Hysteresis Effects during Martensitic Transformation in Cu-Zn-Al Shape Memory Alloys

J.Stoiber, R.Gotthardt, Insitut de Génie Atomique, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne.
J. Van Humbeeck, Departement Metaalkunde, Katholieke Universiteit Leuven, B-3030 Heverlee-Leuven.

Introduction

The general knowledge of martensite and martensitic transformations in Cu-base alloys, like Cu-Zn, Cu-Zn-Al or Cu-Al-Ni, has already developed considerably and it is generally accepted that a thermoelastic character of the martensite in these alloys is responsible for their capability of reversible shape changes during transformation. However one of the most important features of martensitic transformations, namely their hysteretic transformation behaviour is not yet fully understood. A large number of practical applications show that required functional properties get irreproducible, if they are obtained during incomplete transformations or if temperature fluctuations as well as applied stresses are present during the transformation (1).

In the thermodynamical analysis of a hysteretic transformation behaviour it is assumed that the observed hysteresis is necessarily related to energy dissipative processes, such as dissipation of work to move the interfaces, local relaxation of elastic energy or nucleation processes. These processes and therefore the transformation hysteresis of an alloy system is essentially influenced by the actual conditions at which a given experiment is performed (2).

In the present study effects on the transformation hysteresis have been carried out in different Cu-Zn-Al alloys especially during partial temperature and stress cycles in the hysteresis domain. Transformation kinetics and transforming interface mobility have been studied using the technic of internal friction (IF), where energy dissipative processes are detected quantitatively in direct relation to the amount of transformed volume. On the other hand transmission electron microscope (TEM) in situ observations have been undertaken in order to get informations about the reversibility of formation and growth of individual martensitic plates.

Experimental

Internal friction measurements have been performed in a special inversed torsion pendulum. This pendulum, which is described in (3), is working at resonance frequencies (f = 0.5Hz - 1.5Hz) and oscillation amplitudes from 10^{-6} to 10^{-4}. Simultaneously to the internal friction (Q^{-1}), the frequency (f), the electrical resistance (R) and the shape change of the sample can be measured. In addition a tensile stress up to 10 MPa can be applied to the specimen, which has a size of $40 \times 2.5 \times 0.6$ mm^3. After a specimen was mounted in the pendulum, several complete transformation cycles have been performed until the thermal hysteresis got stable. Subsequently the influence of external parameters such as heating or cooling rate $\dot{T}$, oscillation amplitude ε and applied stresses σ on the IF-curve has been estimated. Partial thermal cycles have been undertaken at different sites of the hysteresis (A_s, M_s, $(A_s+A_f)/2$, $(M_s+M_f)/2$) observing the evolution of Q^{-1}, f and R.

TEM observations have been performed in a microscope operating at 200 kV using a special specimen holder with the possibility to transform a sample in situ either by heating or by applying an external stress. An external stress has been applied to the specimen (size $6 \times 2 \times 0.2$ mm^3) by a pneumatic system. Thin foil samples have been prepared by the jet polishing technic in an electrolyte of methanol/H_2SO_4 (4:1). The transformation behaviour of individual martensitic plates has been observed during temperature and stress cycles around M_s.

The nominal compositions, the M_s-temperatures and the heat treatments of the Cu-Zn-Al polycrystals used for both types of measurements are listed in table I.

Table I:

number	alloy composition (weight %)	heat treatment	M_s	A_f
1 (TEM)	Cu-26Zn-4.5Al-0.5Co	60'at 1130K ⇒quenched to 290K	250K	260K
2 (IF)	Cu-26Zn-4Al	15'at 1023K ⇒ 90'at 363K	290K	300K

Results and Discussion

a) IF measurements

i) Internal friction spectrum in dependence of temperature rate ($\dot{T}$), applied stress (σ) and oscillation amplitude (ε)

A typical temperature spectrum of Q^{-1}, f and R during the forward and reverse transformation in the studied alloy is shown in figure 1, where connected curves are drawn in stead of measured data points in order to clarify the evolution of the interesting parameters. The transformation region is characterized by an

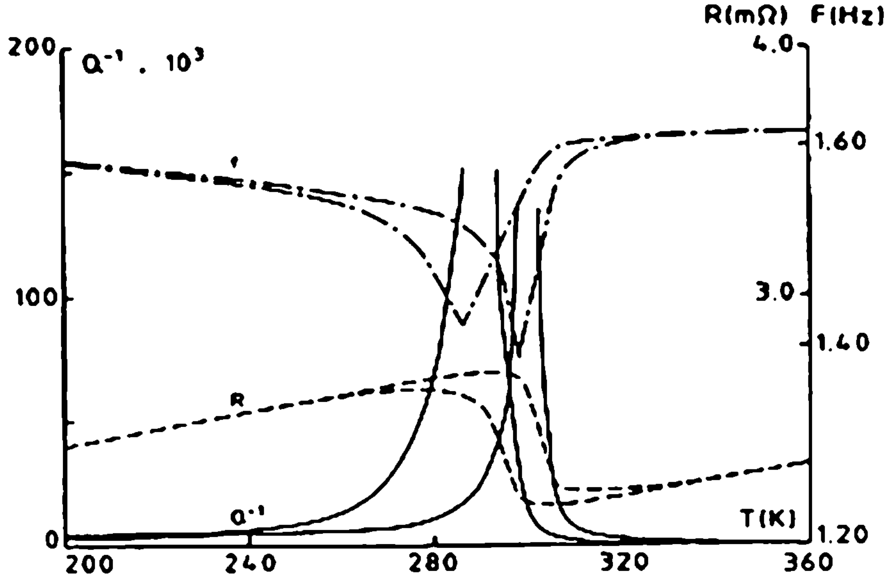

Fig.1: Q^{-1}, R and f as a function of T, $\varepsilon = 7.5 \cdot 10^{-6}$, $\dot{T} = 1$ K/min).

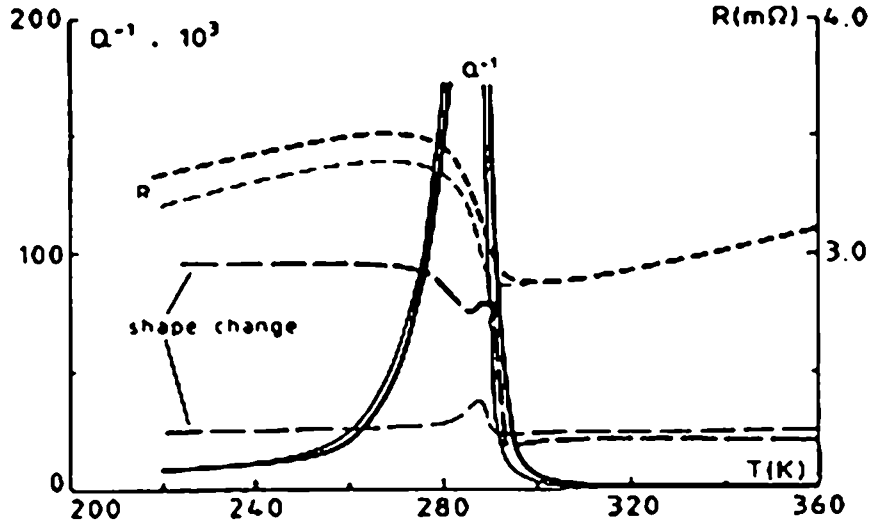

Fig.2: Q^{-1}, R and shape change for $\sigma = 0$ (thin lines) and $\sigma = 10$ MPa (broad lines), $\varepsilon = 2.2 \cdot 10^{-5}$, $\dot{T} = 0.5$K/min.

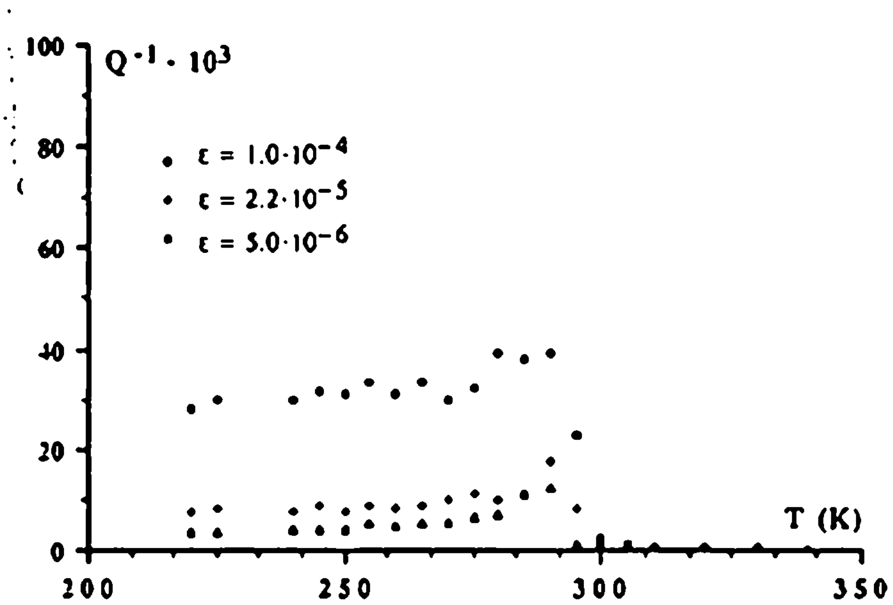

Fig.3a: IF($\dot{T}$=0) for different amplitudes.

extremely high damping capacity and accompaniing shape changes even for relatively low temperature rates, which make the estimation of Q^{-1}-values often impossible in this region. Therefore exact values of Q^{-1}_{max} have not been obtained, but they are certainly above 0.2.

The influence of an applied stress on Q^{-1}, R and the shape change presents figure 2, in which two successive cooling curves have been measured, the first with $\sigma=0$ and the second with $\sigma=10$ MPa. The spectra of all parameters are slightly shifted to higher temperatures, if a stress is applied, indicating that M_s has been increased. The form of the IF-curve remains almost constant, but the evolution of the resistance and the shape change of the sample changes significantly during the transformation. Since both, the amount of shape change and the resistance increase compared to the curves for $\sigma=0$, it can be concluded that the applied stress caused an elongation of the sample due to the growth of preferentially oriented martensite variants.

The effect of the oscillation amplitude has been established by decomposing the measured IF in a transient term and in a static term. The transient term IF_{Tr} can be related to the amount of transformed volume per unit of time and represents therefore the propagation of the transformation, which is done by dislocation motion. In existing models for the internal friction behaviour in the transformation region, this contributions is thought to be proportional to $\dot{T}/f$ (4). The static term, measured at constant temperatures, is related to the mobility of parent-martensite or martensite-martensite interfaces and to the IF-contributions of each phase. $IF_{Tr}=0$ for $\dot{T}=0$ and can therefore be calculated as: $IF_{Tr} = IF(\dot{T}\neq 0) - IF(\dot{T}=0)$.

Figures 3a and 3b show the dependencies of the static and the transient term on ε respectively. It can be seen that $IF(\dot{T}=0)$ increases with increasing amplitude , while IF_{Tr} decreases. In isothermal conditions the amount of interface movement and therefore the amount of dissipated energy during one oscillation cycle is proportional to the amplitude. This can explain a positive amplitude dependence of $IF(\dot{T}=0)$. On the other hand, an amplitude dependence of IF_{Tr}, as it is observed in fig.3b, is rather unusual, since IF_{Tr} was often observed to be independant of the oscillation amplitude (5). However other authors found also that IF_{Tr} decreases as ε increases but only for lower amplitudes (6,7). Morin (6) explains this behaviour with the influence of the oscillation amplitude on the amount of reorientated martensite, while Bidaux (7) assumes that the oscillation stress can participate to the quantity of phase, which is transformed during one cycle. Both calculate IF_{Tr}, but using different models for the transformation strain. The model of Morin yields decreasing IF_{Tr}-values for increasing oscillation amplitudes only for $\varepsilon < 2.5\cdot10^{-5}$, while the model of Bidaux predicts this dependence of IF_{Tr} also for higher amplitudes. Recent TEM in situ observations (8) showed a high sensibility of interface arrangement to external stress

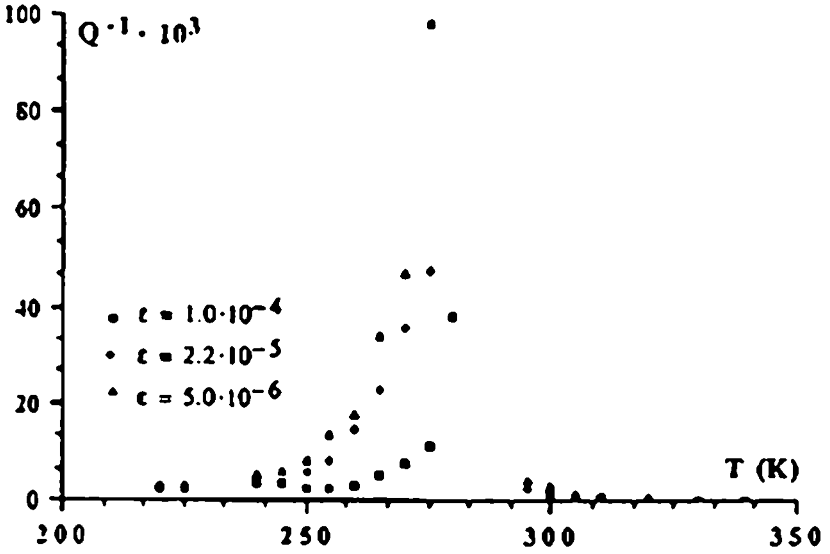

Fig.3b: IF_{Tr} for different amplitudes, $\dot{T}$=0.5K/min.

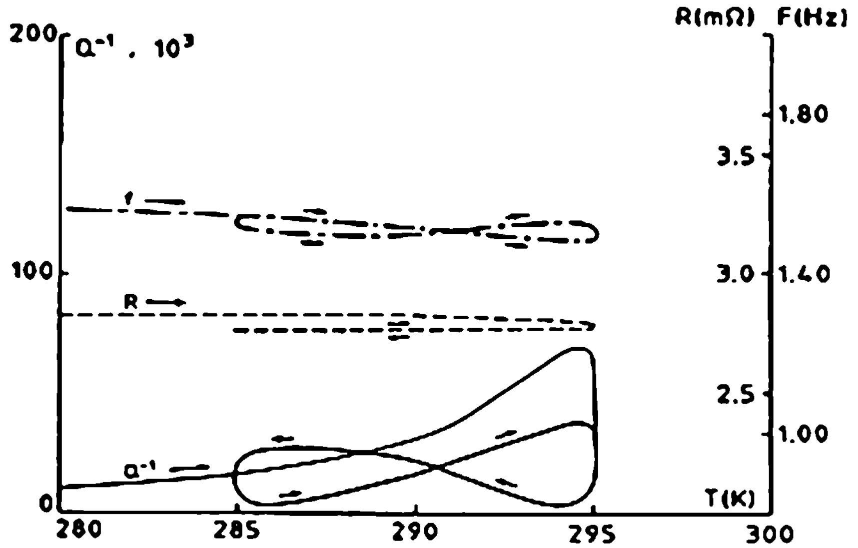

Fig.4a: Q^{-1} and R during partial thermal cycling around A_s, $\dot{T}$=0.5K/min, ε= $7.5\cdot10^{-6}$.

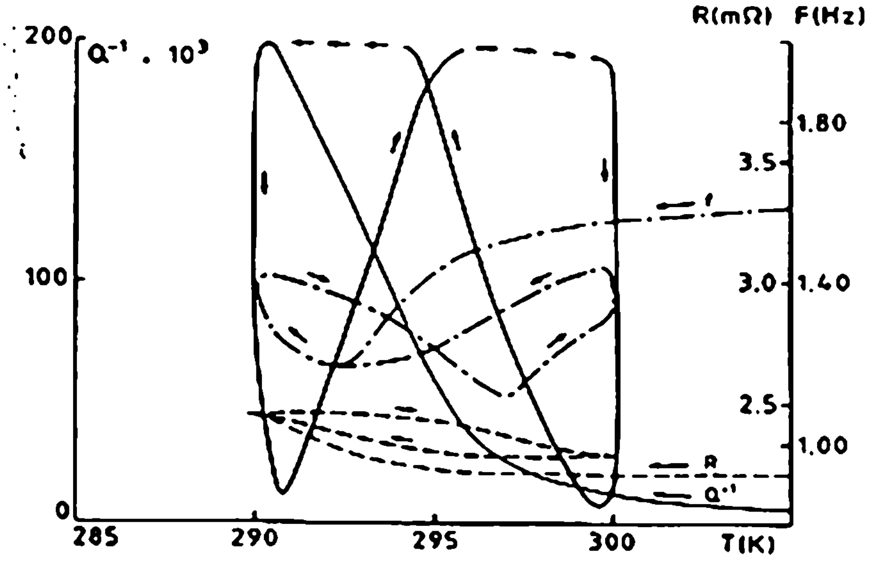

Fig.4b: Q^{-1} and R during partial thermal cycling around $(M_s + M_f)/2$, $\dot{T}$ = 0.5K/min, ε= $7.5\cdot10^{-6}$.

variations, confirming that reorientation mechanisms have to be considered for the explanation of IF_{Tr}.

ii) Internal friction (IF) during partial thermal cycling in the hysteresis domain

Figure 4a and 4b show two examples for IF-measurements during partial thermal cycling. In figure 4a thermal cycling with an amplitude of ±5K has been performed around A_s. The sample has been heated up to 295K (thin lines) and then cycled ten times between 285K and 295K (broad lines). While the electrical resistance remains constant during cycling, the internal friction varies following a "∞"-shaped path due to $\dot{T}$-effects. Every time, as the sign of temperature rate changes (at 285K and 295K respectively), Q^{-1} passes a minimum corresponding to $\dot{T}=0$. Further temperature change leads to an increase of Q^{-1}.
Figure 4b represents thermal cycling around $(M_s+M_f)/2$. After the sample had been cooled to 290K (thin lines), ten partial cycles between 290K and 300K (broad lines) have been performed. In this case R shows a partial hysteresis in between the hysteresis of a complete temperature cycle. The developement of Q^{-1} is in principle the same as in fig.4a, but much more pronounced. Big changes of Q^{-1} can be observed (between 1% and 20%), even while R remains constant, confirming the important influence of $\dot{T}$ on the internal friction in this alloy.

Comparing the results of electrical resistance and IF_{Tr} during partial thermal cycling in the transformation region, it can be concluded that changes in the IF are not necessarily related to significant changes in the transformed volume and could be related to changes in the interfacial arrangement. Interface migration can be induced by changing internal stresses of the specimen as soon as the temperature rate increases.

b) TEM-observations

In thin foil samples of alloy 2 small martensite plates were already present at room temperature (RT) in the observable region around the hole in spite of the lower M_s-temperature. These plates were probably stress induced due to high stress concentrations around the hole. Three different types of experiments have been performed observing the developement of the amount of transformed martensite and the number of martensitic plates:

- thermal cycling between RT and 395K
- stress cycling
- combined stress and thermal cycling

i) thermal cycling

Several individual plates have been observed during temperature cycles between RT and 395K. The observations show that the number of martensitic plates as well as the transformed volume are increasing with the number of thermal cycles. Furthermore the temperature at which individual plates disappeared during heating increases with the number of cycles until these plates have been stable even at 395K.

ii) stress cycling

Stress cycles have been carried out by applying increasing and decreasing pressures to the pneumatic system. It is assumed that constant pressure levels correspond to constant stress levels in the specimen, even if for individual martensitic plates the resulting stress components are probably more complex. During stress cycling reversible moving of martensitic plates has been observed, i.e. the amount of transformed martensite volume has not changed significantly.

iii) combined stress and thermal cycling

The way of the performed cycles was the following:

- 3x stress cycling like ii)
- 1x thermal cycling
- 1x stress cycling

While the first three stress cycles turn out more and less reversibly, after the following thermal cycle the proceeding of the stress induced martensitic transformation is completely different than before: During loading the number of martensite nuclei increases obviously and after the whole stress cycle the amount of transformed martensite is higher than before.

In order to discuss the discribed observations it is necessary to point out that in thin foil samples special conditions are present for the martensitic transformation itself as well as for a quantitative description of external parameters. Especially the influence of surface martensite (9) and the contribution of internal stresses due to the inhomogeneous shape dimensions of the specimens are not known.

The present study of the transformation behaviour around M_s in thin foil samples show that the earliest stages of martensitic transformation are strongly influenced by small thermal or stress cycles, which do not lead to a complete transformation. An increasing number of growing martensite plates indicate that nucleation events can be energetically favoured as against the growth of already formed plates. Especially small temperature cycles lead to an increasing activation of nucleation sites.

Conclusion

Hysteresis effects of the martensitic transformation in Cu-Zn-Al alloys have been investigated especially during partial thermal and stress cycles in the transformation regime.

Internal friction measurements show that the transient IF-contribution is strongly influenced by the oscillation amplitude and small variations in temperature rate without significant changes of the transformed volume. This indicates that the transient part of IF is not only a function of transformed volume per time unit but also depends on the amount of reoriented martensite variants, which is a function of the applied oscillating stress and internal stresses. The contribution of internal stresses can be modified during the transition from isothermal to constant temperature rate conditions.

TEM in situ observations of the first stages of martensitic transformation reveal that especially small temperature cycles increase the number of growing martensitic plates as well as the amount of transformed volume.

References

(1) Delaey L., Aernoudt E., Proc. ICOMAT 1986, Nara, Japan, 926.

(2) Delaey L., Ortin J., Van Humbeeck J., Proc.Phase Transf.1987, Ed.: Lorimer G.W., The Inst.of Metals, London, 1988, 60.

(3) Gotthardt R., in "Die martensit. Phasenumwandlung", Ed.: Hornbogen E., DGM, 1986, 75.

(4) Van Humbeeck J., in "Internal Friction in Solids", Proc.of the summer school on IF, Cracow, Poland, 1984, 131.

(5) Delorme J.F., Gobin P.F., Métaux No 573, 1973, 185.

(6) Morin M., Guénin G., Gobin P.F., Proc.ECIFUAS 1980, Manchester, England, 275.

(7) Bidaux J.-E., Schaller R., Benoit W., Acta met.37, 1989, 803.

(8) Gotthardt R., see contribution to the same conference.

(9) Lovey F.C., Ferron J., De Bernandez, Ahlers M., Scripta Met., 17, 1983, 501.