

**STUDY ON THE MOBILITY OF THE MARTENSITIC INTERPHASES ON THE Cu-Al-Ni SHAPE MEMORY ALLOYS**

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Abstract- In this work we have studied the mobility of martensitic interphases on Cu-Al-Ni polycrystalline shape memory alloys with different concentrations. For that reason we have used a microdeformation technic very useful for the study of the polycrystalline alloys. This microdeformation measurement has let us to observe two transformation stages linked to  $\gamma_1'$  and  $\beta_1'$  phases nucleation. Finally we discuss the effect of the internal stresses, stored during the quenching treatment, on the nucleation of the different martensitic phases.

## 1. Introduction

As it is well known martensitic transformation on the shape memory alloys is of a thermoelastic kind and it could be induced by an applied stress. A great number of studies have been carried out on the nucleation and growth of the different martensitic phases by tensile tests where the transformation was induced by stress. However, these studies have been mainly carried out on single crystals, due to the Cu-Al-Ni alloys tendency towards the intergranular fracture in the polycrystals. For that reason, we have used, in this work, a microdeformation technic that come to be very useful for the study of the polycrystalline alloys. The use of stresses in the anelastic range allows us to follow the microdeformation associated to the martensitic transformation thermically induced, avoiding as well, the risk of intergranular fracture.

On the other side, in the last years, a great number of works have been published related to the influence of the quenching treatment on the nucleation of the martensitic phases, induced thermically or by stress. In this direction, we think that the influence of the internal stresses stored in the material during the quenching process has not been enough considered. And we also believe that, as discussed in this work, these stress can play a main role in the nucleation and growth on the different martensitic phases.

## 2. Experimental procedure

An alloy series with a fixed concentration of Al, and changing the Ni concentration was prepared from 99.99 % Cu, 99.99 % Al and 99.97 % Ni, in an induction furnace in argon atmosphere. The obtained ingots were homogenized at 1000 °C during 6 hours in argon atmosphere. After the treatment, the concentrations of the alloys were analyzed in a plasma

emission spectrometer. Table 1 shows the analysis in weight percentage as well as the e/a relation of the alloys.

Table 1

Alloy	wt%	Cu	Al	Ni	e/a
A		81.3	13.75	4.95	1.526
B		81.8	13.75	4.39	1.528
C		82.9	13.75	3.30	1.534

To carry out the microdeformation measurements we cut 0.8\*5\*50 mm samples with a low speed diamond saw. In order to retain the  $\beta$  phase, the samples were annealed at 1123K during 30 minutes and quenched into water at 90 °C. Afterwards they were aged at 473K during 20 hours, in order to stabilize the atomic order and to reduce the internal stresses produced by quenching.

The microdeformation and modulus measurements have been carried out in an inverted torsion pendulum operating at 1 Hz in a temperature range between 80K and 750K and that allow us to work with a superposed static stress /1/. The measurements were carried out at a heating rate of 60K\*h<sup>-1</sup> or 120K\*h<sup>-1</sup> and with a oscillation amplitude of  $\epsilon_m=5*10^{-6}$ . Static stresses with values between  $\sigma_s=10^{-4}*\mu$  and  $\sigma_s=2.5*10^{-5}*\mu$  were also used. Two kinds of microdeformation measurement have been carried out, depending on whether the static stress is applied, either in  $\beta$  phase or in martensitic phase. In the first case, afterward the static stress is applied in  $\beta$  phase, the temperature was decreased and increased again in order to measure the microdeformation during the transformation cycle. Finally the static stress is removed. In every time the microdeformation and the dynamic modulus is recorded Vs. temperature.

### 3. Experimental results

The microdeformation curves obtained under a static stress of  $\sigma_s=10^{-4}*\mu$  ( $\dot{T}=120k/h$ ) are shown in Fig.1. The figures 1-a, 1-b and 1-c correspond to the sample A, B and C respectively. In the three cases the hysteresis associated to the transformation appears perfectly clear, being bigger for the samples A and B, than for sample C, presenting the last an hysteresis cycle much more narrow. The microdeformation curves of samples A and B show two microdeformation stages clearly identified, showing two maximums on its derivate curves. On the other side the sample C shows only one microdeformation stage with bigger slope than on the alloys A and B.

In order to study the effect of the stress on each one of the two stages observed, microdeformation measurements with different applied stresses have been carried out on sample A.

Fig. 2 shows the microdeformation curves of the alloy A, ( $\dot{T}=60k/h$ ), under two different static stresses of  $\sigma_s=5*10^{-5}*\mu$  and  $\sigma_s=2.8*10^{-5}*\mu$ , Fig. 2-a and Fig. 2-b respectively. Again it is easy to appreciate two microdeformation stages, and the general shape of the microdeformation curves is the same as in the case before. However we can remark for a smaller static stress both microdeformation stages appear mark in a stronger way.

## 4. Discussion

The microdeformation measurements, carried out by the method described before, come to be a technic very useful for the study of the martensitic interphases mobility, as well during the nucleation of the martensitic plates as during the following growth when the transformation progresses.

Owing to the fact that the static stress we have used for the microdeformation measurements are smaller than the stresses necessary to produce the nucleation induced by stress, we can consider that the transformation temperatures obtained from the microdeformation experiences are the same as in the absence of stress. This can be perfectly justified if we compare the microdeformation and the internal friction results /2/. These measurements have allow us to observe the presence of two microdeformartion stages in the case of the alloys A and B, (Fig. 1-a and 1-b). The presence of two transformation stages has been also observed by internal friction measurements /2/ and it can be attributed to the coexistence of two martensitic phases  $\gamma_1'$  and  $\beta_1'$ . Indeed, the observation carried out by optic microscopy with a heating-cooling stage have allow us to identify both phases  $\gamma_1'$  and  $\beta_1'$  /2/ agreeing with the observations done by Van Humbeeck et al. /3/ and Sakamoto and Shimizu /4/. Besides, for the concentration of the alloy A, Vasilenko et al./5/ phases diagram previews the coexistence of both phases  $\gamma_1'$  and  $\beta_1'$ . Though the alloy B has a much lower Ni concentration, it shows an e/a relation which is really closed to that of the alloy A, being located in the range in which a mixture of both phases  $\gamma_1'$  and  $\beta_1'$  can be expected.

In the case of the alloy C, with a very lower Ni concentration, only one microdeformation stage (Fig. 1-c) can be observed, due to the transformation of a unique martensitic phase. Though we have not identified it yet, it could be probably the  $\gamma_1'$  phase, because the e/a relation is higher than those of the alloys A and B /6,7/.

Transformation temperatures can be easily calculated from the derivate curves of the microdeformation curves, as well as the hysteresis width of the transformation cycle and the temperatures characteristic of the transformation  $T_0$  /2/. Otherwise, it is necessary to notice that the transformation temperatures, when two stages are overlapped can not be determined with the same precission as the extreme ones. In table 2 we show the results obtained for the three alloys.

Table 2

Alloy	Phase	T(K)	M <sub>s</sub>	M <sub>f</sub>	A <sub>s</sub>	A <sub>f</sub>	T <sub>0</sub>	Hysteresis
A	$\gamma_1'$		297	216	245	327	277	27
A	$\beta_1'$		251	185	213	282	241	30
B	$\gamma_1'$		315	*	*	337	312	26
B	$\beta_1'$		*	227	242	*	*	17
C			416	352	331	425	391	10

\* Very difficult to determine

The presence of two stages, that is to say, the presence of the two martensitic phases depending on the concentration range, point out us how it is necessary to be careful when indicating the transformation temperatures of the alloy. This way, the diagram proposed by Xinming et al. /8/ consisting on the variation of the transformation temperatures along with the Ni concentration for 13,75 % Al, is, in our opinion, not correct because they do not have in mind the presence of two phases  $\gamma_1'$  and  $\beta_1'$  in the range of high Ni concentrations. Probably, it is the presence of the two phases, the responsible for the curvilinear aspect of the diagram. On the other side, the hysteresis cycle width decreases along with the decreasing of the Ni concentration (Fig. 1), becoming very narrow when we have a unique transformation stage (alloy C). All this can be clearly seen on the derivative curves of the microdeformation measurements (Fig. 3), and it is also opposing Xinming et al. observations /8/.

The  $\gamma_1'$  and  $\beta_1'$  phases transformation, at temperatures which are so close, is coherent with the fact that the chemical free energy changes associated with the transformation of  $\gamma_1'$  and  $\beta_1'$  phases are very similar /9,10/. This double transformation has been also observed by Van Humbeeck et al. /3/ and by Friend et al. /11/. The difficulties this authors met when trying to observe the direct transformation  $\beta_1-\gamma_1'$ , but that we have not met, can be analyzed in terms of the internal stresses of the alloy.

During the thermomechanical treatments, two operations are carried out usually:

- The hard hot-working ( extrusion, rolling, etc )
- The quenching process ( into iced water or NaOH solution )

These operations can strongly increase the internal stresses of the material. Specially, in the case of quenching process, we have verified, that during the quenching process in NaOH solution an important number of intergranular fissures is produced, and it produces in many cases the fracture of the sample. Even in the case of iced water quenching, intergranular fissures have been observed. This means that in the case of Cu-Al-Ni alloys, the quick cooling produces an increase of the internal stresses until so high levels as to fracture the alloy. In these conditions the internal stresses stored in the sample, make easier the martensite nucleation under stress, this is  $\beta_1'$ , not allowing it to reach at  $\beta$  phase the transformation temperature of the  $\gamma_1'$  phase. At a given temperature, the nucleation of a phase, induced by stress, will be reached when the addition of the applied stresses  $\sigma_a$  plus the internal stresses  $\sigma_i$  reaches the value of the nucleation critical stress  $\sigma_c$ , that is when  $\sigma_c = \sigma_i + \sigma_a$ . This way, if the internal stresses, produced by cooling reach the stress  $\sigma_c$  of a martensitic phase, this will be immediately induced by stress. This is probably the reason why Sakamoto and Shimizu /4/, depending on the quenching rate, obtain the  $\beta_1'$  phase or the  $\gamma_1'$  phase for the same alloy. The influence of the internal stresses has been analyzed in detail in a model developed in other paper /12/.

In our case the samples are as cast, the quenching has been more or less slow, besides we have carried out a long enough annealing treatment. For that reason, we can think that the internal stresses in our alloys are very weak and therefore, the  $\gamma_1'$  can be thermally induced. Along with the advance of the transformation the internal stresses get bigger owing to the accommodation of the deformation in a polycrystal (that in  $\gamma_1'$

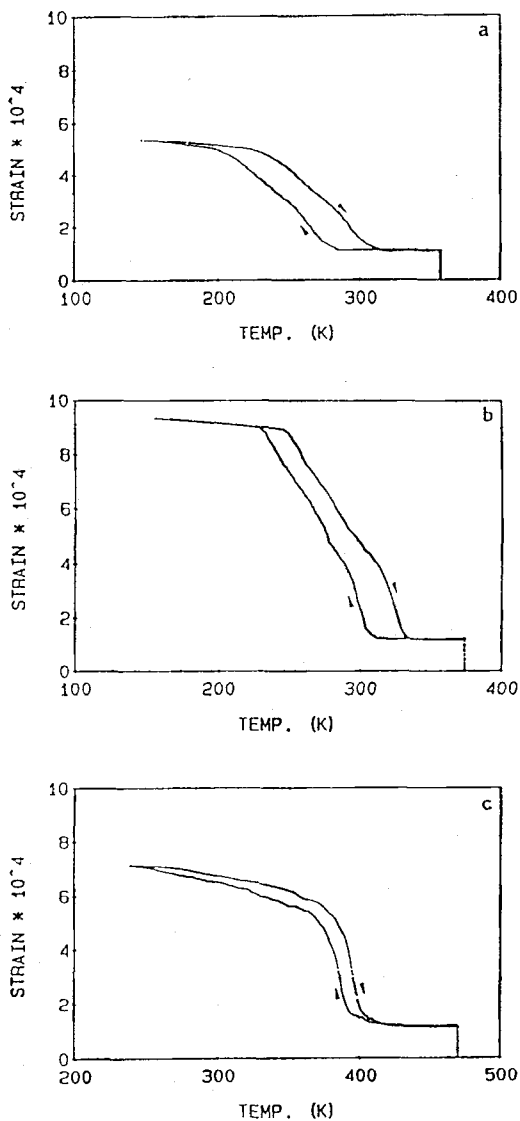


Fig.1. Microdeformation curves obtained with a static stress of  $\sigma_s=10^{-4} \mu$  applied in  $\beta$  phase when the temperature increases and decreases. (a) alloy A, (b) alloy B, (c) Alloy C.

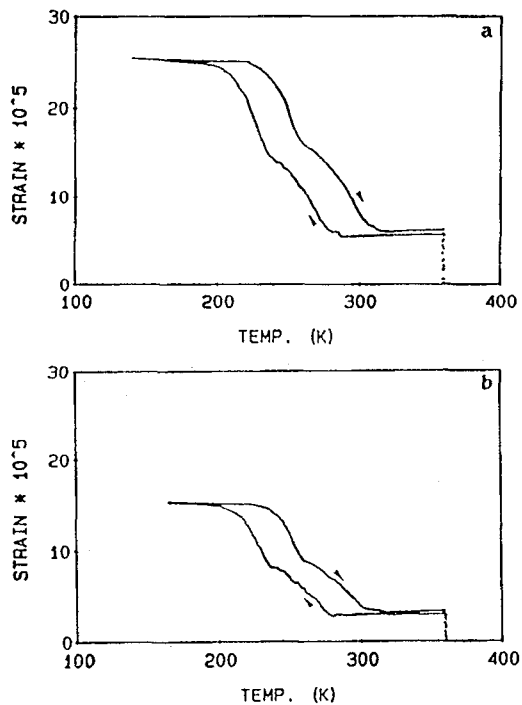


Fig.2. Microdeformation curves of alloy A when the temperature increases and decreases with a static stress of  $\sigma_s=5 \times 10^{-5} \mu$  (a), and  $\sigma_s=2.8 \times 10^{-5} \mu$  (b), applied in  $\beta$  phase.

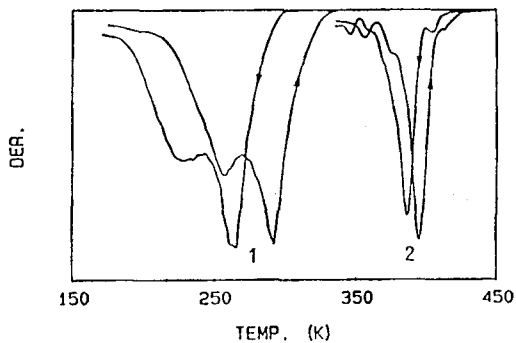


Fig.3. Derivate curves of the microdeformation curves shown in Fig. 1-a (1), and Fig. 1-c (2).

is produced by twinning), making more difficult the nucleation and growth of the  $\gamma_1'$  phase and making easier the nucleation and growth of the  $\beta_1'$  that accommodates a bigger shear deformation.

This nucleation and growth process of both kinds of martensite plates is very sensitive to the applied stress, just as it can be seen comparing the microdeformations on Fig. 1-a, Fig. 2-a and 2-b, that have been carried out over the same sample at different stresses. It can be observed how, the less is the applied stress the clearer way can be differenced both stages. All this seems to be owing to the fact that the temperatures characteristic  $T_0$  ( $\gamma_1'$ ) and  $T_0$  ( $\beta_1'$ ) are affected by the stress in a different way, and it can be linked to the mobility of the variants interphases of both kinds of martensite. These last matter must be cleared in further works. We can conclude that the internal stresses stored in the material during the quenching process can have a great influence on the nucleation and growth process of the  $\gamma_1'$  and  $\beta_1'$  phases, specially on those concentration ranges in which both phases can coexist.

In this direction, the effect of the annealing treatment at around 200°C would be not just to stabilize the atomic order degree, as it has been suggested by many authors, see /7/ for a review, but also to reduce and stabilize the internal stresses level existent in the material after the quenching.

#### 5. Acknowledgment

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