JOURNAL DE PHYSIQUE IV
Colloque C4, supplément au Journal de Physique III, Vol. 1, novembre 1991

CHARACTERISATION OF THE MICROSTRUCTURAL STATE OF A CuZnAl INDUSTRIAL SHAPE MEMORY ALLOY

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Abstract : The thermomecanical treatments used for the industrial production have a great effect on the transformation temperatures of the CuZnAl shape memory elements.
We characterize the microstructural state of samples submitted to several kinds of thermomecanical treatments.
We used the transmission electron microscopy and X-ray diffraction. A particular effort was made on the observation of the alloy long range order state.
The observations show different default structures and different long range ordered domain sizes according to the kind of treatment.
The order state is characterized by a size and a number of long range ordered domains B2 and L21, but it seems to be necessary to estimate the short range order degree.

Introduction :

The martensitic transformation temperatures of an alloy of given chemical composition depends both on thermal and thermomechanical treatments. In a previous paper[1], we presented some results about the influences of the treatments on the martensitic transformation. These results exhibit great differences in the aging and in the mechanical hysteresis of the transformation depending on the treatments used.
In order to understand the physical mechanisms involved in the alloy, we have undertaken an other set of investigations, using : Differential Scanning Calorimetry (DSC), Quenching Dilatometry and physical observation method : Transmission Electron Microscopy (TEM).

I - Experimental Procedure :

I.2 - The alloy :

The results presented here are obtained from the same industrial shape memory alloy (SMA) as that used in reference [1].
It is composed of Cu 24,4% Zn 8,8% Al 1,1%Ni and additives such as Zr to control the grain growth.
In order to understand what are the physical mechanisms involved in the thermal and thermomecanical treatments, and during the aging of the alloy we focused on that particular alloy.

We chose to use samples with a spring geometry. This ensure us that the thermal and mechanical stresses are exactly the same as in our previous experiments [1].

The CuZnAl are known to have two chemical order transformations [2]. The first one happens at 770 K between the disordered high temperature b phase and a B2 ordered one, noted β2. The second one happens at 500/550 K, depending on the alloy composition. This second transformation gives a L21 ordered phase, noted β3.

The nature (B2 or L21) of the chemical order has a great influence on the martensitic cristallography and on the transformation temperatures [3].
It is the reason why we wanted to characterize the state of order of our alloy.

I.2 - Treatments

We used four treatments that can be classified as Direct or Inverse treatments :

- The Direct Treatments are constituted of the betatisation, the quenching, the annealing and the training treatments.
- The Inverse Treatments are constituted of the betatisation, the quenching, the training, and the annealing.

The difference between the Direct and the Inverse treatments is the **inversion in the sequence of application for annealing and training.**

The parameters of the treatments are :

- Betatisation : 15 min at 1103 K
- Quench : water at 295 K
- Annealing : 1 h at 373 K
- Education : 15 thermal cycles under stress, as defined in reference [1]

The samples are treated with :

- just an annealing --> Samples named : **Annealed**
- an annealing then a training --> Samples named : **Direct**
- just a training --> Samples named : **Trained**
- a training then an annealing --> Samples named : **Inverse**

For each of this treatments three springs have been made.
The isothermal holding time is contant for all treatments and equal to 15 min.

I.3 - Methods of investigation :

The caracterization of the martensitic transformation is made by differential scanning calorimetry. This methods gives us acces to the technological aspects of the transformation : Ms, Mf, As, Af, ΔH. From these parameters, we can describe the transformation. But we can use other characteristics of the hysteresis cycle such as :

-H=M50%-A50% , the hysteresis whose width is attributed to dissipative processes.

-ED=Ms-Mf or EI=As-Af , the temperature spreading of the direct and reverse transformation respectively. They depends on the flaws concentration.

- To=1/2(Ms+Af) , the thermodynamical equilibrium temperature between austenite and martensite which depends on the chemical composition and on the chemical order of the alloy [3].

It is better to use these characteristics of the martensitic transformation.

The quenching dilatometry is used to determine the chemical order transformations critical temperatures. In this method the sample is a small cylinder. We record the dilations or the contractions of the sample when it is rapidly cooled at 150 K/s.
X rays diffraction has been used to quantify the order present in the alloy. But this technique needs samples of planar geometry. So the experiment can not be directly performed on the spring.
We tried to annalyse some specially designed samples to show that the thermal treatments have an influence on the chemical ordering of our alloy.

Finally, we used the Transmission Electron Microscopy to analyse the ordered microstructure of our alloy. The observations are made on a 200CXS Jeol of the CEMES-LOE (CNRS) laboratory.

Parts of the springs were electrolytically thinned down for TEM observation. As the spring wire diameter is 0,8 mm, we encountered some difficulties to make observable thinned samples.
The TEM observation of the ordered microstructure uses the superlattice diffractions. Figure (1) shows the positions of these diffraction patterns in two different zone axis ([110] and [112]. With the double tilt sample holder, we can observe at least one of these zone axis.
Dark field observations have been made, using B2 and L21 superlattice reflections.

II - Results :

II.1 - DSC :

The DSC measurements where made after approximately one year of aging at ambiant temperature, when the transformation temperatures are stabilised.
The results, presented in table (I) show that :

-A difference in the microstructure is still existing between direct and inverse treatments even after one year of aging : the To temperature depends on the type of treatment, it is 10

-Training introduces flaws that increase the hysteresis, H is 3 to 4 K larger for a trained sample, the treatment being direct or inverse.
-Education introduces more flaws in an inverse treatment than in a direct one : the transformation spreadings are larger for an inverse treatment [4].

II.2 - Quenching Dilatometry :

When the sample is rapidly cooled from 1123 K to ambiant temperature, a small contraction is recorded from 490 ± 20 K to ambiant temperature. This event could be associated with the L21 transition order.
This temperature is very low, as it could be expected from the composition of the alloy [5].
The disorder <->B2 transition has not been detected.

II.3 - X-Ray Diffraction :

We never have detected the superlattice reflections due to B2 or L21 orders.
A calculation of the relative intensities of the superlattice reflections for the composition of our alloy and for a maximal order degree gives for the (1,1,1) diffraction : 17/1000.
The X-Ray detector used was sensitive enough to detect a diffraction with 2/1000 relative intensity.
We attributed the default of superlattice diffraction to a crystallographic texture of the sample or to a very low degree of order of the alloy. Some more investigations are in progress.

II.4 - TEM observations :

The more important observation is that **our alloy is only partially B2 ordered: a volume fraction of the alloy is still disordered.** Whatever the treatment is, we found the disordered β phase.
This observation is surprising, as it is usually admitted that the B2 ordering in the CuZnAl SMA alloys cannot be avoided even by rapid quenching. We observed the samples with a stereographic method using two different superlattice patterns. Then, we could observe the volume of the thinned down blade. It appeared that the alloy is constituted of B2 ordered domains contained in a disordered matrix.
The state of order of the alloy depends on the treatment. We observe that a direct treatment gives a less imperfect order than an indirect one.

The diffraction patterns in the [110] and [112] zone axis show that all the samples are B2 ordered.

As it can be seen on figures (2a to 2d), the domain size and the volume fraction of the B2 ordered β phase are greater for the "Annealed" and "Direct" samples than for the "trained" and "Inverse" samples.

One can think that this causes the difference of To temperature observed between direct and inverse treatment. But, the more the CuZnAl alloy B2 ordered is, the lower the transformation temperatures are. This is in contradiction with our results [6].
We must consider the L21 order. Its effect is the inverse of that of B2 order and the amplitude of that effect is larger (30 K) than that of the B2 order (10K).

The L21 state of order is very imperfect.
In the samples "Annealed" and "Direct", the L21 superlattice diffraction patterns appear weakly and are diffuse.
The L21 superlattice diffraction patterns of the samples "Trained" and "Inverse" are practically invisible. One can distinguish very weak and diffuse patterns.

The direct treatment results in a partially and weakly L21 ordered alloy. An inverse treatment results in an alloy which is not L21 ordered.

We could only observe the L21 dark field of the "Annealed" sample, figure (3). One can see that the ordered domains are very small (50 Å) and represent only a part of the alloy.
The L21 microstructure in the "Direct" sample was perturbed by surface martensite and no ordered domains can be observed.

In an other hand, the observations of the samples confirm that the education introduces more flaws (dislocations and martensite plates) when the treatment is inverse than when the treatment is direct.

III - Discussion :

The differences observed in the martensitic transformation after direct and inverse treatments are due to microstructural differences. We put in evidence that the ordered structure of the alloy is made of a mixing of two or three phases : β + β2 or β + β2 + β3.
The chemical composition of the alloy certainly explain the presence of the disordered b phase. But it seems that the ordered part of the alloy depends of the annealing and training treatments.
The presence of several phases indicates that the order transitions in our alloy certainly involve chemical demixtion.
The annealing treatment effect is the increase of the ordered part. The training effect is the increase of the flaw concentration. From this conclusions it seems that an interaction between the flaw and the atomic diffusion can explain the differences observed between the direct and inverse treatments.
The metallurgical mechanisms involved into the CuZnAlNi alloy are certainly controlled by the interactions between the state of order and the flaws of the alloy with the atomic diffusion.

REFERENCES

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(2) Rapacioli R., Scripta. Met., 11 (1977) pp 1147-1150
(3) Rapacioli R., Acta Met., 27 (1978) pp 777-784
(4) Torra V., J. therm. Anal., 36 (1990) pp 1545-1577

Sample	To (K)	Direct Transformation Spreading (K)	Inverse Transformation Spreading (K)	Transformation Hysteresis (K)
ANNEALED	272,0	12,5	8,5	6,5
TRAINED	262,8	21,6	12,5	9,7
DIRECT	271,3	17,5	8,8	10,3
INVERSE	261,3	20,0	10,5	9,3

Table (I) : DSC results

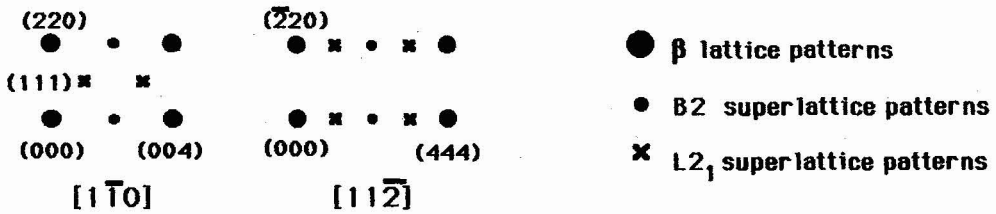


Fig (1) Indexation of the superlattice patterns.

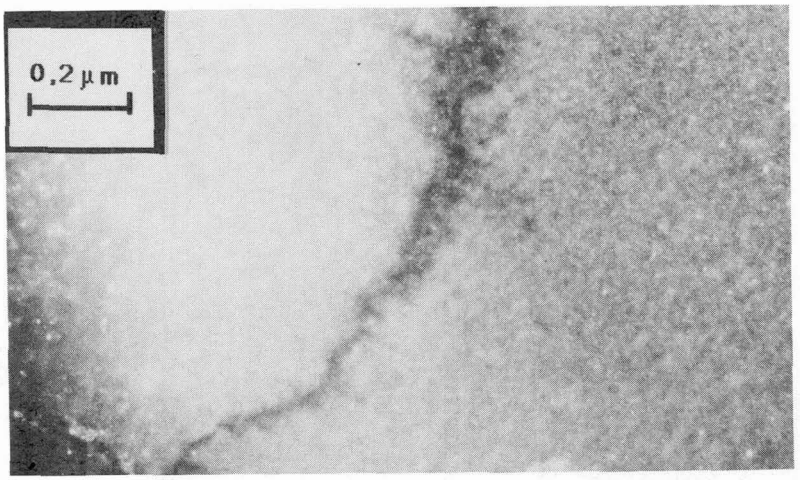
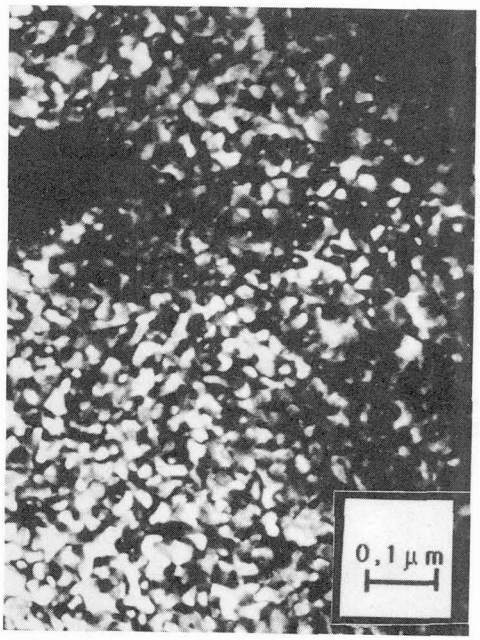
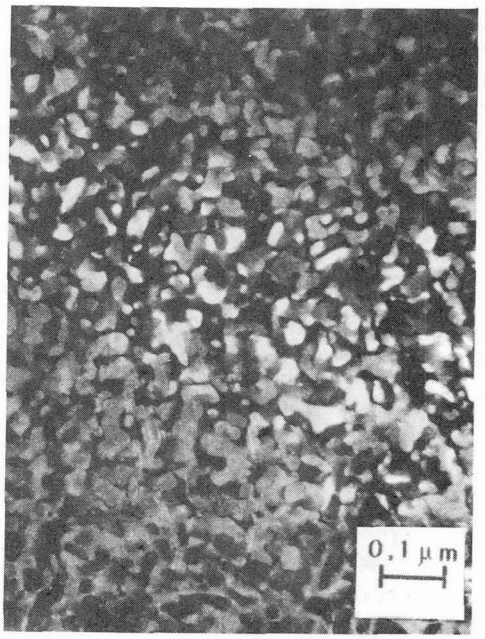


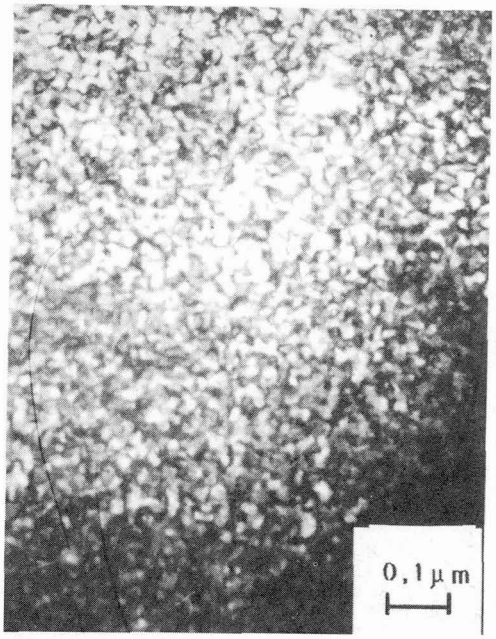
Fig (3) Dark field micrograph showing $L2_1$ ordered domains of Annealed sample



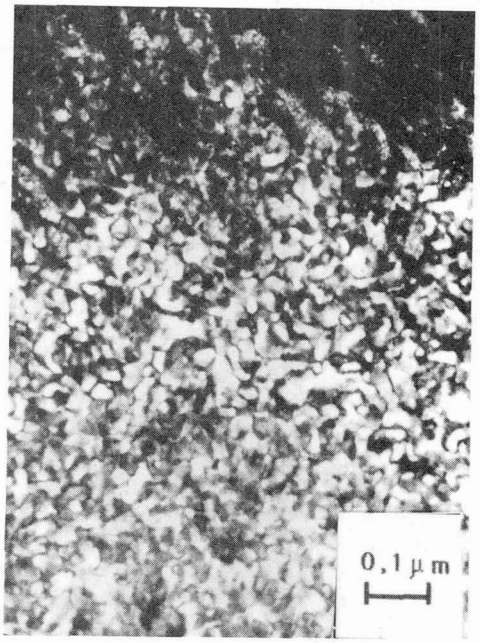
(2a) Annealed sample



(2b) Direct sample



(2c) Trained sample



(2d) Inverse sample

Fig (2) Dark field micrograph showing B2 ordered domains