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# Influence of heat treatment on internal friction spectrum in NiTiCu shape memory alloy

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## Abstract

Internal friction (IF) and storage modulus evolution during the martensitic transformation were measured using the DMA technique in order to compare the effect of heat treatment on the behavior of IF in Ti<sub>44.6</sub>Ni<sub>5</sub>Cu (%at.) shape memory alloy. Two kinds of experiment were performed: IF measurements as a function of temperature and IF measurements at a fixed temperature to obtain the static term of the intrinsic internal friction. The results are compared with those obtained from DSC measurements. IF results show a clear dependence on the temperature of the heat treatment with distinctive regions that could be attributed to microstructural changes.

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*Keywords:* Internal Friction; Shape Memory Alloys; NiTiCu; Heat Treatment

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## 1. Introduction

The shape memory properties of SMAs are a strong function of composition, thermal treatments, microstructure, functional temperature and stress state [1,2]. These effects are often intertwined, a factor that disguises their true relationships. Consequently, modifications to the microstructure through thermomechanical treatments such as cold-working and annealing processes have been shown to modify shape memory properties in NiTi-based materials by severely altering their transformation characteristics.

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Because the damping capacity is determined by the mobility of the interfaces, any changes in the microstructure caused by thermomechanical treatments greatly affect this capacity. Therefore, microstructural changes produced by cold work (increased dislocations density) and annealing (precipitation process) can lower interface mobility [3] and affect internal friction values. Thus the Dynamic Mechanical Analysis (DMA) technique can be used as an efficient tool for characterizing microstructural changes and for investigating martensitic transformation of binary NiTi and ternary NiTiCu alloys [4].

This study used a DMA technique to measure internal friction (IF) and storage modulus evolution during the forward and reverse martensitic transformation in order to systematically compare the effect of the heat treatment (HT) on the behavior of the Ti44.6Ni5Cu (%at.) shape memory alloy. These results are expected to provide insight into the relationship between damping behavior and microstructural changes caused by thermomechanical treatments.

## 2. Materials and Methods

Ti44.6Ni5Cu (%at.) wires with a diameter of 1mm and a length of 250 mm were used in this study. After 30% cold-work, different HTs were carried out for 60 minutes (400, 450, 500, 550, 600 and 650°C) in an Ar protective atmosphere followed by water quenching to stop the precipitation process.

Martensitic transformation temperatures and heat flow exchanges were determined by means of DSC tests using a Mettler DSC-821e calorimeter. Samples weighing about 25 mg were placed in aluminum pans in a nitrogen atmosphere and non-isothermal tests were conducted from 0°C to 100°C at a heating and cooling rate of 10°C/min.

The  $\tan \delta$  and storage modulus measurements were carried out using a dynamic mechanical analyzer, (TA Instruments DMA Q800) equipped with a liquid nitrogen cooling system. Two kinds of experiment were performed:

- **Experiment 1: Internal Friction (IF) as a function of temperature**, with a flexural loading 3-point bending configuration and at a heating/cooling rate of 3 °C/min, from 0 to 100°C;  $f = 0.2$  Hz and  $\Delta\epsilon(\text{amplitude}) = 0.02\%$ .
- **Experiment 2: IF at fixed temperature**, with the same configuration and parameters in order to obtain the isothermal damping characteristics of austenite (B2) and martensite (B19'). Samples were cooled from 120°C at 3°C/min and kept isothermally for at least 30 minutes at the set temperatures of 100°C (austenite state) and 0°C (martensitic state).

## 3. Results and Discussion

Figures 1(a-b) show DMA curves on cooling and heating for two heat treated NiTiCu samples (HT400 and HT650) along with the  $\tan \delta$  (or internal friction IF) and storage modulus evolution with temperature. As can be seen in Fig. 1, the phase transformation process is clearly detected and shows a maximum in the internal friction curve and a sharp variation in the storage modulus. Both HT samples present one stage B2-B19' transformation IF peak during cooling, which is characteristic of Ti50Ni50-xCux for  $x < 5\%$  [5], and a reverse transformation IF peak B19'-B2 during heating. The higher internal friction values of B2-B19' are associated with the high mobility of the twin boundaries of the parent/martensite and martensite/martensite interfaces [2]. The storage modulus decreases drastically with temperature on cooling, and shows a deep minimum associated with the martensitic transformation that coincides with the corresponding IF peak. This softening of the storage modulus as the temperature decreases is a precursor phenomenon of the martensitic phase transition. Beyond the transformation process, IF remains almost constant in a rather wide temperature range as the structure is completely transformed (to B2 on heating and to B19' on cooling).

In order to analyze in greater depth the IF evolution in the HT samples, the intrinsic internal friction of martensite (B19') phase ( $IF_1^{B19'}$ ) and austenite phase ( $IF_1^{B2}$ ) were measured under isothermal conditions. As is well known, it has been proposed that the IF associated with a first-order phase transformation decomposes into three terms:  $IF_{Tr}$ ,  $IF_{PT}$  and  $IF_1$  [2]. The first term  $IF_{Tr}$  is a transitory internal friction which appears only at low frequency and non-zero  $dT/dt$ . The second term ( $IF_{PT}$ ) is the internal friction due to phase transformation, and it does not depend on  $dT/dt$ . The third term  $IF_1$  is the intrinsic internal friction of the austenitic or martensitic phases and depends strongly on microstructure properties, such as dislocations, vacancies, precipitates and twin boundaries. The intrinsic internal friction  $IF_1$  of the B19' and B2 phases can be calculated by means of isothermal tests which measure the IF until it

reaches a steady value that remains constant with time. A comparison of the evolution of this intrinsic term  $IF_1$  in all HT samples can give us a more accurate analysis of the effect of the heat treatment because  $IF_1$  is strongly dependent on the microstructure of each phase [2].

Figure 2a shows the  $\tan \delta$  values versus time at 0°C (B19' martensite) for 0-40 minutes. The measured  $\tan \delta$  of the B2 parent phase is not represented as it presents an almost steady behavior during the entire isothermal interval. Also, this value was comparatively very low ( $\tan \delta \approx 9 \cdot 10^{-4}$ ). Fig. 2a shows that, for all HT samples, the measured  $\tan \delta$  values of B19' decrease as time increases reaching the steady value ( $IF_{ISteady}^{B19'}$ ) after 30 minutes approximately. While this behavior is similar for all HT samples (see Fig. 2b), the steady values are quite different for all the HT and present the same tendency as the  $IF_{B2-B19'}$  peak shown in Fig. 3a.

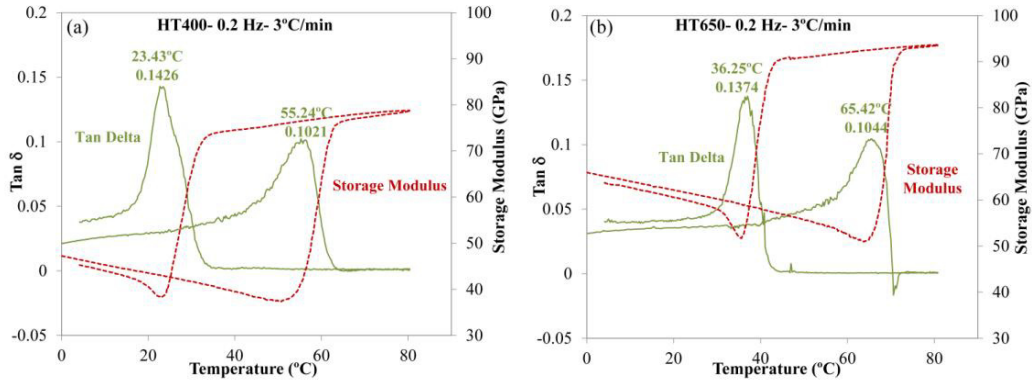


Fig. 1. Internal Friction and storage modulus evolution with temperature (heating and cooling) for (a) HT400 and (b) HT650.

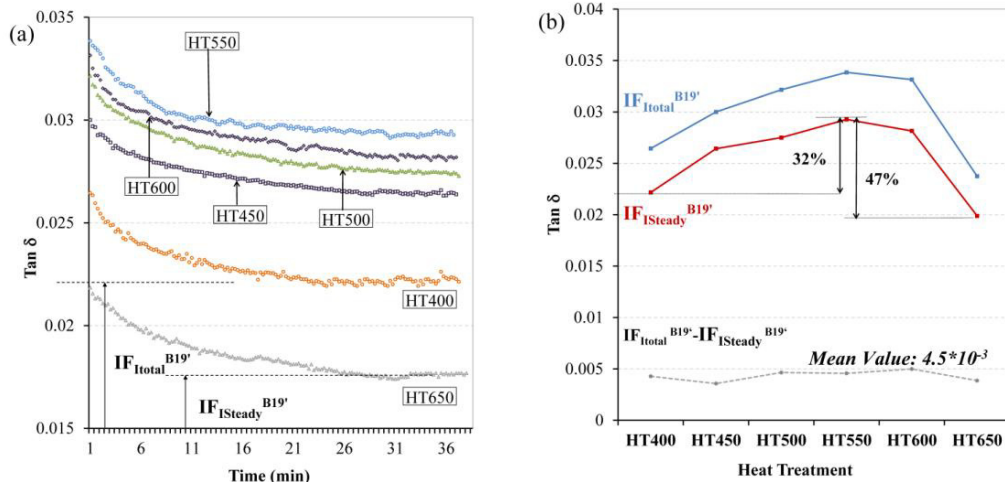


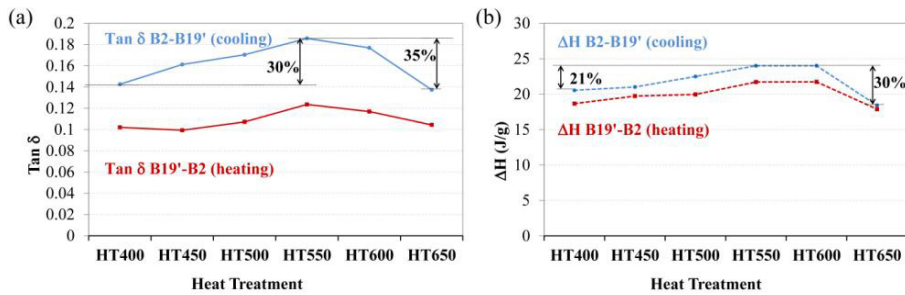
Fig. 2. (a)  $\tan \delta$  evolution at 0°C (B19') as a function of time for all HT. (b)  $\tan \delta$  values of  $IF_1^{B19'}$  for all HT.

The transformation behavior can also be analyzed by calorimetric methods; thus, DSC measurements were performed to study the effect of the heat treatment on the phase transformation behavior of the NiTiCu alloy in order to compare the results with those obtained by DMA. Phase transformation temperatures and their hysteresis for all the heat treated samples are presented in Table 1.

Table 1. Transformation characteristics obtained from DSC results.

Sample	Mf (°C)	Ms (°C)	As (°C)	Af (°C)	Hysteresis (°C)
HT400	25.1	37.5	46.2	60.9	23.5
HT450	28.2	39.4	49	61.9	23.8
HT500	30.3	41.6	53.6	65.9	25.1
HT550	39.2	50.1	61.6	71.5	23.6
HT600	39.5	49.7	61.1	70.8	24
HT650	33	43.6	58.2	68.8	29.5

Fig. 3(a-b) shows  $\tan \delta$  and  $\Delta H$  values for all HT samples. When comparing DSC results with DMA results, it can be seen that  $\tan \delta$  and  $\Delta H$  present the same tendency as the temperature of the HT increases. On both heating and cooling, HT400 and HT650 samples present the lowest values and are significantly lower than HT550. At low temperatures, the low values of  $\Delta H$  and  $\tan \delta$  can be attributed to high dislocations density caused by the cold work, and at high temperatures (beyond the recrystallization temperature), the decrease in the  $\Delta H$  and  $\tan \delta$  values can be attributed to competition between the reduction in dislocations and a precipitation process with a heterogeneous distribution.

Fig. 3. (a)  $\tan \delta$ -peak values for all HT and (b)  $\Delta H$  values for all HT.

#### 4. Conclusions

The results obtained in this study on a NiTiCu alloy show a clear relation between the IF spectra and the HT temperature due to microstructural changes. This relation is also observed in the DSC results. Different behaviors have been detected depending on the HT temperature: from HT400 to HT550  $\tan \delta$  and  $\Delta H$  increase as the HT temperature increases; from HT550 to HT600 they do not seem to change; and from HT600 to HT650  $\tan \delta$  and  $\Delta H$  appear to decrease as the HT temperature increases. All these changes may be due to competition between two factors: the progressive elimination of the dislocations generated by the cold work and a precipitation process. Future work should be aimed at demonstrating this through microstructural analysis using X-ray powder synchrotron diffraction.

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