

NiTi and CuAlNi Martensite Studied by Isothermal Mechanical Spectroscopy

V. Pelosin and A. Rivière

Laboratoire de Mécanique et de Physique des Matériaux, UMR 6617 du CNRS, ENSMA, BP. 109, 86960 Futuroscope cedex, France

Abstract: Internal friction has been measured in isothermal conditions over a large frequency range (5×10^{-4} Hz-40 Hz) in NiTi (49.6 at.% Ni) and CuAlNi (12 wt.% Al, 3 wt.% Ni) alloys. A low frequency increase which depends on temperature has been found on NiTi sample in the martensitic phase. This damping effect has been ascribed to interface motions between martensite variants. As to confirm that the process is linked to the martensitic structure, CuAlNi alloy was also studied. It has been observed that the low frequency damping behaviour of two samples looks totally different whether the sample has been slowly cooled from 1073 K or if it has been water quenched. Indeed, the low frequency increase is clearly evidenced in the first case contrarily to the water quenched sample where the effect is reduced and delayed as it appears only at much higher temperature. Several annealings have been performed on the quenched sample and the ageing effects have also been observed by modifications on the internal friction level. In addition, the structural evolution of this last sample has been observed by X-ray diffraction experiments.

1. INTRODUCTION

The shape memory alloys are commonly considered as high damping materials. In fact, the high damping capacity concerns mainly the martensitic state and of course the transition domain. It has been established that various contributions are constituting the measured damping [1, 2]. On the present study, isothermal internal friction measurements were performed in order to eliminate all the transient effects. The damping is obtained by sweeping in a very large frequency range for various temperatures in the martensitic state ($T < A_s$). First, we have focused our study on a NiTi sample where a low frequency effect, associated to variant interface motions, has been observed. The aim of this work is to clearly link the damping effect with the presence of the martensitic structure and to confirm variant interface influence. Then, in order to explore a wider temperature range in the martensitic domain, a CuAlNi alloy where A_s determined by DSC has been found to be higher than 700 K, has been chosen.

Concerning the CuAlNi, it is well known that thermal treatments can modified the martensitic structure [3] and the mechanical properties as well. Two CuAlNi samples were then studied. After a 1073K treatment, the first sample was furnace cooled when the second one has been water quenched. X-ray measurements have been performed to associate the damping evolution with the structural modifications.

2. EXPERIMENTAL PROCEDURE

Two industrial shape memory alloys were studied, Ni Ti (49.6 at.% Ni) and CuAlNi (12% wt. Al and 3% wt. Ni). The samples were cut in flat bar of typical dimensions: $64 \times 6 \times 1 \text{ mm}^3$. The NiTi and CuAlNi samples were initially annealed for ten hours at 1073K then furnace cooled. The characteristic transformation temperatures measured by DSC are $M_s = 350\text{K}$, $M_f = 325\text{K}$, $A_s = 370\text{K}$ and $A_f = 385\text{K}$ for the NiTi sample and $A_s > 773\text{K}$ for the CuAlNi. A second CuAlNi sample was annealed at 1073K for ten hours then water quenched at 293K: in that case $A_s = 714\text{K}$ and $A_f = 763\text{K}$.

Internal friction measurements were carried out with an inverted torsional pendulum subjected to subresonant forced vibrations with a 5×10^{-6} torr vacuum. The apparatus allows isothermal damping

measurements over a large frequency range (from 4×10^{-4} Hz to 40 Hz) with ten discrete measurements by frequency decade. Q^{-1} is equal to $\tan\phi$ where ϕ is the phase lag between the applied stress and the resulting strain.

X-ray diffraction experiments were performed using θ - 2θ Siemens diffractometer fitted out with a copper anode.

3. RESULTS

3.1 NiTi alloy

Figure 1 shows the internal friction evolution versus frequency measured on isothermal conditions by increasing the measurement temperature from 293K to 367K in the martensitic state and from 383K to 438K in-austenite. As it has been exposed elsewhere [4], the structural stabilization of the martensite when it is heated or cooled could be very long. It is the reason why all the spectra where realized after a 27h stabilization at each temperature. As expected, the damping is much higher in the martensitic phase. Considering the dependence on frequency, it could be observed an increase of the damping level at low frequency for every curves. Nevertheless, in the martensitic domain only, this effect depends highly on temperature. For the 367K spectrum, the increase begins before 10^{-1} Hz and reaches an amplitude higher than 40×10^{-4} while at 293K it only begins at 10^{-2} Hz for a total amplitude of a few 10^{-4} .

The low frequency effect on damping is thermally activated and could be due to motions located at the interfaces between martensite variants [5]. In fact, the motion could be directly ascribe to the interfaces themselves or to the displacement of dislocations located at these interfaces [6]. In order to check and confirm that the effect is directly linked to the martensitic structure (or just a NiTi intrinsic phenomenon), the study has been extended to a martensitic copper-based alloy.

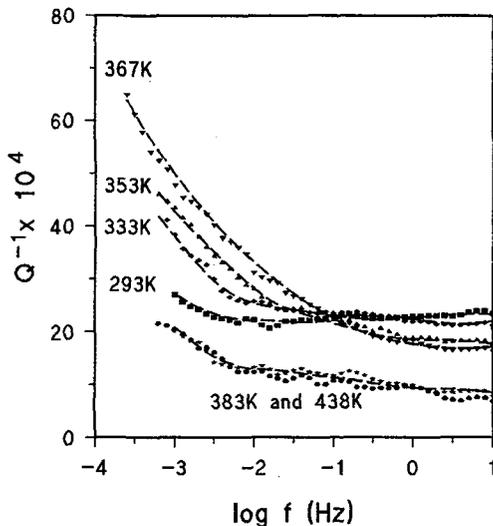


Figure 1. Internal friction versus frequency measured in isothermal conditions on the NiTi sample at various temperatures both in the martensitic state ($T=293\text{K}$, 333K , 353K and 367K) and in the austenitic phase ($T=383\text{K}$ and 438K).

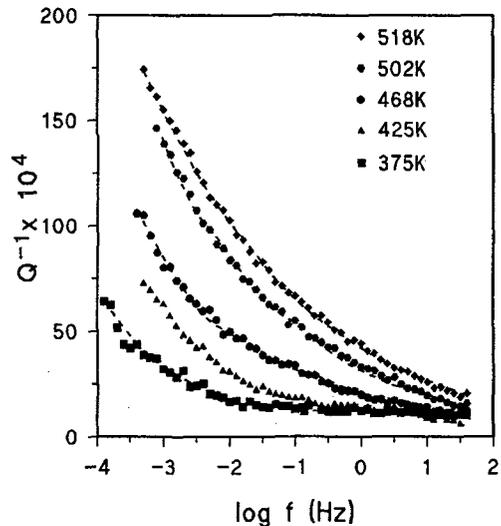


Figure 2. Internal friction versus frequency measured in isothermal conditions on furnace cooled CuAlNi sample at various temperatures below A_s .

3.2 CuAlNi alloy

The present alloy has been chosen because of its low aluminum content (12 % wt.) that implies a quite high value of the transformation temperatures [7]. As measured in the present samples is upper than 773K, that enables to study the martensite damping in a much larger domain of temperature.

The copper based alloy martensite being sensitive to thermomechanical treatments, experiments have been focused first on a stabilized martensite (by furnace cooling), secondly on a as quenched structure.

3. 2. 1. Isothermal measurements on the furnace cooled sample

The same experimental procedure than for the NiTi has been followed between 375K and 518K. The results obtained on isothermal conditions are reported on figure 2. For the five measurement temperatures, the low frequency effect is checked i.e., a damping increase at low frequency. As previously, the effect is developed with the temperature increase.

3. 2. 2. Isothermal measurements on the water quenched sample

The transformation temperature A_s has been determined by DSC to be 714K. The direct comparison between the two CuAlNi samples is then possible, by performing isothermal measurements of the damping. Several temperatures have been studied but on figure 3 we have only reported the most characteristic ones, that is to say 375K, 518K and 579K (full symbols). The open symbols correspond to the damping obtained at 375K and 518K, on the furnace cooled sample. As shown by the figure, the value of the damping measured on the water quenched sample is considerably reduced by comparison to the slowly cooled alloy. In fact, the damping level is quite low both at 375K and 518K as it lies around 10×10^{-4} in a large part of the frequency range as a weak increase is only detected below $10^{-2.5}$ Hz. However, the damping measured at 579K exhibits an exponential increase from 10×10^{-4} until 110×10^{-4} . Then the thermally activated low frequency effect is still valid even if it is considerably delayed in the water quenched sample.

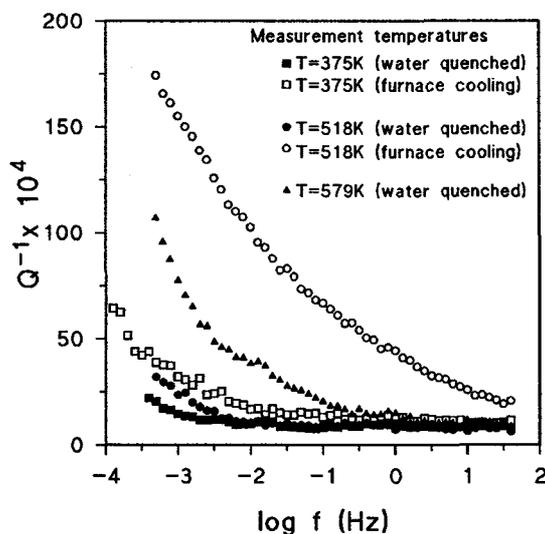


Figure 3. Internal friction versus frequency measured on the CuAlNi water quenched sample at successively 375K, 518K and 579K, full symbols. The open symbols are relative to the damping obtained on the furnace cooled CuAlNi at 375K and 518 K.

The second step of the CuAlNi sample study concerns the ageing effect. The damping has been measured a first time, in the quenched state, at various temperatures then at these same temperatures but after thermal treatments. Figure 4 shows the damping spectra obtained at 314 K, 375K and 482K on the water quenched sample by increasing steeply the temperature (full symbols) and after annealings at respectively 375K, 482K and 579K (open symbol). As shown on the figure 4a, the damping determined at 314 K does not depend on frequency whatever the thermal treatment, however it is reduced from a few 10^{-4} after annealing. Concerning the 375 K and 482 K spectra (4b and 4c), one could observed that before annealing the damping is increased at low frequency unlike the curves obtained after heating which lay below 10×10^{-4} in both cases. In a general way, the damping is reduced by annealing. Subsequent measurements had been performed at 375 K and 314K after the 579K annealing showing that the damping does not evolved anymore.

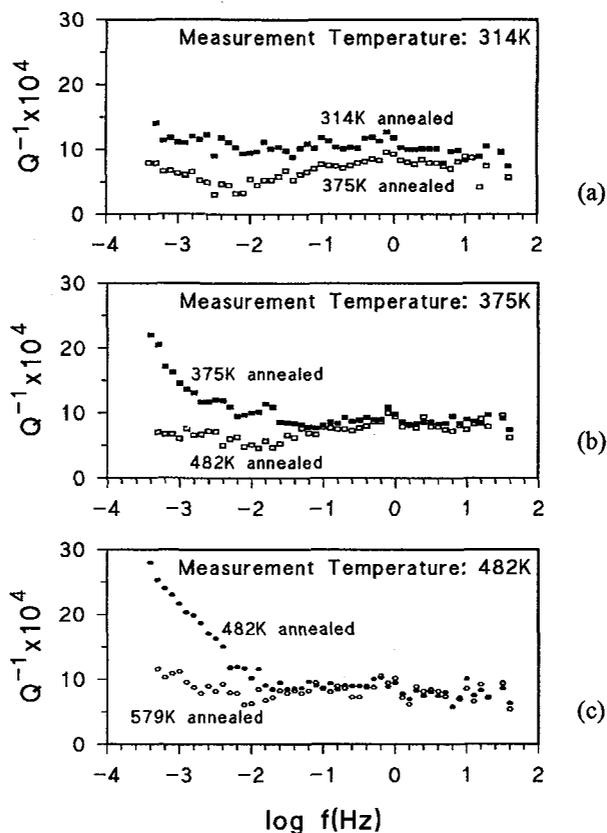


Figure 4. Internal damping spectra obtained at 314K, 375K and 482K on the water quenched sample in isothermal conditions by increasing the temperature, full symbols and after annealing, open symbols, at 375K (a), 482K (b) and 579K (c).

Complementary X-ray experiments have been performed as to determine the structural evolution of the water quenched sample when submitted to thermal treatments. Spectra has been recorded at room temperature after water quenching then after 10 h anneals at successively 375K, 482K and 579K. The x-ray diffractograms are reported on the figure 5. The initial spectrum is indexed in the orthorhombic system of the martensite (β'_1). Two diffraction peaks located at 47.5° and 40.8° has not been clearly identified but does not belong to the β'_1 system. They could indicate the presence of another phase. The spectra obtained after the 375K and 482K annealings are very closed. The general pattern of the initial state is still valid but the 47.5° and 40.8° peaks are vanishing. This trend is confirmed by the last thermal treatment. In addition,

after the 579K annealing, a peak located at 44.2° clearly rises up and another one appears at 46.2° . These two peaks could correspond respectively to the (330) and (331) diffraction of the γ_2 phase.

It seems that some precipitates generated by the quenching are eliminated by further annealings that could explain the presence and vanishing of peaks which do not concern the martensitic structure. Unfortunately, the present phase has not been determined. A second effect of the annealing is the precipitation of the γ_2 phase.

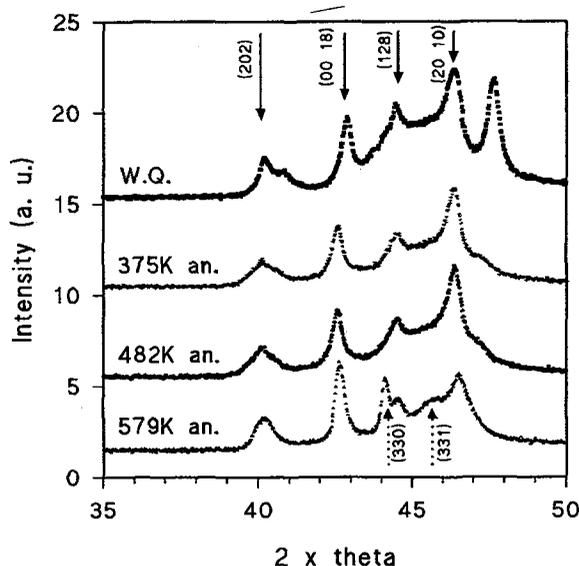


Figure 5. X ray spectra obtained at room temperature on a CuAlNi after water quenched then after successively 375K, 475K and 579K annealings. The two dotted arrows are relative to the 579K annealed sample, their indexation concerns the γ_2 phase.

4. DISCUSSION AND CONCLUSION

The low frequency effect of internal damping has been observed both on NiTi and the furnace cooled CuAlNi. The damping increase is thermally activated in the two cases. The damping effect is then observed in the martensitic state of two different alloys that confirms the direct link with the martensite morphology more particularly to the interface motions between martensitic variants.

Concerning the water quenched CuAlNi sample, the damping is much lower by comparison to the one of the furnace cooled sample. As a consequence, the low frequency effect could not be clearly evidenced below 518K. But, at higher temperature the damping evolves exponentially when frequency is decreased. It has been assumed that the defects introduced by the quenching prevent the variant interfaces from moving unlike the furnace cooled sample where the martensite is stabilized and the internal stresses are relaxed. Particularly, it could be considered that the martensite-martensite interfaces mobility is reduced because of the pinning effect of the vacancies introduced by quenching [8]. In addition, x-ray experiments show the presence of a very instable phase in the water quenched sample which is eliminated for anneals as low as 375K. These precipitates could contribute as well to the frozen of the interface (or dislocation) motions. On the other hand, it could be supposed that the martensite variant size is much lower in the quenched sample and the high density of interfaces could lock their motions.

The second effect observed on the water quenched sample concerns the damping drop after annealing. Once again it could be associated to the formation of precipitates when the material is annealed. Indeed, it has been already established that the thermal ageing could lead to the precipitation of γ_2 phases [9, 10]. That assumption is here confirmed by X-ray diffraction. These structural modifications are obstacles both to the interface and the dislocation motions that involve a diminishing of the damping level.

Of course further information is needed to conclude definitively on the present effects. A complementary TEM in situ analysis is undertaking.

References

- [1] J. Van Humbeeck, J. Stoiber, L. Delaey and R. Gotthardt, *Z. Metallkd*, **86**, (1995), 176-183
- [2] J. S. Zhu, R. Schaller and W. Benoit, *Phys. Stat. Sol. (a)* **108**, (1988), 613-618
- [3] I. Hurtado, *Katholieke Universiteit Leuven Thesis*, 1994.
- [4] F. Deborde, V. Pelosin and A. Rivière, *Scripta Met*, **33**, (1995), 1993-1998
- [5] F. Deborde, V. Pelosin and A. Rivière, *J. de Phys. IV*, **6**, (1996), C8-401-404
- [6] R. Gotthardt and O. Mercier, *J. de Phys.*, **10**, (1981), C5-995-1000
- [7] M. Fremond and S. Miyazaki, *Shape Memory alloys* (SpringerWienNewYork, 1996), pp 129-130
- [8] M. Chandrasekaran, E. Cesari, J. Wolska, I. Hurtado, R. Stalmans and J. Dukiewicz, *J. de Phys.*, **4**, , (1995), C2-143-152
- [9] P. Rodriguez and G. Guenin, *Mat. Sciences and Eng. A*, **129**, (1990), 273-277
- [10] N. Kuwano and C.M. Wayman, *Met. Trans A*, **15**, (1984), 621-626