Journal of Alloys and Compounds, 211/212 (1994) 204–207
JALCOM 134

Effects of thermal and thermomechanical cycling on the phase transformations in NiTi and Ni–Ti–Co shape-memory alloys

L. Jordan[a], M. Masse[b], J.-Y. Collier[b] and G. Bouquet[b]
[a]*Faculté de Chirurgie Dentaire, 5 rue Garancière, 75006 Paris (France)*
[b]*Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, 75005 Paris (France)*

Abstract

Thermal cycling carried out on Ni–Ti–X alloys leads to a stabilization of thermal properties (well-defined transformation temperatures) and mechanical characteristics (elastic modulus).

1. Introduction

A previous study [1] by differential Scanning Calorimetry (DSC) on Ni–Ti shape-memory alloys showed the unstable character of structural states resulting from a single annealing treatment at high temperature (700–800 °C). Indeed, it was observed that thermal cycling, performed in the DSC apparatus through the direct and reverse martensitic transformations, was necessary to reach a stable thermodynamic state. The present work concerns the same stabilization phenomenon studied by internal friction (IF) measurements, which allow correlations to be made between structural evolutions and the corresponding mechanical characteristics, i.e. shear modulus changes. In Ni–Ti shape-memory alloys, the structural transformation sequence is, on cooling: B2-CsCl (denoted “A” in figures) → R-phase → martensitic phase (M), the reverse phenomena being capable of occurring on heating.

2. Experimental

Equiatomic Ni–Ti and ternary $Ni_{47}Ti_{50}Co_3$ alloys have been elaborated in our laboratory by melting pure metals in an electric high-frequency furnace. The ingots (10 mm diameter, 20 mm long) are hot-rolled at 800 °C until a 1 mm thick sheet is obtained, then the material is cold-rolled with intermediate annealing treatments to reach a thickness of 0.5 mm. At this stage $0.5 \times 8 \times 70$ mm^3 samples are cut, then annealed under vacuum (10^{-5} Pa) at 700 °C for 10 h and slowly cooled in the furnace. This last thermal treatment gives rise to our reference structural state.

3. Results

Internal friction evolutions are shown in Fig. 1 for NiTi alloys. In Fig. 1(a), the damping behaviour of the material after the first thermal cycle is characterized by a single Q^{-1} maximum on cooling as well as on heating.

This maximum corresponds to the direct and reverse martensitic transformations. Taking the highest Q^{-1} values as the transformation temperature, we can estimate the hysteresis to be 25 °C. The modulus evolutions (Fig. 1(a)) exhibit a mininum value associated with the Q^{-1} maximum. The lowest modulus values have approximately the same level, though the profile of the modulus curve on cooling is sharper than on heating.

In Fig. 1(b) we show the internal friction spectrum of the same specimen after 21 thermal cycles. Note the presence of a shoulder at the start of the maximum described on cooling. This shoulder is associated with the occurrence of the R-phase, and we note that the minimum modulus temperature corresponds to this R-phase structural transformation temperature [2]. Furthermore, the value of the minimum modulus is lower than that observed during the first thermal cycle. On heating, a single Q^{-1} maximum is observed and the curve profile is unchanged. Between the first and the 21st cycle, the internal friction evolution consists mainly of a lowering of the transformation temperatures, as detailed in Table 1.

Our experiments have shown that after 16 cycles the material can be considered as thermomechanically stabilized, because no additional shift of the transformation temperatures is detected. If we study the internal friction behaviour of a Ni–Ti–Co alloy, we note that the result obtained for the first thermal cycle (Fig. 2(a)) is some-

0925-8388/94/$07.00
SSDI 0925-8388(94)00134-X

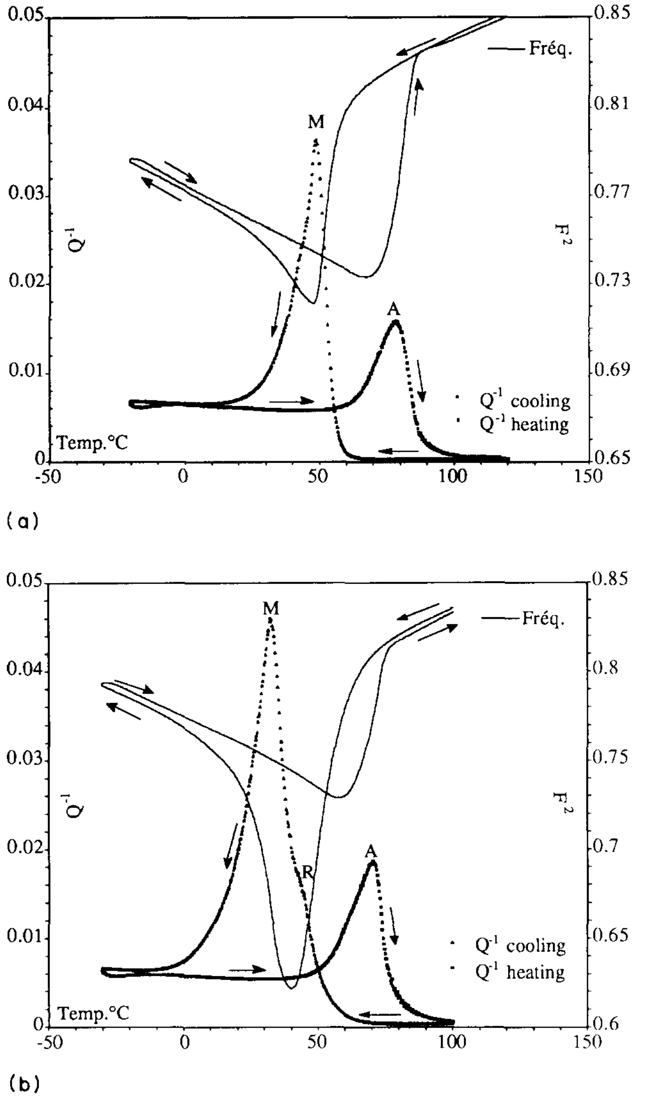

Fig. 1. Internal friction and modulus evolutions of NiTi: (a) first thermal cycle; (b) 21st thermal cycle.

TABLE 1. NiTi transformation temperatures as a function of thermal cycles

Cycle	T_{rs} (°C)	M_s (°C)	A_s (°C)
1	–	56	65
2	–	53	62
3	–	52	61
4	–	50	58
21	54	44	53

what similar to that of the thermomechanically stabilized NiTi alloy (Fig. 1(b)), in that sense that:

1. the R-phase is detected on cooling by a shoulder at the foot of the Q^{-1} maximum;
2. a clear difference appears between the modulus minimum values measured on cooling and on heating;

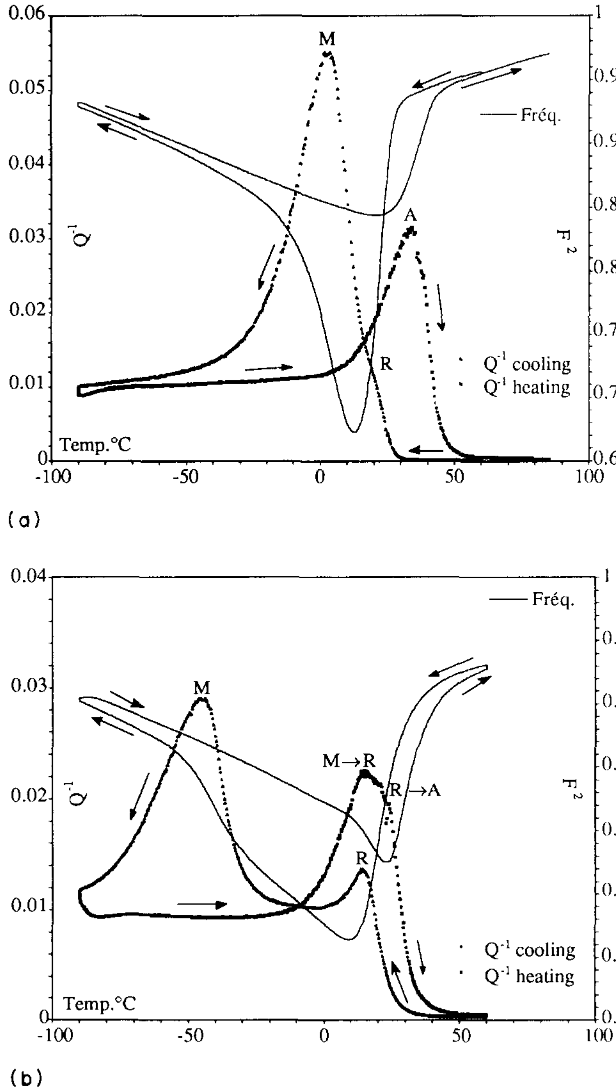

Fig. 2. Internal friction and modulus evolutions of Ni–Ti–Co: (a) 1st thermal cycle; (b) 21st thermal cycle.

3. a single maximum is observed on heating.

If we consider now the 21st cycle (Fig. 2(b)) on cooling, the main result is the occurrence of two clearly separated Q^{-1} maxima. The first one, at 15 °C, is associated with the R-phase (verified by X-ray diffraction experiments performed as a function of temperature) while the second one, at approximately −45 °C, corresponds to the martensitic transformation. We must emphasize that the R-phase maximum is placed at the same temperature when the shoulder was observed during the first cycle.

This means that the R-phase is insensitive to thermal cycling; however, the martensitic transformation Q^{-1} maximum is considerably shifted (Table 2) as a function of the cycle order: 0 °C for the first thermal cycle, −45 °C after 21 cycles.

Another remark concerns the Q^{-1} maximum observed on heating: we note that the profile of this maximum

TABLE 2. Transformation temperatures evolution of Ni–Ti–Co as a function of thermal cycles

Cycle	T_{rs} (°C)	M_s (°C)	A_s (°C)
1	–	−27	12
2	28.5	4	11
3	28.5	0	9
4	28.5	−4	8
21	26	−23	−4

is uneven at its top, as if a second maximum interfered with the one observed, for instance, during the first cycle. This assumption is supported by the modulus evolutions. Indeed, a comparison of the various modulus changes in NiTi and Ni–Ti–Co shows that when the R-phase transition takes place, a sharp modulus variation is detected, proving a rapid structural modification (narrow temperature range), while the modulus variation associated with the martensitic transformation spreads over a wide temperature range. The shape of the modulus curve obtained on heating in Fig. 2(b) shows a sharper variation than the corresponding one in Fig. 2(a). It can therefore be concluded that there is a separate contribution of the R transition to the internal friction level, which leads to a splitting of the initially single maximum.

4. Discussion

Important results have been obtained from this study. The first one is that in order to reach equilibrium it is necessary to submit the material to thermal cycling in the temperature range where the direct and reverse transformations take place. However, after such a thermal treatment is performed, it is revealed that the martensitic transformation is in fact the superimposition of two structural transformations which are, on cooling:

$$B_2(CsCl) \longrightarrow \text{R-phase then R-phase} \longrightarrow B19' \ (M)$$

The second result, and the most striking feature, is that the main modulus effect is concerned with the $B_2 \rightarrow R$ transformation, the R-phase being characterized by the lowest modulus value. This last remark is important because of the 80 °C separation between the R and martensitic phases. As some mechanical work is surely accessible at the R transformation temperature, so the memory effect can act as soon as this temperature is reached. Consequently, for practical applications this alloy has to be considered as having a transformation temperature at 20 °C and not at 60 °C if the martensitic transformation is only taken into account.

On heating, the reverse transformations sequence would occur, i.e. martensitic phase $\rightarrow R \rightarrow B_2$, but the separation between these structural changes depends on the chemical content of the alloys and on the thermal treatments adopted for the specimens.

For example, in Fig. 3, we have reported the internal friction spectrum of a Ni–Ti–Co alloy submitted to a reference annealing performed at 600 °C. We note, in this figure, that the corresponding internal friction spectrum exhibits, on heating, two maxima associated with the martensitic phase $\rightarrow$ R and $R \rightarrow B_2$ transformations respectively. This result is difficult to explain because we have to find a reason why, in some cases, it is possible to observe two separate transformations. It is obvious that structural causes must be invoked. Various assumptions can be put forward, such as an incomplete elimination of structure defects (mainly dislocations), some anomalies in ordering of the B_2 phase, the occurrence of a precipitation phenomenon, residual stresses around precipitated particles, or some combinations of all these.

The assumption of an ordering effect is suggested by the comparison of the equiatomic NiTi and ternary Ni–Ti–Co alloys' behaviour. In this last material, Co atoms are substituted for Ni, implying some disturbance in the ordering degree, which could eventually influence the transformation mechanism. As for the effect of dislocations, these defects would act on the mobility of interfaces between the martensitic and R (or B_2) phases.

Thermal cycling is performed at such low temperatures that an elimination of dislocations is inconceivable. However, it is possible that the network of dislocations undergoes some rearrangement under the combined effect of temperature and internal stresses resulting from interactions between moving interfaces or precipitated particles. Whatever the implied phenomenon is, it leads to a decrease either of the nucleation energy or of the driving force for the martensitic phase

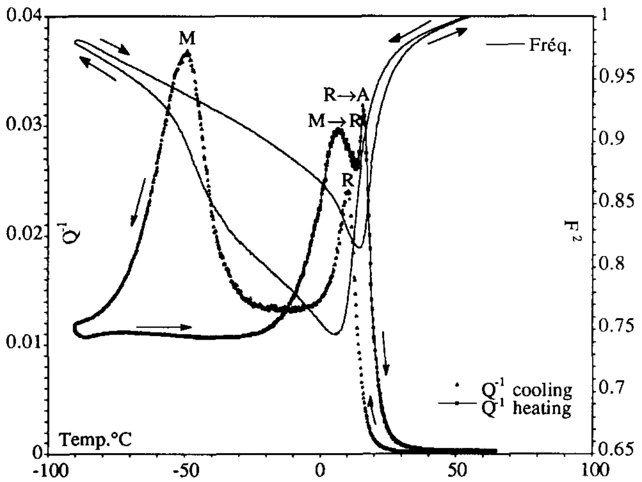

Fig. 3. Internal friction and modulus evolutions of Ni–Ti–Co after annealing at 600 °C; 21st cycle.

growth. Consequently R → M and reverse M → R transformations take place at lower parameters as thermal cycling proceeds until an optimal transformation path is reached [3]. This shift allows the B2 → R and R → B2 internal friction maxima to be observable because this transformation appears at fixed temperatures, and thus there is no more interference with the Q^{-1} maximum associated with the martensitic phase. That the R transformation appears at fixed temperatures can be explained by the fact that this transformation results from crystallographical distortions, implying short-range atom displacements that are not impeded by network defects. In that case the R-phase temperature is insensitive to thermal cycling.

Probably the same transformation sequence occurs in NiTi alloys, but the two transformation temperatures are less separated. This could be due to a thermal cycling apparently less effective in shifting the martensitic transformation than in the case of Ni–Ti–Co alloys, because of an initial structural state that is more stable.

Another point we have to discuss is the modulus variation. This variation seems to be reduced to a curve exhibiting a single minimum, as illustrated in Fig. 4. As in the case of internal friction, these curves correspond to the superimposition of two moduli related to the R and martensitic phase respectively.

The various shapes of experimental curves obtained on cooling in Fig. 4 can be reproduced by displacing a spread modulus curve, related to the martensitic transformation, with regard to a fixed sharp modulus curve associated with the R-phase [4].

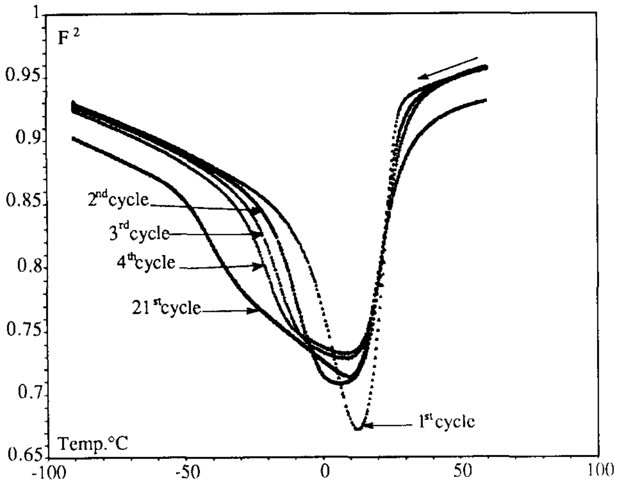

Fig. 4. Modulus evolution of Ni–Ti–Co as a function of thermal cycles, on cooling.

5. Conclusions

This work definitively allows the elimination of imprecisions concerning the occurrence of the R-phase in Ni–Ti(–X) alloys. We ascertain that whatever the alloy is, binary or ternary, we have the transformation sequence: B2 (high temperature) ↔ R-phase ↔ martensitic phase M (low temperature). If this sequence is not observed it is only because the R and M transformations proceed in too narrow a temperature interval, as it generally occurs on heating.

This study showed two important features concerning practical applications of Ni–Ti(–X) shape memory alloys.

The first one is the necessity of using the materials after structural stabilization, i.e. after the materials have been submitted to sufficient thermal cycles.

The second one is that care must be taken in characterizing the material with respect to its transformation temperature (M or R, for example). Indeed, when the R-phase is clearly separate from the martensitic transformation, according to modulus effects related to the R-phase, shape memory phenomena can acts as soon as this transformation takes place. Consequently, we can refer to this transformation temperature, though the mechanical efficiency of this phase has to be verified.

One point remains unexplained: the reason for the shifting of the martensitic transformation temperature towards low temperatures under the effect of thermal cycling. Dislocations and ordering effects have been suggested, precipitated particles being another possibility. The precipitation phenomena in rapidly solidified Ni–Ti–Co alloys is currently being studied.

References

1 L. Jordan, M. Masse, J.-Y. Collier and G. Bouquet, *J. Phys. (Paris) C3* (4) (1994) 157.
2 O. Mercier, B. Tirbonod and E. Torok, *J. Phys. (Paris) C5, 42* (1981) 1037.
3 H.C. Ling and R. Kaplow, *Met. Trans. A, 12* (1981) 2101.
4 L. Shenyen, Z. Xiaoping and Z. Rusong, *J. Phys. (Paris) C9, 44* (1983) 223.