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Phase transition and mechanical damping properties: A DMTA study of NiTiCu shape memory alloys

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ABSTRACT

Internal friction measurement is a well-known investigation technique of the damping property of shape memory alloys (SMAs). It has already been demonstrated that this practice conducted in temperature scanning at a constant solicitation frequency is also useful in determining the path of the martensitic transformation and also the influence of hydrogen content on the martensitic properties. There is indeed a lack of studies about SMA internal friction as a function of solicitation frequency; systematic and rigorous analysis has not been reported yet. In this work the path of the martensitic transformation of $Ni_{50-x}TiCu_x$ alloys ($x = 3–10$at%) is investigated through Dynamic Mechanical Thermal Analysis (DMTA): internal friction as a function of temperature at a constant flexural frequency and internal friction as a function of flexural frequency at a constant temperature were evaluated. Results show that the two scans are both sensitive to phase transitions and microstructural changes.

1. Introduction

$Ni_{50-x}Ti_{50}Cu_x$ alloys derived from the equiatomic binary NiTi system present different martensitic transformation paths as a function of Cu content: the direct B2–B19′ transformation, typical of the equiatomic NiTi, changes into the B2–B19–B19′ when Cu substitutes Ni in the 7.5–16at% range and into the B2–B19 direct transformation for Cu higher than 16at% [1–9].

When B2 transforms into B19 no lattice invariant shear occurs; the two types of admissible twinning are an effect of self-accommodation with a triangular morphology [2,7]. Fig. 1 reports the optical micrograph of $Ni_{41}Ti_{50}Cu_9$ sample taken at room temperature where the characteristic B19 triangular surface reliefs are clearly visible.

The path of the martensitic transformation as well as the phase transformation temperatures and the alloy structure of NiTi and NiTi-based alloys are commonly studied under stress-free condition by means of pure thermal analysis as differential scanning calorimetry (DSC) and electrical resistance measurements (ER) [5,10–16].

Besides these standard techniques, the path of the martensitic transformation may also be detected through internal friction (IF) measurements. Lo et al. studied the $Ni_{40}Ti_{50}Cu_{10}$ alloy through different methods, and demonstrated that IF measurements are more sensitive in the highlighting of the multi-stage B2–B19–B19′ transformation as respect to DSC and ER scans [13].

IF measurements by DMTA (Dynamic Mechanical Thermal Analysis) technique in different conditions of deformation, applied force and temperature control, are usually employed to study the damping properties of NiTi and NiTi-based shape memory alloys. When an SMA material is under a cyclic applied stress, internal friction or "damping", Q^{-1}, is calculated as the ratio between the energy absorbed during one load cycle, ΔW, and the maximum stored energy during that cycle, W. In complex notation, the internal friction is also linked to the real (storage modulus, E') and to the imaginary (loss modulus, E'') part of the elastic complex modulus [17]. Hence, it can be written:

$$Q^{-1} = \Delta W/(2\pi W) = E''/E' = \tan\, delta$$

In addition to the damping capacity derived from Q^{-1} peak value, however, also the IF trend as a function of temperature at a fixed strain and deformation frequency can be studied [18–24]. During this kind of test, Q^{-1} increases when the material goes into a phase transition; therefore the shape and the position in temperature of IF peaks could be used to obtain information about the subsequent steps in the martensitic transformation. In particular, two types of IF peaks may appear during cooling both for NiTi and NiTiCu alloys: the first typology of peaks is related to the martensitic transformation while the second one is a relaxation type.

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The transition peak typology finds its basis in the thermoelastic martensitic phase transformation due to the mobility of martensite variant interface and twin boundaries and is responsible of the damping properties of the material; frequency does not alter the peak position but affects the peak height which is also influenced by the cooling rate. Moreover, if the material is held isothermal at the transformation peak temperature and the strain and the frequency are kept at a constant value, a reduction in IF peak as a function of time can be observed. This kind of analysis is therefore useful to distinguish phase transitions to relaxation phenomena [25].

The phase transition is also visible in the storage modulus curve; as a matter of fact, the maximum of the IF peak due to the phase transition corresponds to a minimum in the analogous storage modulus curve.

Besides these transient peaks, many authors also observed an extra peak, of the so-called relaxation type, which is situated around 250 K for the $Ni_{50-x}Ti_{50}Cu_x$ alloys (200 K for the NiTi system); its position depends on frequency and its height is not affected by the cooling rate. This peak is stable in isothermal conditions and corresponds to a sharp increase in the storage modulus curve [25–27]. Moreover, hydrogen doping was demonstrated to be essential for observing the relaxation peak [28–31].

Finally, Fan et al. [32] found one smaller peak at low temperatures which they associated to the martensitic transformation of precipitates.

The frequency scanning at a fixed temperature value is one more interesting possibility to investigate the material by DMTA technique: in this case, the study concerns the measure of IF peaks in isothermal condition at different frequencies.

There are many effects associated to a frequency variation in an anaelastic material: thermo-elastic phenomena, movement of valence electrons, grain boundary viscosity, interstitial atoms movement, and dislocation relaxation. IF peak height and frequency position depends on the composition, on the sub structural state and on temperature. Probably due to the amount of features which respond to a frequency variation, a detailed frequency scanning of IF measurements at a constant temperature is scarcely employed in SMAs field and very few examples can be found in published literature [21,22,33].

Therefore, the aim of the present work is an attempt to use the DMTA technique in different kind of experimental conditions for the correlation between some mechanical responses and microstructural properties of SMA. In particular, the attention was focused on a series of $Ni_{50-x}Ti_{50}Cu_x$ alloys ($x = 3–10$at%) alloys and to the study of the correspondent path of the martensitic transformation by means of internal friction measurements as a function both of temperature at a constant applied stress frequency and of solicitation frequency at a constant test temperature. In addition, Scanning Electron Microscopy (SEM) equipped with Energy Dispersed Spectroscopy (EDS) was employed to verify the occurrence of precipitates.

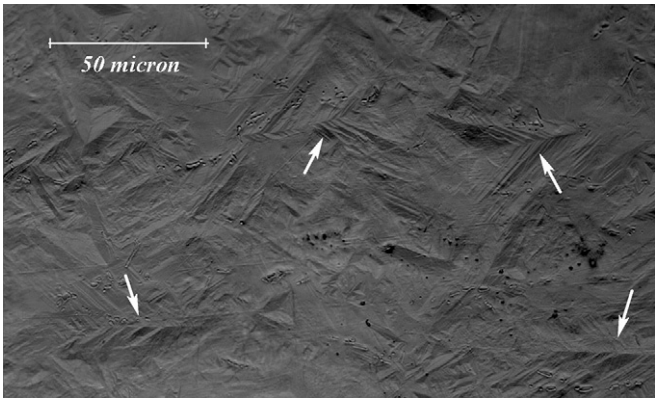

Fig. 1. $Ni_{41}Ti_{50}Cu_9$ optical microscopy image. Optical microscopy taken at room temperature of $Ni_{50-x}Ti_{50}Cu_x$ sample with $x = 9$at%; arrows indicates the triangular surface reliefs typical of the orthorhombic structure.

2. Materials and methods

$Ni_{50-x}TiCu_x$ ($x = 3–10$at%) buttons were prepared by a non-consumable electrode vacuum arc furnace, Leybold LK6/45, under protective atmosphere. Samples were then hot-rolled at 900 °C till a 3 mm of thickness, cut and then cold-rolled to a 1 mm square section wire. Samples were fully annealed at 850 °C in vacuum for 1 h [16], water quenched and electro-polished. Phase transformation temperatures of each $Ni_{50-x}TiCu_x$ sample were measured through pure thermal measurements, as reported in [8]. Table 1 reports the temperatures derived from the DSC cooling curves.

IF and storage modulus measurements were carried out by a dynamic thermal mechanical analyzer, (DMTA, Q800 TA Instruments) equipped with a liquid nitrogen cooling system. IF as a function of temperature measures (T-scan) were conducted with a continuous heating/cooling rate of 2 K/min in the 233 K–373 K (−40 °C–100 °C) temperature range and with a frequency of 1 Hz; samples were subjected to flexural loading in the 3-point bending configuration at a strain amplitude of $2\cdot10^{-4}$ (0.02%). Cooling segments were finally analyzed.

DMTA was also employed to register IF signal as a function of applied stress frequency (f-scan) at constant temperature. Tests were conducted at a fixed strain of $5\cdot10^{-4}$ (0.05%) in the dual cantilever mode to avoid abrupt movements at high frequency solicitations. During these tests, frequency was varied in the 0–50 Hz spectra; values higher than 50 Hz were not considered in order to exclude interaction with the typical resonance frequency of the DMTA device. Moreover, during the f-scan data analysis the frequency spectra was restricted to 8–22 Hz, because important IF variations were observed just in this range. For the f-scan measurements, $Ni_{50-x}TiCu_x$ samples were tested at different temperature values, which were selected from the T-scan measurements in order to test each sample in different crystalline phases.

IF samples were prepared to have length suitable for the DMTA measuring systems: both the 3-point bending and the dual cantilever modes need sample length of about 5 cm.

Optical microscopy images were obtained using Leitz-ARISTOMET light microscope; scanning electron microscopy observations were performed using a SEM LEO 1430 instrument equipped with Energy Dispersed Spectroscopy (EDS) systems for elemental analysis.

Table 1
Martensite phase transformation temperatures: M_s, M_f and M_s', M_f' represents the monoclinic and orthorhombic start and finishing temperatures respectively. ΔH is the transformation latent heat during cooling.

Cu [at%]	Monoclinic		Orthorombic		$\Delta H_{cooling}$ [J/g]
	M_s [°C]	M_f [°C]	M_s' [°C]	M_f' [°C]	
3	58.7	43.5			36.7
4	59.4	43.1			36.3
5	55.4	42.2			38.4
6	50	37.8			33.6
7	53.5	44.8			34.7
8		27.9		46.2	32.5
9	38.6	8.1	55.3	49.2	21.1
10	29.8	−13	57.7	51.6	21.1