

Internal Friction Study of Cu-Zn-Al Martensite.

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Introduction.

The martensitic phase of copper based shape memory alloys, like Cu-Zn-Al can present a stabilization effect. This phenomenon is characterized by a progressive increase of the reverse transformation temperatures A_s and A_f when the alloy is maintained a long time at temperature below A_s [1,2].

The stabilization of the martensite is a thermally activated process which kinetics depends of the vacancy concentration: the higher is the vacancy concentration, the faster is the stabilization. The stabilization effect can be reduced by a quench from the high temperature stable beta-phase region to a temperature T_B just above M_s . This treatment is called "Step Quenching". The two main hypothesis to explained the stabilization of the martensite are the vacancy pinning of the martensite interfaces and the reordering in the martensitic phase [1,2]. According to these hypothesis the stabilization is controlled by the concentration and the migration activation energy of the vacancies in the martensitic phase.

Some measurements of the activation energy for the vacancies migration in the martensitic phase have then been made :

- In a martensite inherited from a disordered beta-phase, the activation energy for the vacancy migration is 0.8 - 0.9 eV (3) (4) (5).

- In a martensite inherited from an ordered beta-phase, this energy is higher (1.2 - 1.3 eV) (4) (6).

In this paper the internal friction technique has been used, because this one is a very sensitive technique to study the motion of the interfaces of the martensite (7). This technique is therefore well adapted to check the validity of first hypothesis for the martensite stabilization phenomenon.

Experimental.

The nominal composition of the alloy used in this study was:

Cu - 23.3 at % Zn - 9 at % Al.

which gives the transformation temperatures :

$$M_s = 350\text{K}, M_f = 328\text{K}, A_s = 338\text{K}, A_f = 360\text{K}.$$

The material was hot extruded into a plate of 2 mm in thickness. This material was next rolled to 1 mm at room temperature after heat treatment at 773K. The samples (35 x 4 x 1 mm) were cut with a slow diamon blade saw from this sheet.

Two heat treatments were performed :

* A Direct Quench. The sample was then homogeneised in the beta-phase at 1123 K during 15 mn, quenched through M_s in wather at room temperature, dried, and quickly immersed in liquid nitrogen. Then, the sample was set in the pendulum at low temperature, this one beeing allways kept below 170 K. After this treatment, an aging at $T < A_s$ rapidly stabilizes the martensite, i.e. the A_s temperature was raised above 500 K [6].

* A Step Quench. The sample was homogeneised in the beta-phase at 1123K during 15 mn, step quenched at $T_B = 273$ K during one hour and then air cooled. This treatment prevents the stabilisation of the martensite. The sample was then named "Standard".

The damping ($\text{tg } \emptyset$) was measured with a forced oscillation torsional pendulum between 170 and 400 K. Measurements have been done at two temperature rates, 5×10^{-3} and 5×10^{-2} K/s, and frequency was in the range of 5×10^{-2} Hz to 5Hz. During the measurements, the maximum strain amplitude was kept constant at $\epsilon_m = 4 \times 10^{-4}$.

Resistivity measurements have been performed after the internal friction measurements.

Experimental results.

* Direct Quench.

After direct quench and mounting in the pendulum, the sample was heated at different temperature rates. During these heatings, the internal friction and the modulus variations were measured.

- At low temperature rate (5×10^{-3} K/s) (Figure 1), the damping exhibits a maximum δ_A at $T_A = 250\text{K}$, and decreases rapidly to a very low value above 285K. During these variations, the modulus only increases, especially when the damping decreases. On further cooling, and for the next thermal cycles between

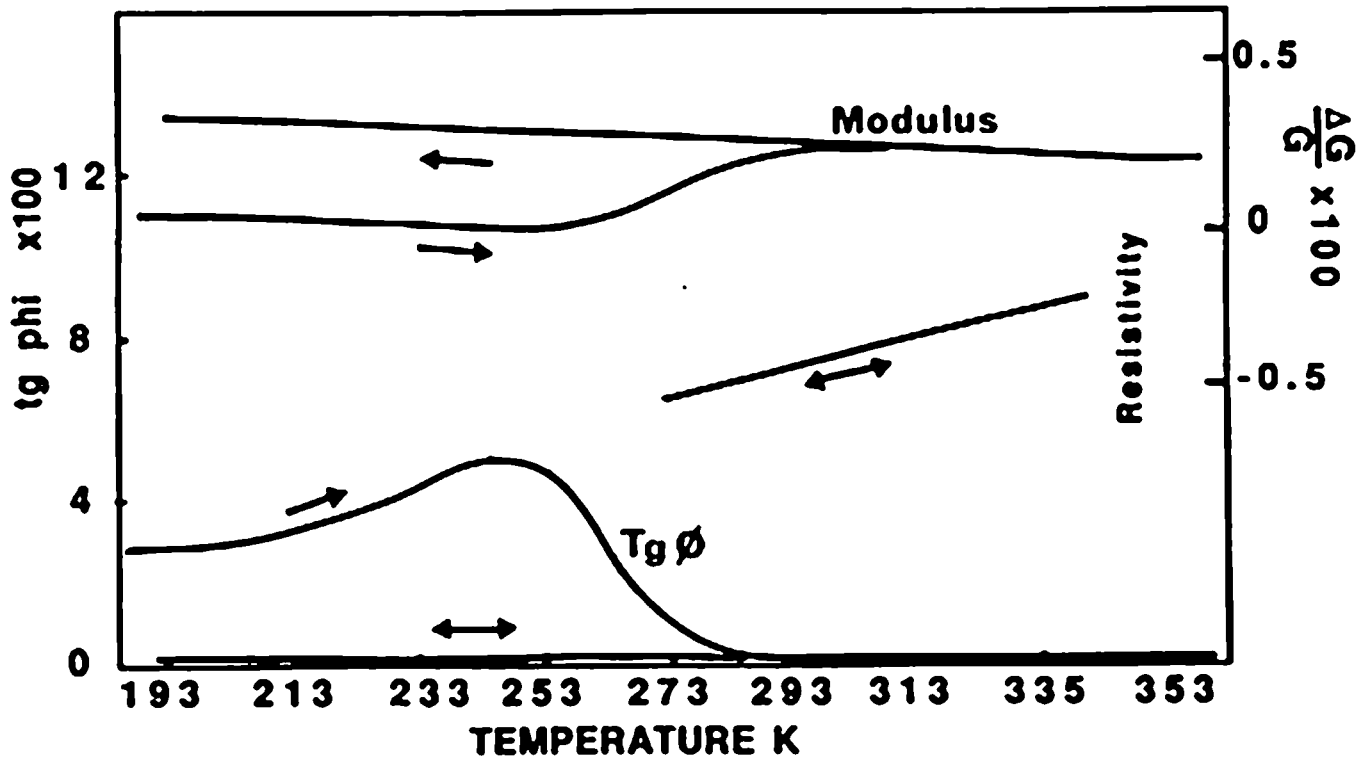


Fig. 1 - Direct Quenched Sample. Internal friction, modulus and resistivity versus temperature. Frequency = 0.5Hz, $dT/dt = 0.3K/mn$.

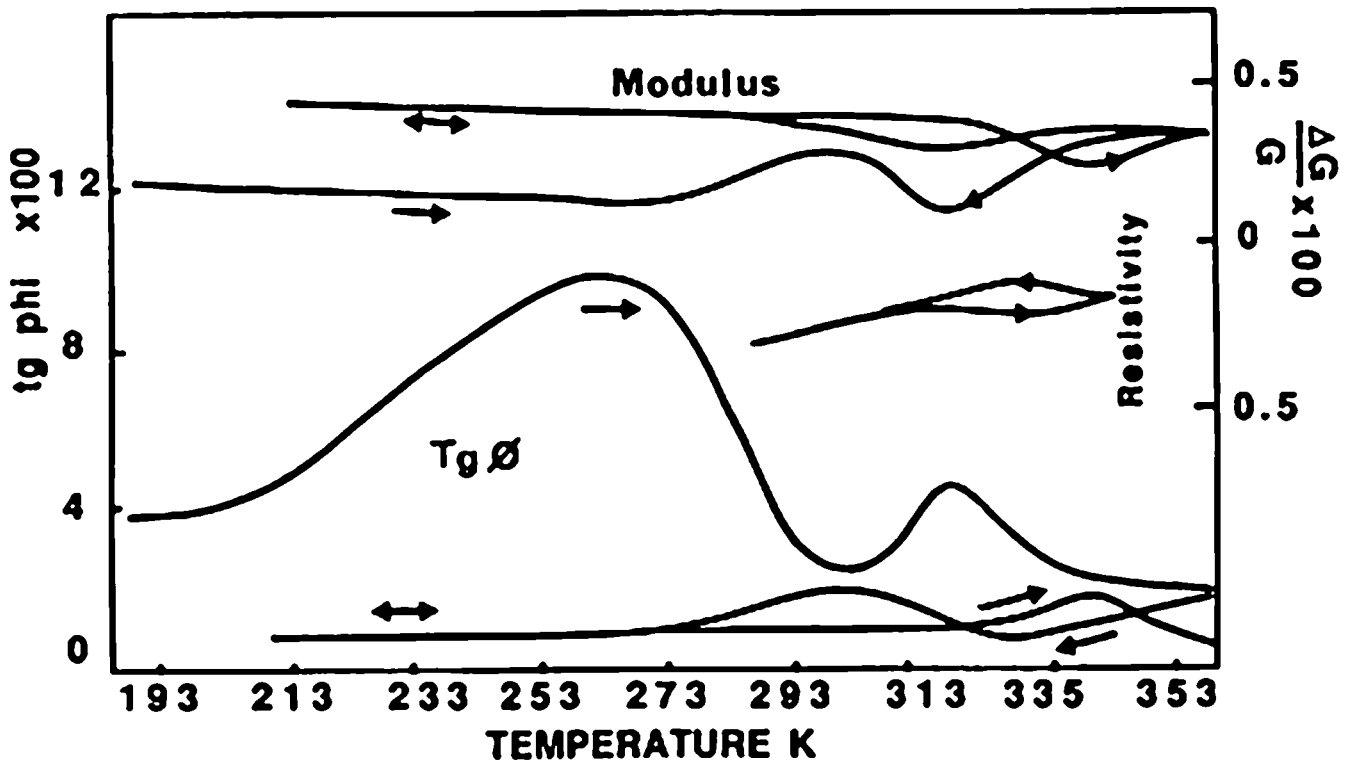


Fig. 2 - Direct Quenched Sample. Internal friction, modulus and resistivity versus temperature. Frequency = 0.5Hz, $dT/dt = 3K/mn$.

- A maximum in the martensite phase δ_m . The temperature of this maximum is temperature rate dependant. According to J. Van Humbeeck [12], the origin of this additional peak is a "peaking effect" due to the vacancies.

The internal friction of a step quench sample versus the time at constant temperature in the martensite has been also measured. The curves (figure 4) shows that a maximum d_T in damping is reached at each temperature. The amplitude of δ_T is maximum near 250 K, and this peak shifts to longer times with decreasing temperature.

The activation energy calculated from these curves is $E_T = 0,39 \pm 0.03$ ev.

The two maxima δ_T measured versus the time at constant temperature and δ_m measured at constant temperature rate have very probably the same origin. For a low temperature rate, the maximum δ_m is located at low temperature and for a low constant temperature measurement the maximum δ_T appears after a long time.

In the same way, the amplitude and frequency measurement dependance of the two peaks δ_T and δ_m are comparable.

Discussion.

The vacancy concentration is strongly dependant of the thermal treatment :

- * For the Direct Quenched samples, this concentration is of course very large.

- * For the Step Quenched sample, the concentration of vacancies must be lower. Just after the aging at T_B , the vacancy concentration of the beta-phase is approximatively the equilibrium one. Due to the diffusionless character of the martensite formation, the martensite inherits from all these vacancies. However, the formation energy of the vacancies of the two phases is very different : approximately 1 ev for the martensite and 0.5 ev for the beta-phase (6). Even if the vacancy concentration is at the equilibrium in the beta-phase, the vacancy concentration in the martensitic phase immediately after the transformation will be higher than the equilibrium one.

At the amplitude and the frequency used for our internal friction measurements, the damping of the martensitic phase is mainly due to the hysteritic movement of the interfaces between the martensite plate variants (7). The internal friction is therefore very sensitive to the breakaway of these interfaces from the vacancies and to their pinning.

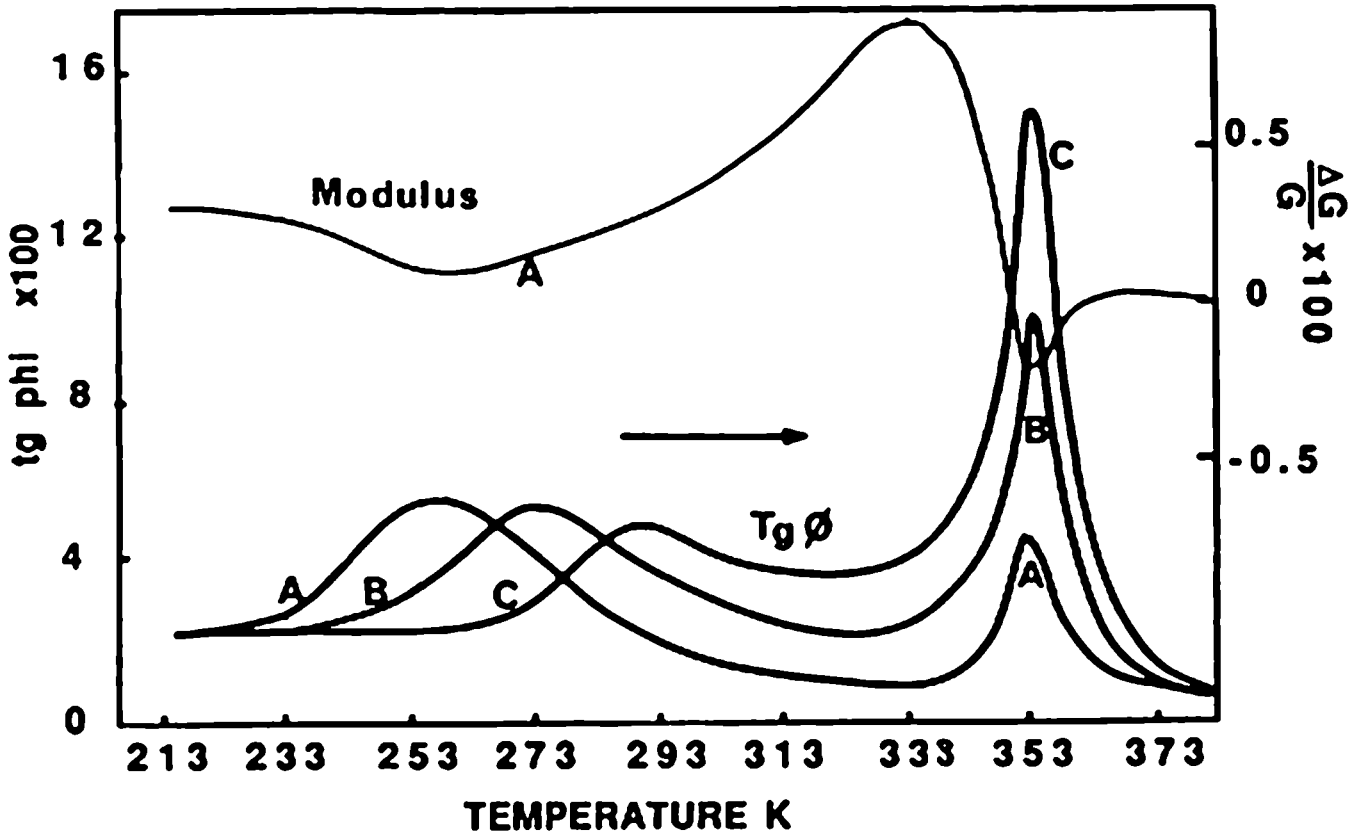


Fig. 3 - Step Quenched Sample. Internal friction and modulus versus temperature. Frequency = 0.5Hz.

A: $dT/dt=0.125K/mn$, B: $dT/dt=1K/mn$, C: $dT/dt=2K/mn$.

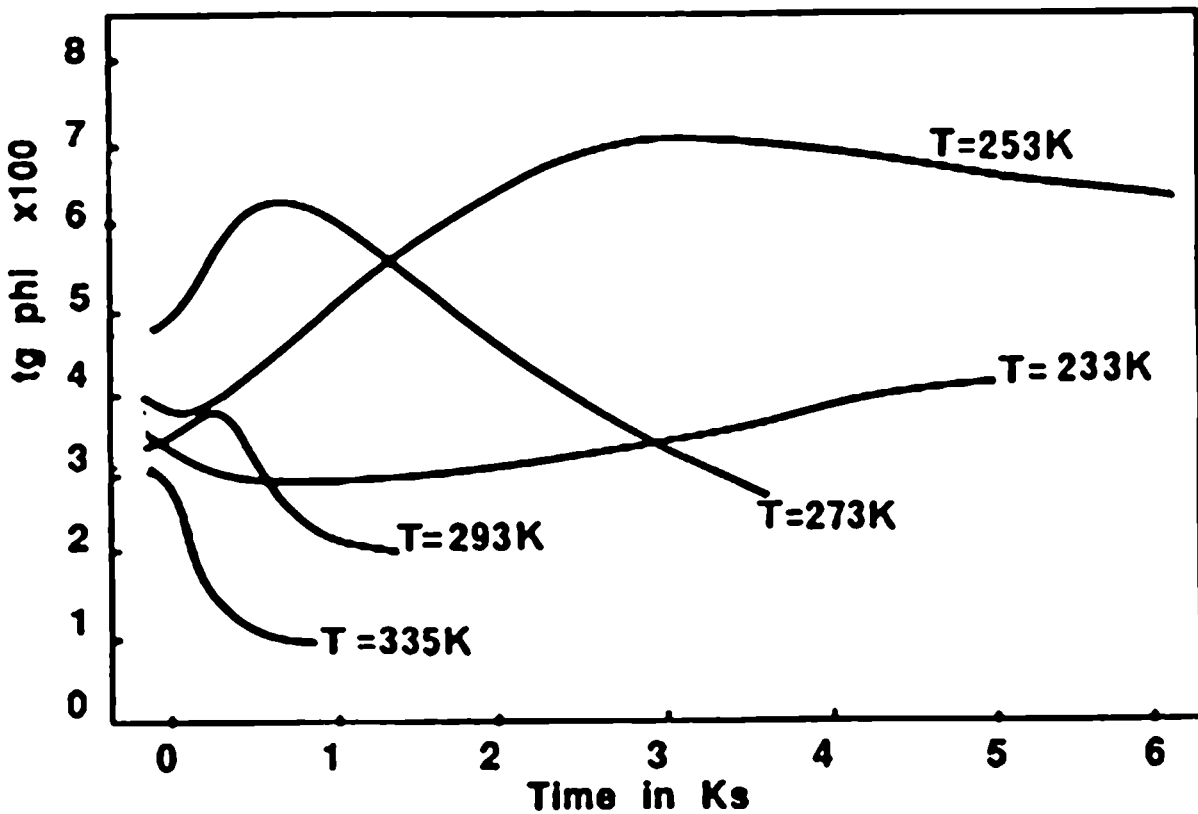


Fig. 4 - Direct Quenched Sample. Internal friction versus the time. Frequency = 0.5Hz, $dT/dt = 0$.

After a Direct Quench, the vacancy concentration in the martensitic phase is very high. At low temperature all these vacancies are frozen-in and do not disturb the interfaces motion. The damping is high. When the temperature is increased, the vacancies begin to move towards the interfaces and progressively interacts with them (breakaway hysteritic process). The internal friction first increases and then decreases when the vacancy concentration becomes too high and induces the strong pinning of all the interfaces. The martensite is then stabilized. If this hypothesis is true the activation energy measured for the pic δ_A is then the migration energy of the vacancies.

After a step quench, the vacancy concentration in the martensite phase is low, but however, this vacancy concentration is not the equilibrium one. Therefore a driving force exists for reducing the concentration of the vacancies.

These excess vacancies can then migrate towards the moving interfaces and be responsible for the maxima δ_m and δ_T . Nevertheless, the activation energy measured for the maximum δ_T is very low compared to the energy E_A measured for δ_A . In fact, the moving interfaces can be pinned by two ways :

- * For the high concentration of vacancies, a direct migration of the vacancies on the interfaces occurs.

- * For the low vacancy concentration, the interfaces, by their movements induced by the measuring stress drag the vacancies (13). This mechanism assists the pinning of the interfaces. The activation energy is then lower than the activation energy for the migration of the vacancies in the bulk material. When the vacancy concentration is high this phenomenon is screened by the direct migration pinning: for the same temperature rate the δ_A temperature is lower than the δ_m temperature.

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