The treatment is a succession of cycles (30 mn at 850°C then quench in water at 20°C) followed by an annealing treatment specific of the alloy.

The effect of the number of cycles on  $A_s$  will be discussed.

### I.3 - Characterization of the sample :

The annealed samples are quenched in water at 20°C before been processed in Differential Scanning Calorimetry experiments for  $A_s$  determination. The surface of the wires is analysed by Scanning Electron Microscopy, X-ray fluorescence and X-ray diffraction.

## II - Results :

Figures 3 and 4 show the variations of  $A_s$  respectively for Cu-Zn-Al and Cu-Al-Ni, as a function of the holding time at 850 °C for a betatization treatment of the first type.

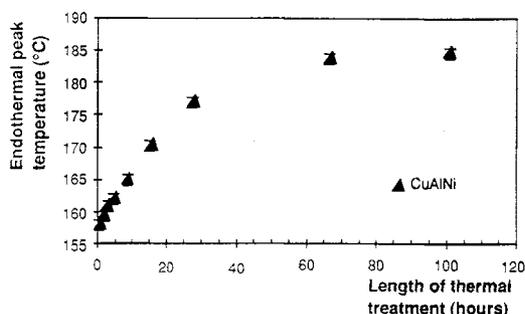
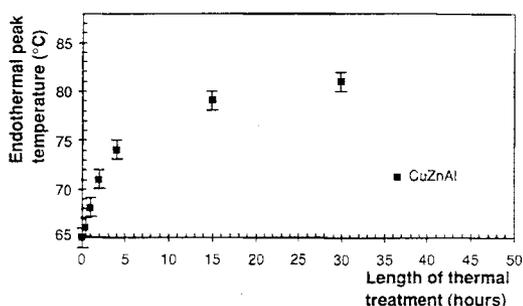


Figure 3 : Transformation temperature as a function of the length of the thermal treatment. Cu-Zn-Al alloy.

Figure 4 : Transformation temperature as a function of the length of the thermal treatment. Cu-Al-Ni alloy.

It can be seen that  $A_s$  increases and exhibits an asymptotic behaviour for large values of the holding time. The trend is similar for the two alloys.

Micrographic observations of the samples show that no significant grain growth occurs even for prolonged betatization. This confirms the efficiency of Zr as a refining element.

At the surface of the wire, a coating is revealed by scanning electron microscopy performed on heat treated samples.

This coating is shown on figure 5 for a Cu.Zn.Al alloy heated at 850°C for 4 hours and air cooled. The layer does not perfectly coat the sample and is partially separated from its surface .

If the sample is tilted it is possible to measure the thickness  $t$  of the coating with a good accuracy. The variations of  $t$  with the holding time are reported in table 1.

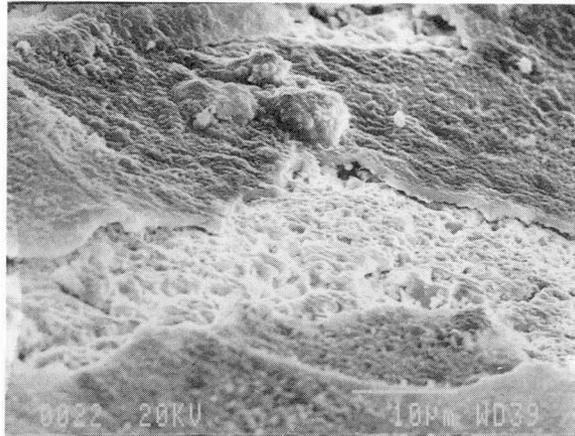


Figure 5 :

Holding time (h)	0,25	2	4	8
Thickness $t$ ( $\mu\text{m}$ )	0,60	0,85	1,10	1,10

Table 1 : Thickness of the layer as a function of the holding time at 850°C.

A limiting value of approximately  $1.1 \mu\text{m}$  seems to be reached after 4 hours of treatment.

The layer has been characterized both by X-ray fluorescence and X-ray diffraction. After being heated for 4 hours at 850°C and air cooled, the samples were cleaned with alcohol in an ultrasonic bath. The layer is separated from the wire and reduced in powder by the ultrasounds. After alcohol evaporation it is collected for analysis.

X-Ray fluorescence (Cr tube and Li F 200 crystal) reveals that all the constitutive elements of the material ( Cu, Zn, Al, and Zr) are present in the coating.

The X-Ray diffraction pattern of the layer is given on fig.6.

Both the number and the width of the reflections make such a pattern difficult to index. However, some possible indexations, corresponding to different oxides of the constitutive elements of the alloy, have been reported on the diagram.

$\text{Cu}_2\text{O}$  and  $\text{Cu Al}_2 \text{O}_4$  as well as  $\text{Al}_2 \text{O}_3$  are certainly present but no Zinc oxide is detected.

In fact, the structure of the layer is probably much more complex. The wide reflexions attributed to  $\text{Al}_2\text{O}_3$  could correspond to a coordinate Zinc-Aluminium oxide exhibiting more than 50 peaks in the explored angular range. A more detailed investigation is necessary to conclude.

In order to study the importance of the oxide layer on the increase of As during the betetization, the **cumulative heat treatment**, presented on figure 2 has been undertaken on the two classes of alloys.

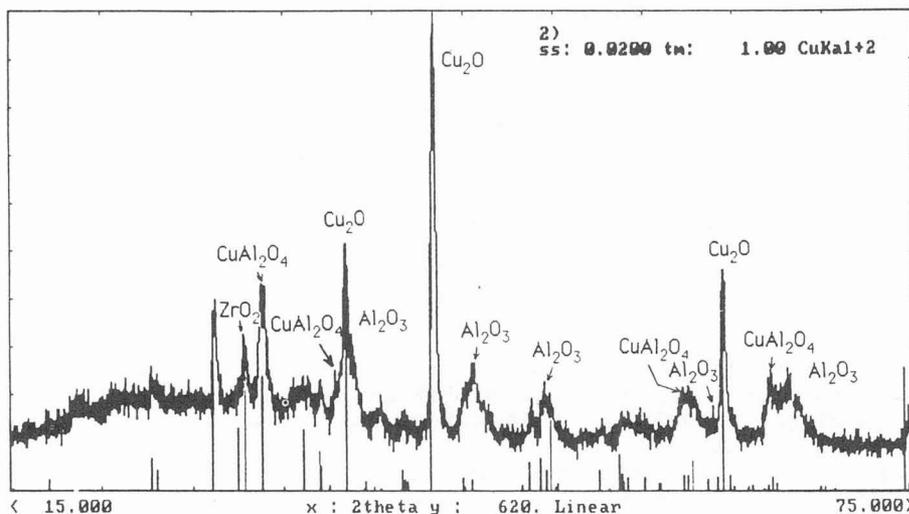


Figure 6 : diffraction pattern of the coating for CuZnAl heat treated alloy.

After each quench in water, the sample is dried and the oxide layer is removed by a light mechanical polishing. A DSC measurement is performed after each cycle and the endothermic peak temperature is plotted against the number of cycles ( Fig.7 and 8).

A linear increase of As is observed for the two classes of alloys but the asymptotic behaviour mentioned for the first treatment is not reached for prolonged treatments, even though the total time of betatization is of the same order.

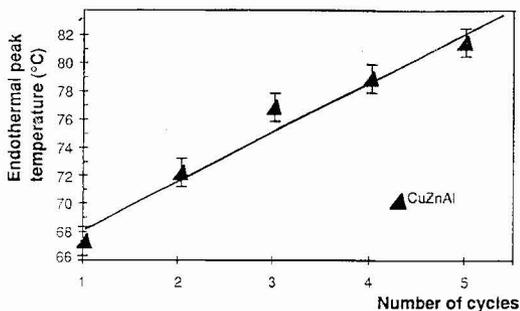


Figure 7 : Transformation temperature as a function of the number of cycles for a cumulative heat treatment on CuZnAl

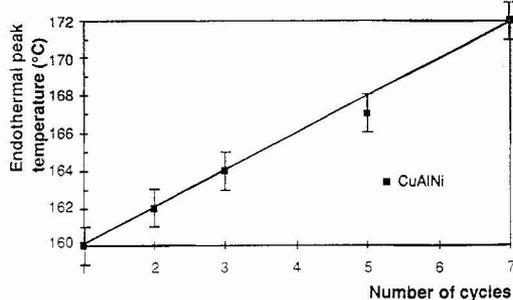


Figure 8 : Transformation temperature as a function of the number of cycles for a cumulative heat treatment on CuAlNi

### III - Discussion :

Controlling the duration of the betatization thermal treatment can be an industrial procedure to reach a suitable transformation temperature for an alloy of given chemical composition.

It has been shown (5) that a loss of Zinc occurs usually for brass heat treated under vacuum . Such a phenomenon is also possible, to a lesser extent, for Cu-Zn-Al heat treated in air, and the increase of As is currently explained by a change of composition of the alloy.

The results presented above (similar behaviour for Cu-Zn-Al and Cu-Al-Ni), clearly show that the so-called **dezincification process**, is not only the result of a loss of zinc, as no Zinc is present in the second class of alloy. But, the increase of As is mainly driven by surface phenomena.

As already mentionned (6) (7), oxidation processes seem to be of great importance and are to be taken into account.

A classical betatization heat treatment (without a cleaning of the surface) seems to favour the growth of an oxide coating of complex structure at the surface of the sample. The composition of this coating is dependant on the chemical composition of the alloy, different oxides such as amorphous and crystalline  $Al_2O_3$ ,  $Cu_2O$ ,  $CuAl_2O_4$  are detected.

This layer, whose thickness is a function of the duration of the thermal treatment, leads to a passivation of the surface responsible for a saturation in the variations of As.

It is possible to accelerate the increase of As and, by the way, to master its final value with an appropriate treatment involving a regular removing of the oxide layer formed at the surface of the sample.

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