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## Martensitic Transformation of NiTi and NiTi-TiC Composites

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**Abstract.** Calorimetry and internal friction were used to study the martensitic phase transformation of shape-memory metal matrix composites consisting of nearly equiatomic NiTi with up to 20 vol.% TiC particles. The start and final temperatures for the austenite-martensite transformation ( $M_s$ ,  $M_f$ ) and martensite-austenite transformation ( $A_s$ ,  $A_f$ ) are lower when measured by internal friction than when measured by calorimetry. In composites, TiC particles lower  $M_f$  and  $A_s$  but do not affect  $M_s$  and  $A_f$ . It is concluded that dissipative work due to twinning takes place to accommodate internal stresses.

### 1. INTRODUCTION

Near-stoichiometric NiTi alloys exhibit a martensitic phase transformation between the high temperature B2 phase with cubic structure (austenite), and the low temperature monoclinic B19' phase (martensite) [1]. This transformation is responsible for the shape memory effect and pseudo-elastic effect in deformed NiTi alloys. The martensitic transformation in NiTi is complicated by the appearance, after thermomechanical treatment, of an intermediate rhombohedral phase (R phase). The sequence of the transformations is then B2->R->B19' during cooling. During heating, either the reverse sequence B19'->R->B2 [2,3] or a direct transformation B19'->B2 is obtained, depending on the thermal treatment [4].

Since martensitic transformation in NiTi shape memory alloys is thermoelastic, stress has a major influence on the transformation temperature and kinetics: the amount of austenite depends on the balance between the chemical driving force and the elastic strain energy [5,6,7]. While the effect of externally applied stresses on the transformation has been investigated [2,8], the effect of internal stresses is not well understood. Sources of internal stress in NiTi are multiple: mismatch between grains, dislocations, second phases and precipitates. Furthermore, growing martensite plates induce internal stresses due to the geometric misfit among different variants.

Because TiC is insoluble in, and unreactive with NiTi, NiTi-TiC composites allow the study of internal stresses due to a mismatching second phase (affecting the strain energy) independently from the chemical and microstructural effects found in nickel-rich NiTi containing precipitates (affecting the chemical driving force). Calorimetry experiments reported in a previous paper on NiTi-TiC composites [9] showed that the TiC particles lower the  $M_f$  and  $A_s$  temperatures of the matrix by producing a back-stress as the transformation proceeds. In the present study, we compare the transformation kinetics of NiTi-TiC composites as observed by internal friction and differential scanning calorimetry.

### 2. MATERIALS AND EXPERIMENTAL PROCEDURES

Prealloyed NiTi powders (99.9 % pure, 70  $\mu\text{m}$  average size, from Special Metals Corp., NY) were mixed with 0 vol.%, 10 vol.%, and 20 vol.% TiC particles (99.5 % pure, between 44  $\mu\text{m}$  and 100  $\mu\text{m}$  in size, from Cerac, Inc., WI). These powder mixtures were vacuum hot-pressed at 1150  $^{\circ}\text{C}$  for 210 minutes under a pressure of 25 MPa, as described in more details in a previous publication [9]. Chemical analysis of the samples by X-ray fluorescence shows that the matrix composition is homogeneous and titanium-rich ( $51.39 \pm 0.34$  at.% Ti). Samples were cut from the disks and annealed at 930  $^{\circ}\text{C}$  for 1 h. under argon for calorimetry experiments, and under vacuum for damping experiments.

Calorimetry experiments, conducted with a Perkin Elmer DSC-7 under nitrogen cover gas, measured the heat absorbed or released by the sample as a function of temperature. Internal friction experiments, performed in a torsion pendulum under vacuum, yielded damping capacity for the free decay of oscillations as a function of temperature. Furthermore, electrical resistivity of the samples was measured concurrently with the damping experiments. Thermal cycling was performed from 280 K (below  $M_f$ ) to 410 K (above  $A_f$ ) at a rate of 3 K/min. for up to 50 cycles (damping measurements) and 100 cycles (calorimetry measurements).

### 3. RESULTS AND DISCUSSION

During the phase transformation, the calorimetry and damping spectra exhibit peaks from which the start- and finish temperatures of the austenite-martensite transformation ( $M_s$ ,  $M_f$ ) and martensite-austenite transformation ( $A_s$ ,  $A_f$ ) can be determined.

The damping spectra of the three samples are shown in Fig. 1. The free oscillation frequency  $F$ , also plotted in Fig. 1, exhibits the characteristic dip corresponding to the phase transformation.

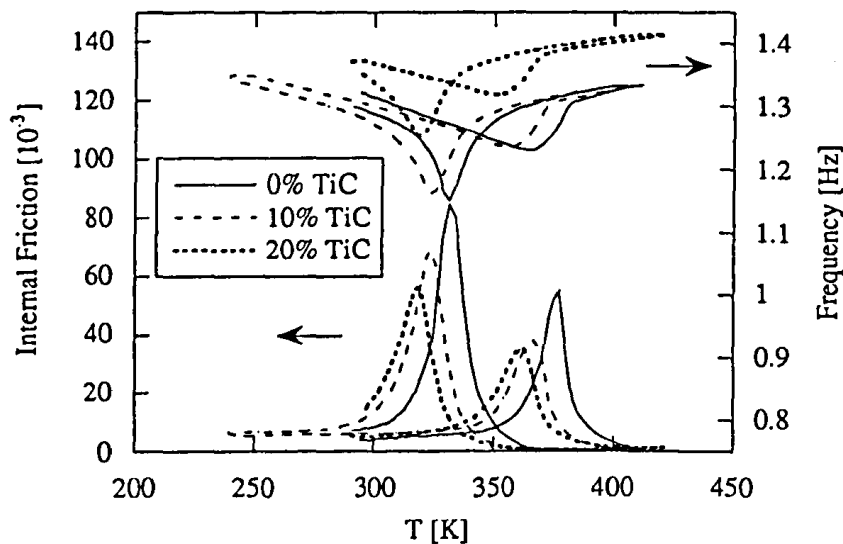


Fig. 1: Internal Friction and frequency  $F$  as a function of temperature for the 6<sup>th</sup> full temperature cycle.

Resistivity curves aligned on the same baseline in the austenite are shown in Fig. 2 for NiTi and NiTi-10%TiC for three different thermal cycles. In an earlier study [9], the evolution of calorimetry peak shape was interpreted as the appearance of the R-phase upon cooling after thermal cycling. In the resistivity curves of the composite a peak appears upon cooling after thermal cycling (indicated by an arrow in Fig. 2) which is characteristic of the two-step transformation  $B_2 \rightarrow R \rightarrow B19'$  [10]. Unreinforced NiTi exhibits a more complicated behavior: upon cooling, a three-step transition is observed both in the as-received samples and after long cycling, while a curve typical of the  $B_2 \rightarrow R \rightarrow B19'$  transition is observed between the 20<sup>th</sup> and the 40<sup>th</sup> cycles. The curves measured upon the 30<sup>th</sup> and the 50<sup>th</sup> cycles look similar on cooling down to 310 K but at lower temperature a new increase of resistivity is observed. A transition from R to two distinct populations of martensite characterized by their respective transformation temperatures has been found earlier in NiTi by the present authors [9, 11] and by Ref. [12]. Therefore, the transitions observed by resistivity in the unreinforced sample (Fig. 2) confirm our calorimetry observations in equivalent specimens [9].

In view of the above remarks, the discussion of the damping and calorimetry results which follows is limited to the first cycle (Fig. 3). The calorimetry spectra (discussed separately in more detail in Ref. [9]) are plotted together with internal friction spectra in Fig. 3 after normalization and background subtraction. Upon cooling, all internal friction spectra exhibit lower peak temperatures than calorimetry spectra. Upon heating, the peaks are similar for the composites with both techniques, while unreinforced NiTi exhibits a higher transformation temperature  $A_f$  in the internal friction spectrum. The results were

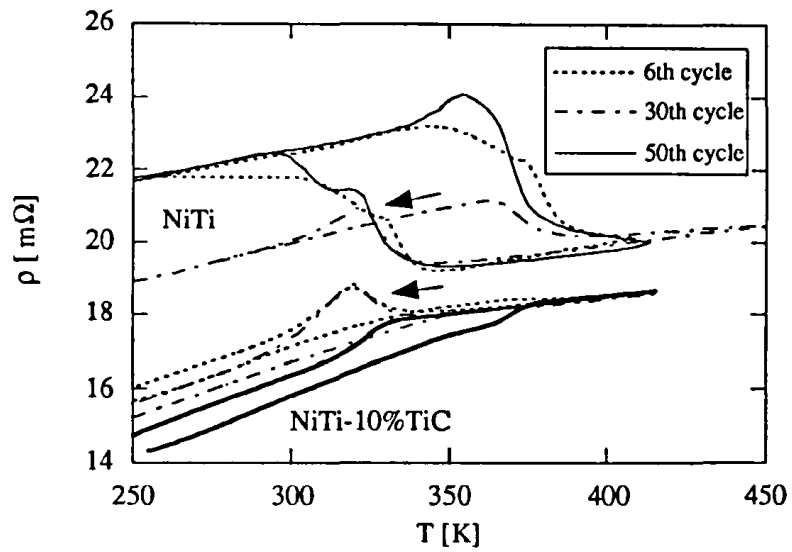


Fig. 2: Resistance of NiTi and NiTi-10%TiC as a function of temperature for 3 cycles. Arrows indicate R->B19' transformation appearing upon thermal cycling.

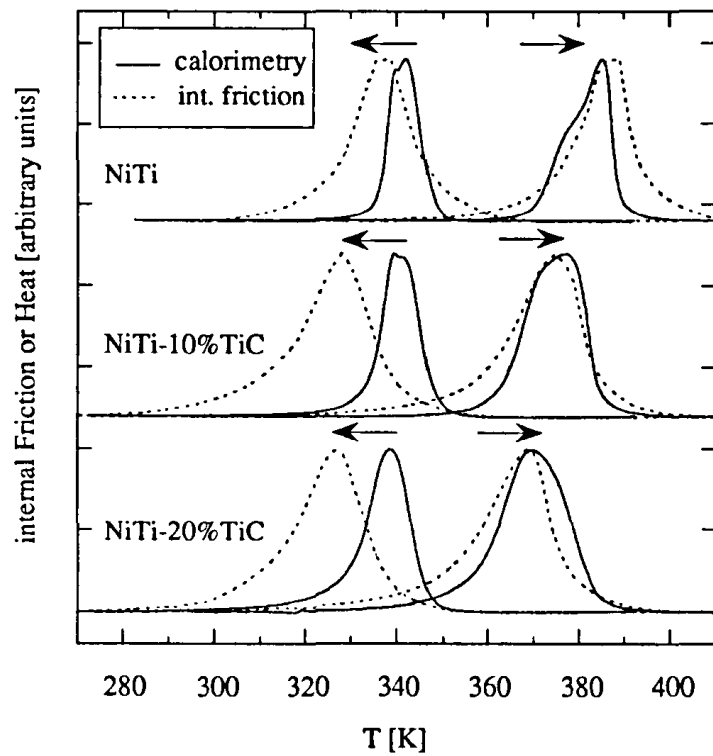


Fig. 3: Damping and calorimetry peaks as a function of temperature for the first temperature cycle. Arrows indicate heating and cooling.

reproducible and systematic temperature measurement errors are unlikely, because the temperature accuracy (estimated from calibration) is  $\pm 2$  K for calorimetry and  $\pm 4$  K for damping.

The composites exhibit different tendencies in the calorimetry and the internal friction spectra. In the calorimetry spectra, the transformation temperature decrease mostly affects  $A_s$  and  $M_f$  while leaving  $A_f$  and  $M_s$  almost unchanged (see Table 1). This effect has been explained by Ref. [9] by a back-stress produced by particles on growing martensite plates which delays the transformation. Salzbrenner and Cohen [13] have shown that the temperature interval ( $M_s$ - $M_f$ ) over which a thermoelastic transformation takes place depends on the stored elastic energy resulting from competing martensitic variants. In a single crystal, the stored elastic energy is higher if multiple martensite variants are growing than if a single variant is growing. In the former case, elastic energy is stored during the transformation and a higher driving force is required to induce the transformation, resulting in a lower final transformation temperature  $M_f$ . Moreover, the elastic stored energy promotes the reverse transformation so that  $A_s$  is lowered too. As a result, a lowering of  $A_s$  and  $M_f$  is expected indeed. The fact that  $M_s$  and  $A_f$  remain constant signifies that the nucleation of martensite is unaffected by the particles. In effect, the thermal residual stresses in the composites in the austenitic phase were found to be negligible by ref. [15], so that internal stress is produced by particles only during the propagation of the martensite.

	NiTi i.f.	NiTi calorimetry	NiTi-10%TiC i.f.	NiTi-10%TiC calorimetry	NiTi-20%TiC i.f.	NiTi-20%TiC calorimetry
$M_f$	324.85	335.82	310.22	333.73	309.70	329.03
$M_s$	347.83	347.83	341.04	347.83	339.48	346.27
$A_s$	369.78	368.73	358.81	362.46	351.49	355.67
$A_f$	393.81	388.58	385.97	384.40	377.61	383.88

Table 1. Transformation temperatures measured by calorimetry and internal friction defined as the intersection with the baseline of the tangent at the point of maximum slope of the peak flank.

In the damping spectra, a decrease of all the transformation temperatures as well as a decrease of peak intensities is noticed when the TiC volume fraction increases. The peak maximum does not provide a valid comparative estimation of the effects as the transformation is extended over different temperature ranges. A parameter quantifying the total amount of damping during the transformation is the "normalized internal friction"  $K$  defined by Delorme and Gobin [15] as:

$$K = \frac{1}{T} \int_{M_s}^{M_f} Q_{tr}^{-1} f dT \quad (1)$$

where  $f$  is the frequency,  $\dot{T}$  is the temperature scanning rate and  $Q_{tr}^{-1}$  is the internal friction due to transformation (determined after background subtraction). The values of  $K$ , shown in Table 2 indicate that, with the exception of NiTi-10%TiC on heating, the damping capacity in the composites follows a rule of mixture within the experimental errors ( $\pm 4\%$ ). This indicates that the particle-matrix interface does not provide significant damping and that the particles have little effect on the global damping capacity of the matrix. However, the decrease of  $K$  for the composites is systematically smaller upon cooling than upon heating: this result can be interpreted by a reduced mobility of twins in the martensite due to particles, as confirmed in the following discussion.

	Peak max. heating	decrease (%)	Peak max. cooling	decrease (%)	K heating	decrease (%)	K cooling	decrease (%)
NiTi	84.6	--	54.3	--	37.6	--	21.9	--
NiTi-10%TiC	68.6	19	38.3	29	30.7	18	19.7	10
NiTi-20%TiC	55.0	35	35.1	35	29.4	22	18.5	16

Table 2: Comparison of damping peak heights and normalized internal friction  $K$  in all samples based on measurements for the 6<sup>th</sup> cycle.

Energy dissipation by twin movement can provide an explanation for the difference between internal friction and calorimetry spectra upon cooling. Stoiber et al. [16] have analyzed damping spectra in CuAlZn alloys and showed that a significant part of dissipative work during damping takes place in the martensite by motion of partial dislocation bordering stacking faults. This phenomenon is likely to take place in NiTi as well, but energy is probably dissipated by twin movement. If the energy dissipation takes place with little heat production, possibly in the form of elastic vibrations as envisaged by Ref. [17], damping will be significant even when the martensite is already formed. Furthermore, the width of the peaks in Fig. 3 indicates that damping covers a temperature range wider than that corresponding to the phase transformation. In the composites, the difference between damping and calorimetry peaks is larger. This effect may be a further confirmation that internal stresses resulting from the mismatching particles lower the mobility of twins. In NiTi composites, non-transforming particles which are at equilibrium with the austenite, are obstacle for the propagation of martensite plates. Elastic energy stored during the transformation is thus larger in the composites but it is progressively relaxed as the transformation proceeds. If the twin mobility is lower, the relaxation takes place over a wider temperature range mostly in the already formed martensite, resulting in a lower  $M_f$  temperature when measured by internal friction. If the end of the martensite-austenite transformation is assumed as  $A_f$  measured by calorimetry, the high level of damping still measured above this temperature is surprising because little damping is expected when most of the austenite is formed. This high damping could be due to phase misfit dislocations in the austenite or to twin movement in residual martensite which are very unstable at high temperature and therefore very mobile. In the composites, the mobility of dislocations or twins is reduced and the effect described above does not appear.

#### 4. CONCLUSIONS

Mechanical damping and calorimetric experiments were performed on unreinforced NiTi and NiTi-TiC metal matrix composites to investigate the influence of internal stress due to inert particles on the martensitic transformation of NiTi. Calorimetry spectra show that particles affect the B2-B19' transformation temperature by lowering  $A_s$  and  $M_f$  and leaving  $A_f$  and  $M_s$  almost unchanged. Comparison with damping measurements shows that a significant amount of energy dissipation takes place below the martensitic transformation range by twinning relaxation of internal stresses. This effect is accentuated by the presence of TiC particles, indicating that the martensite relaxes a major part of the mismatch stresses.

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