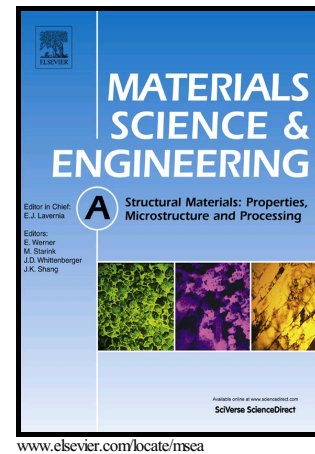


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Identifying the effects of heat treatment temperatures on the Ti50Ni45Cu5 alloy using dynamic mechanical analysis combined with microstructural analysis

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Abstract

The properties of NiTiCu alloys strongly depend on their microstructure, which is greatly influenced by the temperature of the heat treatment (HT) carried out as a final step in their processing. This study investigates the effect of HT temperatures on the Ti50Ni45Cu5 alloy using dynamic mechanical analysis (DMA). To confirm the results obtained by the DMA as regards the effects of HT on the microstructure, they were checked against differential scanning calorimetry (DSC), synchrotron X-ray diffraction (SXRD), hardness measurement and stress-strain tests. By combining all these experimental techniques with the DMA measurements, the effects of the HT were determined and attributed to different factors: density dislocation morphology introduced by prior cold work, recovery and recrystallization processes with texture changes, grain growth, precipitation processes and wt(%) of retained martensite. The results showed that low HT temperatures (400 and 450°C) are not high enough to eliminate the effects of the cold work but do provide suitable mechanical properties and lower transformation temperatures. Medium temperatures (500 to 575°C) lead to higher transformation temperatures and maximum martensitic transformation capacity (ΔH and $\tan \delta$) because of the recovery and recrystallization process, but they also cause a reduction in the mechanical properties (slip stress). High temperatures (600 and 650°C) produce a reduction in transformation capacity and a huge decrease in the mechanical properties (slip stress and ultimate tensile stress).

Keywords

SMA; shape memory alloys; NiTi; NiTiCu; XRD; DMTA

Introduction

Because of their peculiar features and functional properties, shape memory alloys (SMAs) have attracted increasing interest over recent years in connection with a number of applications such as actuators, fittings, biomedical applications, clamping systems, etc. [1,2]. The underlying mechanism behind these special functional properties is the reversible thermoelastic martensitic transformation between austenite (A) and martensite (M) phases in solid state. This diffusionless martensitic transformation can be induced either upon cooling from the austenitic phase or upon application of stress. As a result, SMAs exhibit two distinct mechanical responses depending on the temperature at which they are deformed. The shape memory effect (SME), which occurs when the SMA is deformed in the martensitic condition, is a result of the detwinning of the martensite (i.e. with an energetically-favored martensite variant growing at the expense of the others). The superelasticity or pseudoelastic effect arises due to stress-induced martensite (SIM) formation when the SMA is deformed in the austenitic state. Both these processes can be reversed, either by increasing the temperature or by releasing the load, respectively. Martensitic transformation in SMAs is characterized by four specific temperatures known as transformation temperatures (A_s and A_f for the initial and final austenitic transformation, and, M_s and M_f for the initial and final martensitic transformation) [3].

NiTi-based alloys and especially NiTiCu are considered to be the most important SMAs with good shape memory effect and superelasticity. This is because NiTiCu alloys have better properties than other SMAs for some applications: lower functional fatigue, higher deformation recovery, higher transformation temperature stability and lower hysteresis range [3].

It is also reported that NiTi and NiTiCu SMAs exhibit high mechanical damping or internal friction (IF) in the temperature range of the thermoelastic transformation and are propitious to the energy dissipation systems that are opening up a new application field in engineering [4–6]. Their high IF, especially during transformation and in the martensitic state, is closely related to the mobility of the parent/martensite and martensite/martensite interfaces. The density and distribution of the structural defects inherent to the martensite phase (vacancies, dislocations, grain boundaries and precipitates) control the global IF spectrum of these alloys [6].

The shape memory properties of SMAs are a strong function of composition, heat treatments, cold work, and microstructure [4,7,8]. These effects are often intertwined, a factor that disguises their true relationships. Consequently, modifications to the microstructure (increased vacancy content, presence of precipitates, dislocations, grain growth changes) through thermomechanical treatments (cold working, pre-aging, annealing) have been shown to modify shape memory properties in NiTi-based materials by severely altering their thermoelastic transformation characteristics. Of these thermomechanical treatments, cold working can cause severe alterations to the SMAs' microstructure leading to lattice defects and dislocation substructure. The role of dislocations is extremely important because they can hinder or favor martensitic transformation [3] and therefore change the SMA phase transformation behavior. These imperfections greatly affect martensitic transformation behavior and can be reduced or released by annealing treatment. In NiTi and NiTiCu, for example, all the mentioned effects can be reflected in changes in the transformation paths from the direct B2-B19' transformation to a two-step transformation (B2-R-B19' in NiTi and B2-B19-B19' in NiTiCu) [3,9,10].

Because damping capacity is determined by the mobility of the interfaces, any changes in the microstructure such as the high density of dislocations and precipitates (produced by cold work and annealing) can lower interface mobility and affect IF values [11]. Thus the dynamic mechanical analysis (DMA) technique can be an efficient tool for characterizing microstructural changes and investigating the martensitic transformation [12].

Apart from the pioneering studies by Y. Liu and J. Van Humbeeck cited earlier [6,13], other research groups have used IF evolution to analyze the transformation paths of SMAs [5,14,15]. Yoshida et al. [11] studied low-frequency internal friction in Ti–Ni alloys with different heat treatments and Chang and Wu performed similar studies [16–18] in severely cold-rolled and post-annealed equiatomic NiTi alloys. Other studies but focused on the damping properties of TiNiCu alloys with different compositions can be found in [19–22].

San Juan and colleagues [8] also carried out a detailed study of damping behavior during martensitic transformation in SMAs but focused on the decomposition of the IF spectrum in its three terms — intrinsic, transitory and phase transition — each related to different microscopic phenomena. Using a completely different approach to the subject, Biscarini et al. [23] and Mazzolai et al. [24,25] analyzed the damping of hydrogen-doped NiTi and NiTiCu alloys. IF analysis has also contributed to explaining some of the intrinsic properties of martensitic phase, such as the anelasticity of B19' martensitic phase in Ni-Ti and Ni-Ti-Cu alloys [26].

Finally and more recently, Nespoli et al. [7,27,28] focused on a series of NiTiCu based alloys in order to study the path corresponding to martensitic transformation by means of IF measurements with the aim of clearly distinguishing the presence or absence of intermediate phase B19.

On the basis of all these previous studies, DMA is found to be particularly suited to the investigation of even more transition effects, providing precise information on physical properties, thereby making it possible to investigate a large number of variables in a fairly straightforward way. As already mentioned, many interesting properties of SMAs are related to the mesoscopic arrangement of the martensitic phase and/or the coexistence of two phases or precipitates.

The objective of this study is therefore twofold. Firstly, to study the effects of different temperature heat treatments on $\text{Ni}_{45}\text{Ti}_{50}\text{Cu}_5$ by means of DMA measurements in order to provide insight into the evolution of its microstructures, damping behavior and shape memory properties. DMA measurements are performed under non-zero heating and cooling rates and under isothermal conditions, as it has been proven that this is the best way to correlate results involving microstructural changes caused by cold work and annealing at different temperatures [6,12,28]. Secondly, in order to confirm the results obtained by the DMA as regards the effects of HT on the microstructure, they were checked using other techniques such as DSC, X-ray diffraction (XRD), hardness measurement and stress-strain tests.

Each of these techniques senses different physical phenomena and thus provides information concerning the changes in various physical parameters that take place during the phase transformations. By combining all these experimental techniques to analyze the DMA measurements of the internal friction and mechanical behavior of the NiTiCu alloys, the present paper provides a complete study of the comprehensive effects of heat treatment on these alloys.

Although several studies have used DMA for evaluating the internal friction of NiTi and NiTiCu alloys, the kind of study presented here is still missing from the literature. In the present study the relationship between the internal friction observed by means of DMA is used to investigate the consequences of carrying out the annealing process at different temperatures (dislocation reduction, precipitation process, recrystallization, grain growth and wt(%) of retained martensite). Also, once the relationship between the IF results and all the other techniques was known, a study was carried out into how the internal friction and mechanical properties of $\text{Ni}_{45}\text{Ti}_{50}\text{Cu}_5$ can be optimized using a suitable heat treatment temperature to produce a favorable combination of mechanical properties.

Materials and methods

The materials used in this investigation were $\text{Ni}_{45}\text{Ti}_{50}\text{Cu}_5$ (at%) wires, which were provided by Saite Metal Materials Xi'an Co., LTD. These were subjected to processes to obtain the final wire of 1 mm diameter with 30% cold work. The cold-worked wire was shape-setting annealed (in a straight constrained shape) by heat treatments at seven different temperatures: 400, 450, 500, 550, 575, 600 and 650°C for 60 minutes under argon atmosphere. After aging, the samples were quenched in water. The nomenclature used from now on is formed by the HT prefix followed by the temperature of the heat treatment (°C). The samples for all the following experimental procedures were obtained from the same heat-treated batch, ensuring that they all had the same microstructure. Before any tests were carried out, all samples were quenched in ice to achieve a fully martensitic state.

Martensitic transformation temperatures and heat flow exchanges were determined by DSC tests using a Mettler DSC-821e calorimeter. Samples of 4mm length (weight about 25mg) 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 thermal mechanical analyzer (TA Instruments DMA Q800) equipped with a liquid nitrogen cooling system. Two kinds of experiment were performed:

- IF as a function of temperature: measurements were conducted with a continuous heating/cooling rate of 3 °C/min in the 0-100°C temperature range and with a frequency of 0.2 Hz; samples were subjected to flexural loading in the 3-point bending configuration (with a low-friction, self-adjusting 3-point bending clamp) at a strain amplitude of 0.02%.
- IF isothermal: in order to obtain the isothermal damping characteristics of austenite (B2) and martensite (B19'), isothermal tests were conducted with the same configuration (clamp, frequency and strain amplitude). The experimental procedure was as follows: samples were cooled from 120°C at a constant cooling rate of 3°C/min and kept isothermally for at least 40 minutes at a set temperature: 100°C (austenitic state) and 0°C (martensitic state).

In order to investigate the effect of the heat treatment on the material's mechanical performance, break tensile tests and microhardness tests were carried out. Samples for break tensile tests were cut to a length of 125 mm and tested at a temperature below M_f to ensure martensitic phase using a Zwick 1445 tensile test machine with specially designed grips at a strain rate of 0.5 mm/min, simultaneously recording the applied force and crosshead displacement. All microhardness tests were conducted by the same operator using a WILSON-WOLPERT 401MVA microhardness tester with a micro-Vickers indenter and a 500g load at room temperature to ensure martensite phase. To obtain a hardness value, ten micro-Vickers indentations were performed on each specimen. A statistical calculation with a 95% confidence level was then carried out to determine the upper and lower limits.

Finally, in order to further understand the phase structures of heat-treated NiTiCu samples, X-ray experiments were performed at the BL04-MSPD beamline of the ALBA-CELLS synchrotron facility. Diffractograms were measured at austenitic state (120°C). The detector employed was a Mythen detector for time-resolved experiments, covering 40 deg in 2 θ . This detector is composed of 6 modules (Dectris/PSI Detectors group) placed at 550mm from the sample and with a strip-pitch of 50 μ m. The shortest wavelength used for the detector was chosen from a crystal Si 111 monochromator and was 0.41322547Å ($\approx$ 30 keV). The precise wavelength 0.4132(1) Å was determined by refining the peak positions of a NIST standard silicon sample. The beam was focused down to 0.7 mm in the vertical direction by bending the mirror appropriately prior to the monochromator. The horizontal beam size was 3 mm as defined by slits after the monochromator.

Before starting the synchrotron analysis of the samples, two standards were separately analyzed at room temperature. They were placed in a glass capillary of 0.7mm: LaB₆ (SRM 660a) and NAC (Na₂Ca₃Al₂F₁₄). These standards were analyzed to obtain the instrumental resolution function of the beam line setup. The resulting diffractograms were refined by convoluting a Lorentzian and a Gaussian function with a dependence of the angle as $\text{cte}/\cos\theta$ and $\text{cte}*\tan\theta$, where cte is a constant refined for each function.

Results and discussion

DMA results: IF as a function of temperature

Figure 1 ((a) to (d)) shows the DMA curves on cooling and heating for all the heat-treated $\text{Ni}_{45}\text{Ti}_{50}\text{Cu}_5$ samples along with the $\tan \delta$ (or IF) and storage modulus (E_0) evolution with temperature. It can be seen that the forward and reverse phase transformation process is clearly detected, showing a maximum in the internal friction curve and a sharp variation in the storage modulus.

All HT samples present a one-stage B2-B19' transformation IF peak during cooling and a reverse transformation IF peak B19'-B2 on heating. No B19'-B19 or R-phase-B19' transformations are detected, as expected in a $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ alloy for $x < 5\%$ [10,29]. Beyond the transformation process, on cooling, the decrease in IF with decreasing temperature reflects the decreasing mobility of the twin boundaries. However, on heating, the IF remains almost constant beyond the transformation process in a rather wide temperature range as the structure is completely transformed to B2. The higher internal friction values of the B2-B19' peak are associated with the high mobility of the twin boundaries of the parent/martensite and martensite/martensite interfaces. On the B19'-B2 transformation, the associated IF peak to B19'-B2 transformation is lower than the B2-B19' one, and this may be due mainly to the movable phase boundaries and stress-induced motion of martensite/martensite interfaces pointed out by other authors [8,17,30,31]. After the DMA thermal cycle finishes, the IF value remains at a higher level compared to the initial value. This may be a result of the re-orientation of the martensitic structure with mechanical stress and was also noted by Aaltio et al. [30].

The storage modulus (E_0) decreases drastically in temperature on cooling, showing a deep minimum associated with martensitic transformation that coincides with the corresponding IF peak. The deep minimum of E_0 is a consequence of the increase in the relative amount of martensite phase, which has an apparent elastic modulus that is smaller with respect to the parent phase due to motions of the twin boundaries under the alternating applied stress [24]. After the B2-B19' transformation is completed, the storage modulus of the B19' martensite continues to gently increase with decreasing temperature. However, on heating, the B19'-B2 transformation is reflected as a sharp increase in the storage modulus at similar temperature to the IF peak until the structure is fully converted to the B2 phase.

By comparing the IF and the storage modulus signals it can be seen that, during the B19'-B2 transformation, the beginning of the transformation can first be detected by the increase in the IF signal and cannot be detected by the storage modulus evolution. This behavior indicates that the IF signal is more sensitive than the storage modulus in detecting the start of the transformation process due to the interface mobility that changes the IF value but does not affect the storage modulus.

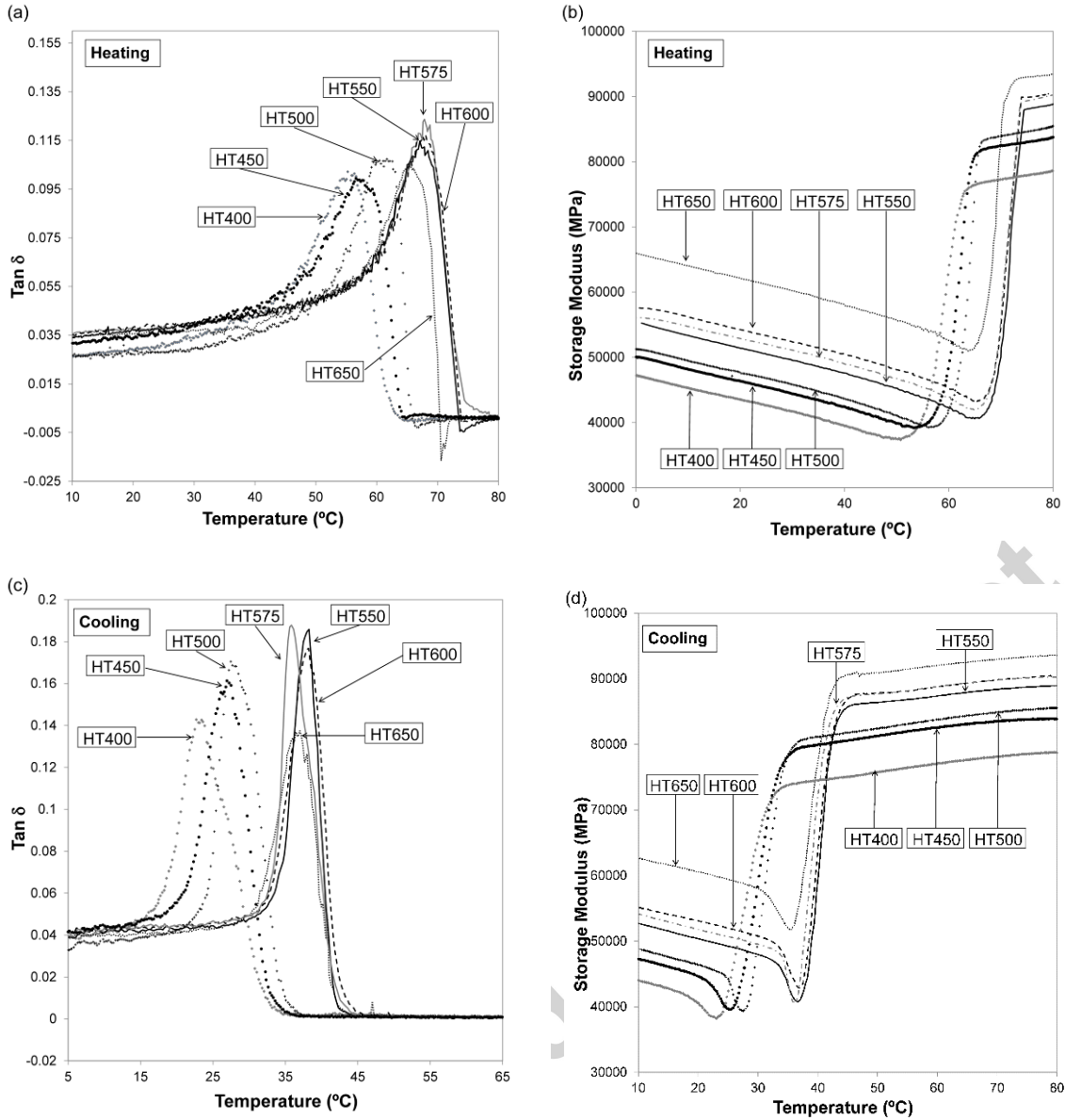


Figure 1. Evolution of internal friction and storage modulus with temperature (heating and cooling) of $Ni_{45}Ti_{50}Cu_5$ for all heat-treated samples.

For a detailed analysis of the difference in IF with all the heat treatments, Figure 2 (upper half) shows the $\tan \delta$ evolution, both on heating and cooling, for all HT temperatures. It can be seen that, on cooling, the IF presents a clear tendency depending on the heat treatment. A similar trend is followed by the heating results but with lower values for $\tan \delta$. Figure 2 shows that for samples annealed between 400°C and 550°C, all IFs present an initial rise that becomes increasingly more pronounced as the heat treatment temperature approaches 550 °C. The values remain more or less stable for HT550 and HT575, when it slowly starts to decrease until HT600, and finally the IF presents a sudden drop at HT650. As shown in this figure, two specimens (HT400 and HT650) present the lowest values of IF peak and are significantly lower than HT575 (32% and 37% respectively).

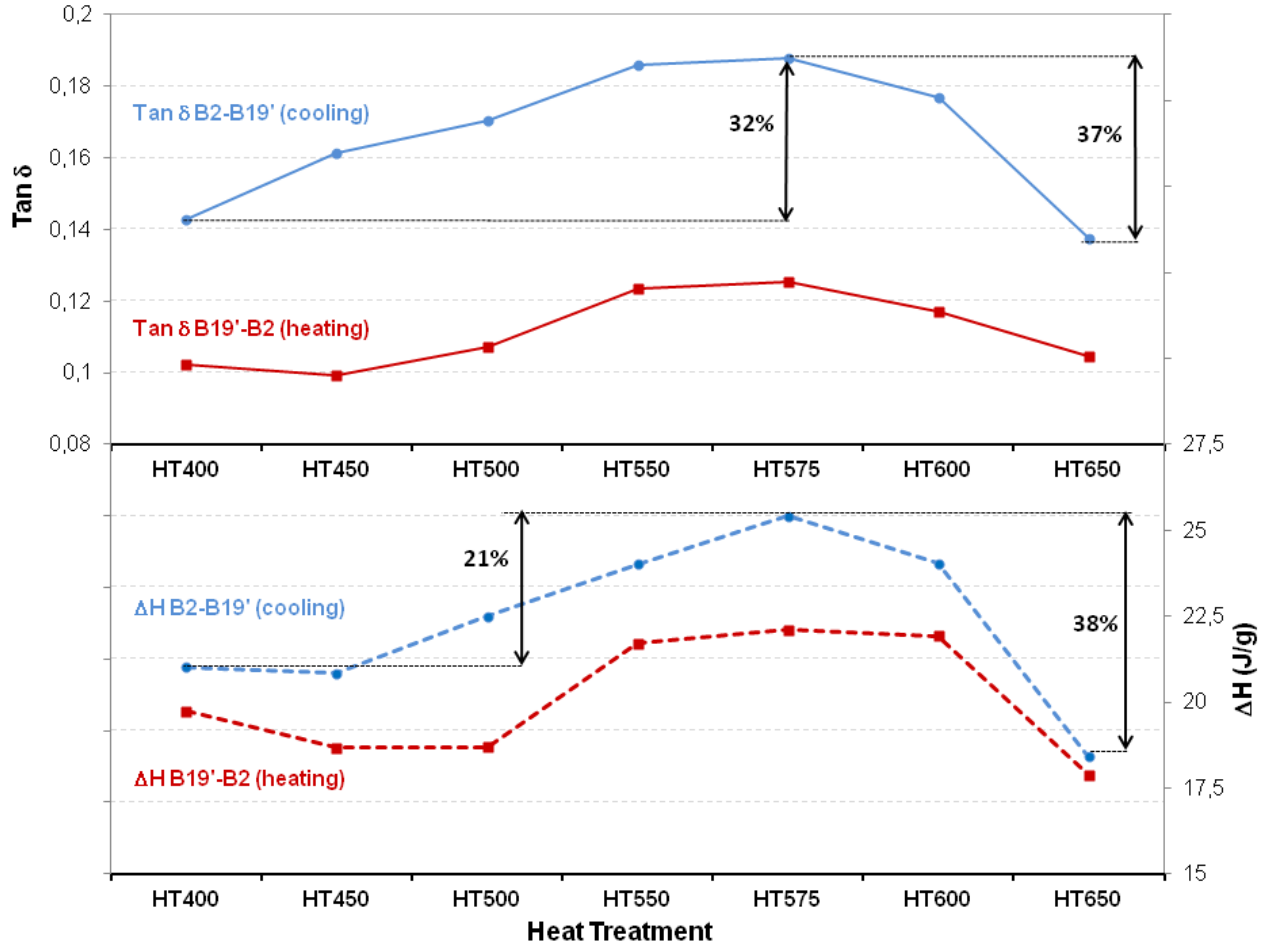


Figure 2. (Upper half) Evolution of internal friction ($\tan \delta$) as a function of heat treatment on cooling and heating. (Lower half) Evolution of heat flow (ΔH) as a function of heat treatment on cooling and heating.

DMA results: isothermal IF analysis

In order to analyze the internal friction evolution in the heat-treated samples in greater depth, the intrinsic IF of martensite (B19') phase ($IF_i^{B19'}$) and austenite phase (IF_i^{B2}) were measured under isothermal conditions. As is well known, it has been suggested that the internal friction associated with a first-order phase transformation decomposes into three terms: IF_{Tr} , IF_{PT} and IF_i [8,18]. The first term (IF_{Tr}) is a transitory IF that appears only at low frequency and non-zero dT/dt , the second (IF_{PT}) is the IF due to phase transformation and does not depend on dT/dt , and the third (IF_i) is the intrinsic IF of the austenitic or martensitic phases and depends strongly on microstructure properties such as dislocations, vacancies, precipitates and twin boundaries [17]. The intrinsic internal friction (IF_i) 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_i in all HT samples can give us a more accurate analysis of the effect of the heat treatment because IF_i is strongly dependent on the microstructure of each phase [8].

Figure 3a 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 shown as it presents an almost steady behavior during the entire isothermal interval. Also, this value was comparatively very low ($\tan \delta \approx 9 \cdot 10^{-4}$) because it comes only from the dynamic/static hysteresis of lattice defects [17]. Figure 3a shows that, for all samples, the measured $\tan \delta$ values of B19' decrease as time increases, reaching the steady value ($IF_{i,steady}^{B19'}$) after approximately 30 minutes. To clearly compare the differences between all HT temperatures, Figure 3b presents the different

internal friction terms ($IF_{I\text{-}Total}^{B19'}$ and $IF_{I\text{-}Steady}^{B19'}$) as a function of HT temperature. The steady values are quite different for all HT temperatures and present the same tendency as the IF B2-B19' peak shown in Figure 2. The static term $IF_{I\text{-}Steady}^{B19'}$ increases slightly with HT temperature from HT400 to HT575 and then drops at HT650. This behavior is probably due to the increase of abundant twin boundaries in between the variants which can easily be moved to accommodate the applied strain [17,18]. Again, HT400 and HT650 present the lowest values due to restrictions in movement. As mentioned earlier, $IF_{I\text{-}Total}^{B19'}$ strongly depends on microstructural properties, hence it can be concluded that severe microstructural changes have come about in the HT process and are clearly manifested in HT400 and HT650.

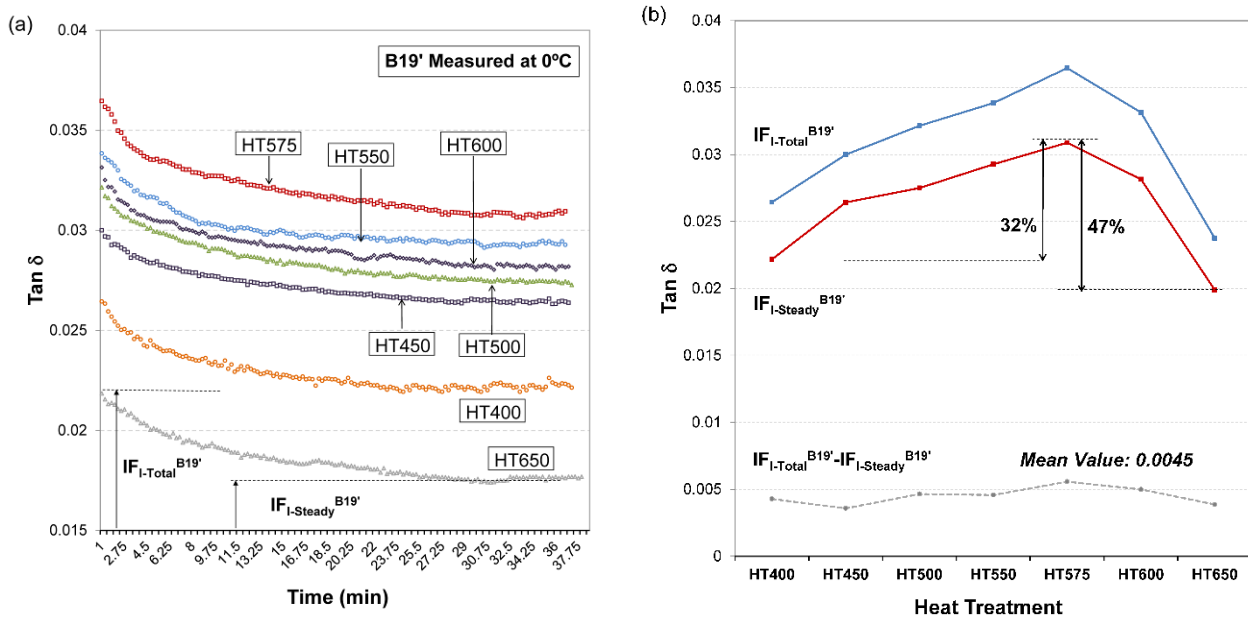


Figure 3. a) Evolution of $\tan \delta$ at 0°C (B19') as a function of time for all HT at 0.2 Hz, 0.02% strain amplitude, b) $\tan \delta$ values of $IF_{I\text{-}Total}^{B19'}$ and $IF_{I\text{-}Steady}^{B19'}$ for HT.

DSC results

The transformation behavior can also be analyzed by calorimetric methods. DSC measurements were therefore performed to study the effect of the HT on phase transformation behavior in order to compare the results with those obtained by DMA. Table 1 presents the transformation temperatures (TT), peak temperatures, hysteresis ($A_{peak} - M_{peak}$) and the transformation heat flow for all the heat-treated samples. For the sake of comparison, ΔH evolution with all HT samples is also presented in Figure 2 above (lower half).

Table 1. Transformation temperatures and heat flow measured from DSC curves at 10 °C/min

	Transformation Temperatures by DSC (°C)						Heat Flow (J/g)		
	Af	As	Ms	Mf	A_{peak}	M_{peak}	Hysteresis	$\Delta H_{cooling}$	$\Delta H_{heating}$
HT400	60.99	46.18	37.48	25.05	54.52	30.99	23.53	21.01	19.73
HT450	61.97	49.01	39.44	28.2	57.5	33.69	23.81	20.84	18.66
HT500	65.94	53.65	41.6	30.35	61.55	34.77	25.03	22.49	18.68
HT550	71.47	61.63	50.05	39.21	67.71	44.11	23.6	24.02	21.71
HT575	71.54	61.64	50.57	40.1	68.02	43.98	23.46	25.42	22.1
HT600	70.83	61.11	49.72	39.47	67.34	43.33	24.01	24.04	21.93
HT650	68.79	58.21	43.63	28.73	64.94	35.41	29.53	18.41	17.88

With respect to the TT (Table 1), it seems that HT temperature has a significant effect on the transformation tendency, and the range of this HT temperature can be divided into three regions: from HT400 to HT550, in which all critical temperatures for transformation (B19'-B2 and B2-B19') increase with increasing HT; from HT550 to HT600, in which the TTs do not seem to change; and from HT600 to HT650, in which the TTs appear to decrease with increasing HT temperature. These results are consistent with similar studies on the effects of annealing on transformation behavior in near equiatomic NiTi and NiTiCu alloys [32–34].

From Figure 2 it can be seen that the latent heats of the transformations (on heating and cooling) present similar trends to the IF peaks for all HT temperatures. As the transformation processes are accompanied by a change in latent heat, this absorbed/released heat can be analyzed to detect microstructural changes because the amount of heat is proportional to the volume fraction of the transformed material [32,35]. The internal stress state associated with dislocations or precipitate processes can restrict the transformation path, thus reducing ΔH . Analyzing Figure 2, the same three regions can be found: an initial rise to HT550, where it reaches a steady value, and a drastic fall in ΔH at HT650, revealing significant changes at microstructural level with different HT temperatures.

As seen in Table 1, the transformation hysteresis (difference between A_{peak} and M_{peak}) shows a completely steady behavior (with a mean value of around 24°C) for all samples except HT650, which again supplies a great deal of information about the different microstructures between HT650 and the other HT temperatures. These differences could be attributed to a combined process of recovery and recrystallization, but also to the probable presence of Ti₂Ni precipitates [32].

Comparing the DSC results with the DMA results, some of the experimentally obtained characteristics ($\tan \delta$ and ΔH) exhibit the same tendency as the temperature of the HT increases. On both heating and cooling, the HT400 and HT650 samples present the lowest values and are significantly lower than HT575. At low temperatures, the low values of $\tan \delta$ and ΔH can be attributed to high dislocation densities caused by the cold work, while at high temperatures (beyond the recrystallization temperature), the decrease in the ΔH and $\tan \delta$ can be attributed to competition between the reduction in dislocations, a precipitation process with an incoherent distribution, and the higher wt(%) of retained martensite.

This distinctive behavior found in the three regions mentioned above may be thought to arise from several factors: (F1) high density dislocation morphology introduced by prior cold work, (F2) recovery and recrystallization processes with texture changes, (F3) grain growth, (F4A) precipitation processes with very narrow precipitates coherent with the matrix, (F4B) precipitation processes with coarser precipitates with incoherent interfaces with the matrix, and (F5) wt(%) of retained martensite.

As commented earlier, the results suggest that samples HT400 and HT450 present lower values of $\tan \delta$ and ΔH because abundant defects and tangled dislocations (factor F1) associated with prior cold-working have generated an internal stress state that restricts the transformation path and causes these lower values. As samples are heat treated at higher temperatures, the dislocations are removed through the annealing process (factor F2) and there is a reduction in the internal stress that facilitates the formation of the martensite phase as M_s and M_f move toward higher values. Several studies on equiatomic NiTi [32,36,37] have reported that 550–600 °C seems to be the critical annealing temperature range. Annealing below or above this range results in different transformation characteristics because two different types of microstructures are formed [3,38]. Both of these microstructures are related to lattice defects and internal stress/strain fields, which affect the mobility of the martensite interfaces. Below the critical annealing temperature (HT575 in our results), the microstructure is related to the internal residual stress/strain lattice defects created during previous deformation processes brought about in the course of fabrication. However, for samples annealed at above the recrystallization temperature, several processes could be involved, e.g. grain growth (factor F3) and precipitation processes (factor F4B)[38]. After analyzing the DSC and DMA results, of all these factors, the most predominant in the specimens annealed up to 575°C seem to be F1 and

F2. In order to clarify the contributions of factors F3, F4A, F4B and F5 to the differences in HT temperatures, other complementary techniques need to be employed. This will be analyzed in the following sections.

Mechanical analysis: break tensile tests and microhardness results

As a first step in uncovering the most predominant factor out of those indicated above (factors F1-F5), break tensile tests and microhardness tests were performed for all HT samples. Figure 4 presents the stress-strain results with an insert in which the enlarged portion of the transformation region (detwinning) is plotted. Figure 5 presents microhardness results combined with ultimate tensile stress (UTS) and slip stress (the plastic stress in the detwinned part of the tensile test where the reoriented martensite might abandon elastic behavior). Several interesting results can be deduced from these figures. In Figure 4, in the transformation region, all samples present an initial drop in tensile stress at the onset of the martensitic reorientation with a typical plateau in the stress-strain curve due to the so-called detwinning process. This critical stress (or barrier stress) is almost the same from HT400 to HT600, with a mean value of 85 MPa. At HT650 it increases slightly to 97 MPa, probably due to defect annihilation processes and factor F4B. These results present slight differences compared to those reported by Liu and Van-Humbeeck [38], which showed a proportionality between the heat treatment temperature and the critical stress. This is likely to be because they studied a near-equiatomic NiTi alloy which is known to be more affected by heat treatment. As these differences are not so evident in the present results, it is clear that at least two microstructural changes interact simultaneously.

With respect to the breaking results (UTS) shown in Figure 5, all samples present similar results and no big differences can be detected between HTs except for HT650, which shows the minimum value. The most interesting result concerns the slip stress, which progressively decays with HT temperature from HT400-450 to the lowest value at HT650. All these results lead to the same conclusion: there is no evidence of big changes in grain growth (factor F3) in HT samples because there is no increment in ductility, and the mechanical strength (UTS) is also almost constant except for HT650, which shows a lower value mainly due to factor F4B, as will be discussed later.

Figure 5 also shows the results of the microhardness tests for all HTs with upper and lower deviation limits. It can be seen that there are two different hardness groups, low HT temperatures (HT400-HT450) and high HT temperatures (from HT500 to HT650). Although there is a difference in hardness between HT400 and HT450, it may not be enough to identify a different behavior because the HT400 upper limit deviation and the HT450 lower limit deviation overlap. The same occurs with HT500 to HT650. The higher hardness value of HT400-HT450 can be attributed to factors F1 and F4A where lower HT temperatures do not eliminate the effects of the cold work (higher dislocation density and fine precipitates with coherent distribution) brought about during the manufacturing process. In contrast, the lower hardness values of HT500-HT650 seem to be attributable to factor F2 because of the reduction in dislocations at high annealing temperatures. F3 seems not to play an important role because, if significant grain growth had existed, a reduction in hardness would have been shown.

The increase in the hardness value of HT650 together with the increase in barrier stress and reduction in UTS and slip stress point to microstructural changes at this temperature. This evidence can be caused by factor F4B, which can also change hardness, not only through the increase in precipitates but also through the incoherence of the precipitates with the matrix [39]. Other authors have also reported higher hardness values with incoherent Ti₂Ni precipitate distribution in nanoindentation studies [40].

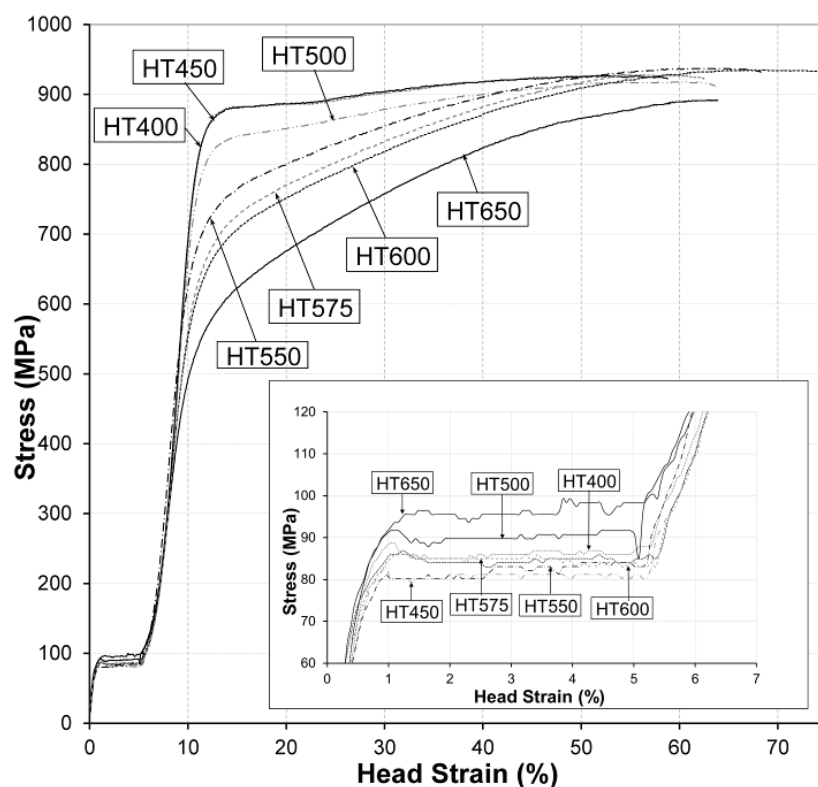


Figure 4. Stress-strain curves of HT samples. Insert figure represents an enlarged portion of the detwinning process.

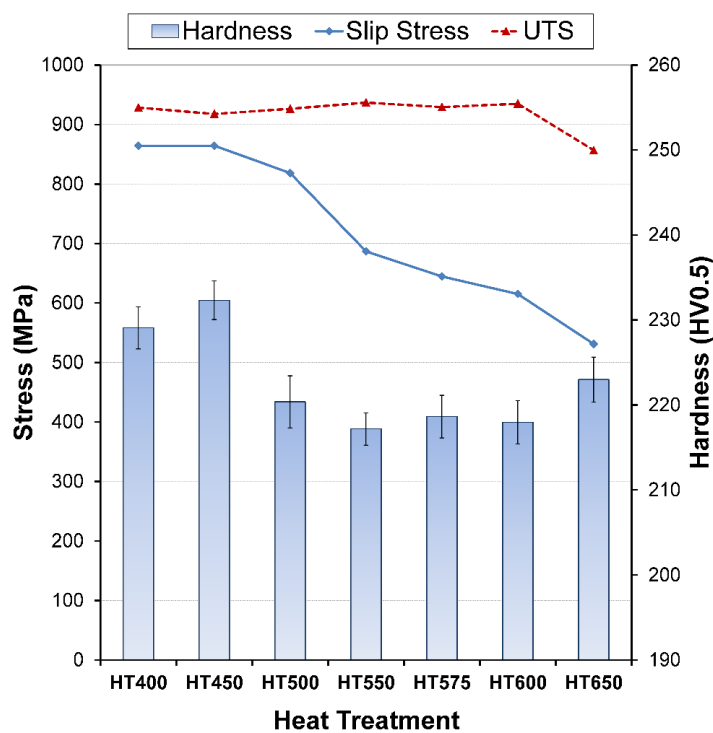


Figure 5. Hardness results of HT samples (right axis) and slip stress and ultimate tensile stress (UTS) obtained from tensile tests (left axis).

Figure 6 makes it possible to compare the evolution of the elastic modulus of all samples obtained from the tensile test with the storage modulus obtained from the DMA results. It provides confirmation that the stiffness of all the HT samples is almost the same except for HT650, where both the elastic modulus and the storage modulus present the highest values.

The modulus defect obtained from the DMA results is also plotted in this figure. This parameter is greatly affected by precipitation processes and was first defined by Mazzolai et al. [24] as the major fractional change of the storage modulus (E_0) that occurs between M_s and M_f . In the present paper, the modulus defect is calculated as the % decrease in total storage modulus that takes place between B2 and B19', i.e. $(E_0^{B2} - E_0^{B19'})/E_0^{B2}$. In Figure 6 the highest modulus defect again corresponds to HT575 and the lowest to HT650. The drastic reduction in the modulus defect is likely due to the pinning of twin boundaries by Ti2Ni precipitates (factor F4B). The presence of these precipitates may also be responsible for the increase in the HT650 storage modulus and elastic modulus [40].

It can be seen, then, that factor F4B (precipitation process with incoherent distribution) is the most likely to explain all the above results for HT650: the lowest $\tan \delta$; the highest storage modulus in B19' and B2; the lowest defect modulus; the lowest UTS and slip stress, and decaying transformation temperatures; the highest transformation hysteresis and lowest ΔH and dissipated energy. The assumption of the existence of Ti2Ni precipitates and their size and distribution in HT650 will be discussed on the basis of the X-ray powder synchrotron diffraction results in the next section.

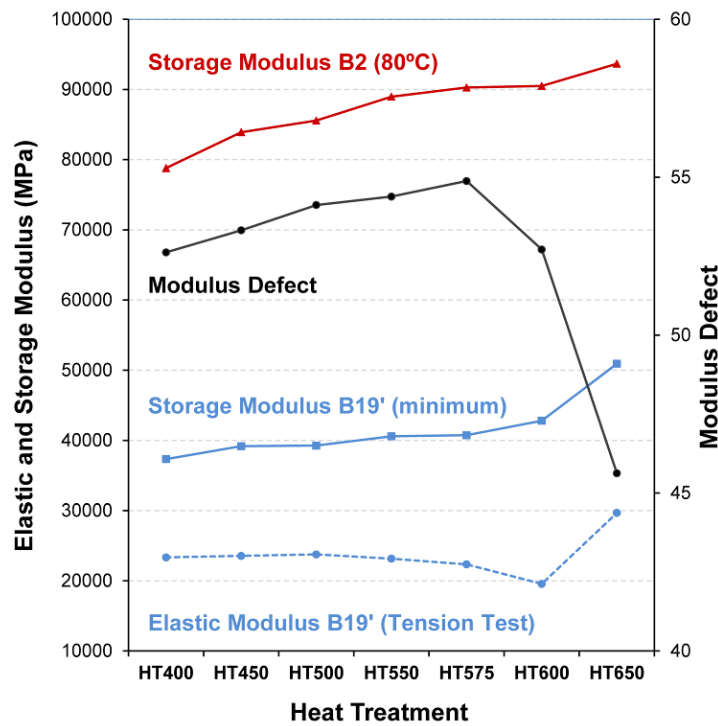


Figure 6. Elastic modulus obtained from the tensile test and storage modulus of B19' and B2 obtained from the DMA results as a function of annealing temperature (left axis). Modulus defect (% of storage modulus decrease between B2 and B19') as a function of annealing temperature (right axis).

Microstructural analysis: synchrotron X-ray powder diffraction results

In order to properly determine what microstructure was present in the specimens and to distinguish between the changes that the HT temperature causes in the microstructure (crystallite size, weight phases (wt%), microstrain and texture), synchrotron X-ray powder diffraction (SXRD) analysis was carried out for all samples. Diffractograms were taken at 120°C because at that temperature the main phase expected is B2 and, due to the high symmetry (i.e. few reflections), minor phases can be detected at the low intensity part of the diffractogram. As expected, B2 was indeed the main phase (92-98 wt%) but minor phases were also detected. The resulting diffractograms were analyzed with TOPAS 4.2 software [41] with local routines. The Rietveld method [42] was applied in order to identify and quantify the minor phases and then study their microstructure (crystallite size and microstrain). Phase identification was carried out using the ICDD PDF-2 database, release 2007. The wt% of each phase present in the samples at 120°C was estimated using the refined Rietveld scale factor and applying the corresponding expressions [43].

The crystal structures used in the Rietveld analysis and the preferred orientation correction employed for each phase are listed in Table 2. The preferred orientation was corrected for the main phase (B2) with the generalized spherical-harmonic description (GSH) of order 8, which implies, for cubic symmetry, the refinement of three independent C_{ij} coefficients. We compared the magnitude of preferred orientation of the samples with the texture index [44], which is calculated from the GSH coefficients, C_{ij} . The resulting texture index is equal to unity for a non-textured material and is infinity for single crystal data and does not have units. The preferred orientation was corrected for the minor phases with the March-Dollase [45] model, where up to two crystallographic directions are specified, and one parameter per direction was refined.

The results of the quantitative phase analysis from SXRD data are shown in Table 3. For the sake of simplicity, Figure 7 only shows the diffractograms for HT400 and HT650, in which the most dissimilar behaviors can be appreciated.

The microstructural analysis was done as a previous paper on NiTi samples [46]. In that paper the authors showed that NiTi-austenite peaks have an anisotropic peak broadening that can be treated with the modified Williamson-Hall plot [47,48]. The peak width (ΔK) was individually measured for each peak by fitting a pseudo-Voigt function and its value plotted against the peak position corrected with the average diffraction contrast factors of dislocations ($K\bar{C}^{\frac{1}{2}}$). The resulting scattered points were fitted with the following function:

$$\Delta K = \frac{0.9}{D_{hkl}} + \alpha' \left(K\bar{C}^{\frac{1}{2}} \right)^2 \quad (1)$$

where D_{hkl} is the apparent crystallite size and α' is related to the density of dislocations. Figure 8 shows the modified Williamson-Hall plot of the NiTi-austenite peaks measured with SXRD at 120°C for different temperatures of training. The same figure shows the resulting fitting of the scattered points with the previous function from which the apparent crystallite size and density of dislocations were obtained.

Table 2. Structure data and reference used for each phase during the Rietveld analysis.

Phase name, composition	System, space group	Crystal parameters	Atomic positions (x, y, z)	Preferred orientation correction and direction	Reference
NiTi	Cubic	a: 3.015 Å	Ni (0, 0, 0)	GSH, order 8	[49]
Austenite (B2)	Pm-3m		Ti ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$)		
NiTi	Monoclinic	a: 2.898 Å	Ti (0.4176, $\frac{1}{4}$, 0.2164)	March-Dollase	[50]
Martensite (B19')	P21/m	b: 4.108 Å c: 4.646 Å β : 97.78°	Ni (0.0372, $\frac{1}{4}$, 0.6752)	(100) and (101)	
Ti ₂ Ni	Cubic Fd-3m	a: 11.3193 Å	Ti ($\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$) Ni (0.912, 0.912, 0.912)	March-Dollase (001)	[51]
TiC	Cubic Fm-3m	a: 4.328 Å	Ti (0, 0, 0) C ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$)	-	[52]
Cu _{0.9} Ni _{1.1} Ti	Tetragonal I4/mmm	a: 3.12 Å c: 7.965 Å	Ni (0, 0, 0.3354) Cu (0, 0, 0.3354) Ti (0, 0, 0)	-	[53]

On the basis of the diffractogram analysis, the following phase results were found:

The NiTiCu-martensite (B19') phase was unexpected because, at the temperature of the analysis (120°C), all martensite is assumed to be transformed into austenite. However, the diffractograms show that a small percentage of martensite is present in all samples (1.41-6.77 wt%). The martensite presents very broad peaks indicating either a very low crystallite size or a high microstrain. Due to the low percentage of this phase, and consequently the lack of well-resolved peaks, it was not possible to determine which of the two phenomena was responsible for the broadened peaks. In order to simplify the calculations, the crystallite size effect was assumed to be responsible and values ranging roughly from 13 to 6 nm were found. The tendency shown in Table 3 from the wt(%) of retained martensite was not expected. Other authors [54,55] have pointed out that higher HT temperatures imply a reduction in retained martensite. However, the lower HT temperature (400 °C) eliminates most of the retained martensite that should be present due to the presence of dislocations which slow down the conversion to austenite. The reason for this is that the specimens were not loaded/trained and dislocations were only produced by cold working before the heat treatment. As a result, HT400 and HT450 show similar low values for wt(%) of retained martensite. HT500, HT550 and HT575 show similar medium values. These values may be due to the recrystallization process (factor F2) and precipitation process (factor F4A). However, HT600 and HT650 show higher values for wt(%) of retained martensite that might be caused by coarser precipitates with incoherent interfaces with the matrix (factor 4B). Both the March-Dollase index and the crystallite size obtained for NiTiCu-martensite should be considered with caution due to the very low content of this phase and to the broad peaks that the phase presents at 120°C.

The Ti₂Ni phase is clearly present in all specimens from 0.52 to 0.67 wt%. It shows very sharp peaks (high crystallite sizes) in comparison with martensite. This phase was identified and described previously [56] as Ti₂(Ni, Cu) with cubic symmetry and a: 11.33Å. The crystal structure found is described as Ti₂Ni, Fd-3m and a: 11.3729. A consideration was made that both phases were the same but the possibility of some Cu content was not discarded. However, at the percentage detected for this phase it is rather difficult to adjust a Ni $\leftrightarrow$ Cu substitution. The tendency in the wt% of Ti₂Ni is characterized by two groups (see Table 3). The first group is formed by HT400 to HT500. These temperatures do not modify the initial quantity of Ti₂Ni. However, from HT550 onwards a slight increase in Ti₂Ni is detected. This could be due to the precipitation process (factor 4B) that also increases the wt(%) of martensite. The precipitation process is also contrasted by the appearance of another phase (Cu_{0.9}TiNi_{1.1}). The relationship between the appearance of the new phase, the increase in the Ti₂Ni phase and the increase in retained martensite may be linked to the change in

microstructure associated with the coarser precipitates with incoherent interfaces with the matrix (factor 4B).

The TiC phase was also found in all specimens and its presence was detected by reflections 111 and 311 of very low intensity. The other reflections for this phase are completely overlapped by the other phases. The wt% of this phase's ranges is very low and can be considered as uniform for all specimens. Therefore TiC was not considered responsible for the behavior changes in specimens. Moreover, the wt% of TiC must be considered with caution because of the few reflections used to estimate it. However, the presence of titanium carbide is not uncommon because it could come from the production process and has been detected and analyzed by other authors [57,58].

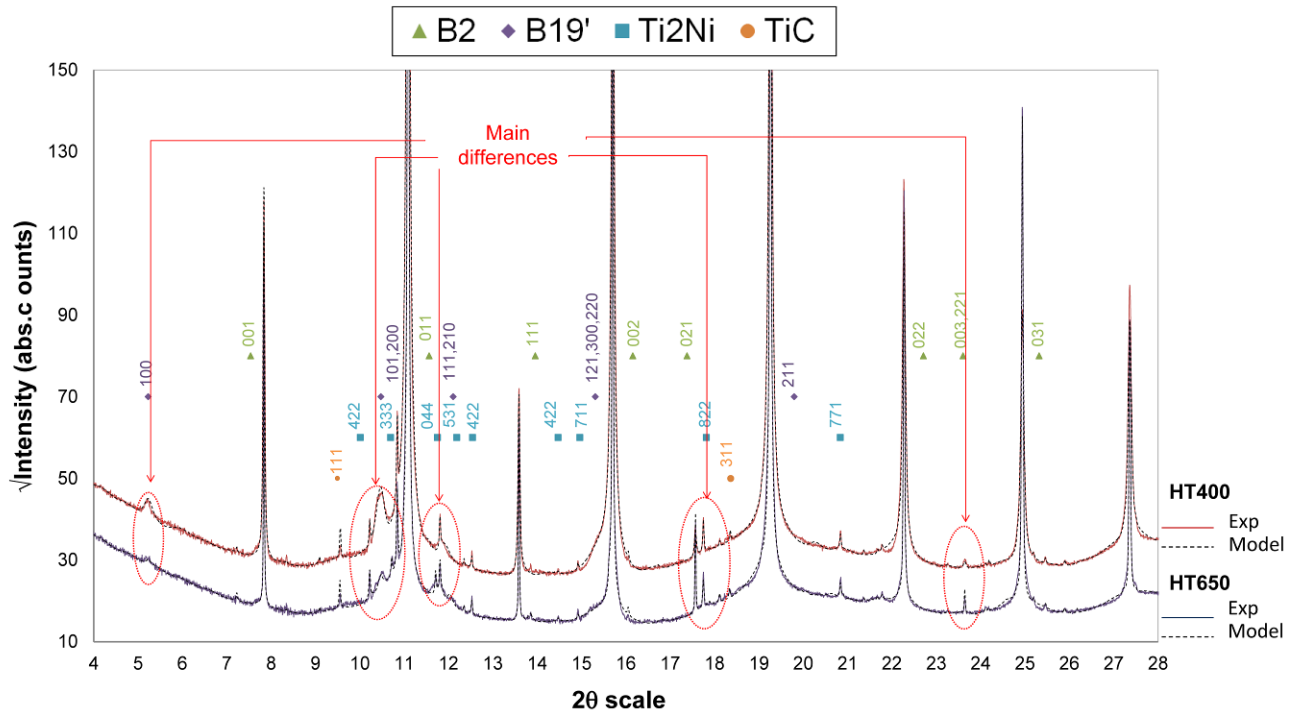


Figure 7. Measured and calculated SXRD patterns for samples HT400 and HT650 at 120°C. The main Bragg peaks with their hkl indexes are indicated for each phase. This plot shows the low intensity part of the diffractogram in order to reveal the peaks of the minor phases.

Figure 7 shows a segment of the SXRD diffractogram measured at 120°C (mainly B2 austenite phase). It can be clearly appreciated that there is a presence of Ti_2Ni precipitates. For the sake of clarity, the reflection peaks that show the biggest differences between HT400 and HT650 are identified by red circles. The main differences are between the B2 and B19' phases. Similar results were presented by Jones and Dye [56].

In Figure 8 below (the modified Williamson-Hall plot) we can elucidate that the tendency for all samples is to decrease the density of dislocations and increase the crystallite size for the NiTiCu-austenite phase as the treatment temperature increases. This tendency can be clearly appreciated with lower HT temperatures (HT400, HT450 and HT500). By fitting the points of the previous figure to the function (1), we have estimated the apparent crystallite size (D_{hkl}) and the density of dislocations (α') for each sample. These are listed in Table 4, which also shows the results of the texture index for the NiTiCu-austenite phase together with the March-Dollase index and an approximation to the crystallite size for the NiTiCu-martensite phase. The tendency in the texture index for the NiTiCu-austenite phase is to decrease as the temperature of the treatment is increased. This is to be expected because of the recrystallization process (factor F2) during the heat treatment that tends to erase the original wire texture. The recrystallization process is also reflected in the apparent crystallite size for the NiTiCu-austenite phase, which grows progressively with the heat

treatment. The density of dislocations for the NiTiCu-austenite phase decreases quickly between 400 and 525°C but at higher temperatures is maintained almost constant. This would indicate that both crystallite growth and dislocation erasing start simultaneously but at different speeds as the temperature of the heat treatment is increased. The values for crystallite size validate the hypothesis made regarding factors 3 and 4B because grain size and coarser precipitates contribute to increasing crystallite size.

Table 3. Results of the relative quantitative analysis (in wt %) by the Rietveld method for the identified phases at 120°C. Also shown is the conventional Rietveld agreement factor R_{wp} . n.d.: not detected.

Sample	NiTiCu-austenite (B2)	NiTiCu- martensite (B19')	Ti ₂ Ni	TiC	Cu _{0.9} TiNi _{1.1}	R_{wp}
HT400	97.65 (0.19)	1.53 (0.18)	0.53 (0.03)	0.29 (0.03)	n.d.	8.43
HT450	97.80 (0.17)	1.41 (0.16)	0.57 (0.03)	0.22 (0.03)	n.d.	9.42
HT500	96.23 (0.24)	2.95 (0.24)	0.56 (0.03)	0.26 (0.03)	n.d.	9.35
HT550	95.07 (0.25)	3.2 (0.25)	0.63 (0.03)	0.28 (0.03)	0.82 (0.06)	8.66
HT575	93.85 (0.27)	4.52 (0.26)	0.67 (0.03)	0.23 (0.03)	0.73 (0.06)	9.4
HT600	91.83 (0.29)	6.77 (0.28)	0.62 (0.03)	0.29 (0.03)	0.49 (0.07)	8.83
HT650	92.49 (0.29)	6.58 (0.28)	0.60 (0.03)	0.33 (0.03)	n.d.	9.61

Table 4. Results of the texture index calculated from the preferred orientation correction by using the general spherical harmonics correction, apparent crystallite size (D_{hkl} , in nm), density of dislocations (α') calculated with the modified Williamson-Hall plot (Figure 8) for the NiTiCu-austenite phase, and the March-Dollase index for preferred orientation correction for NiTiCu-martensite phases and precipitates at 120°C.

Sample	at 120°C	NiTiCu-austenite (B2)			NiTi-martensite (B19')	
		Texture index	D_{hkl}	α'	March-Dollase index	D_{hkl}
HT400		1.145 (0.002)	39 (5)	4.3 (0.5)	1.19(0.06) ; 0.2(0.1)	6.4(0.3)
HT450		1.113 (0.002)	76 (6)	2.8 (0.4)	1.3(0.1) ; 0.2(0.2)	6.3(0.4)
HT500		1.139 (0.002)	49 (10)	3.3 (0.5)	1.6(0.1) ; 0.2(0.2)	6.4(0.4)
HT550		1.033 (0.001)	161 (17)	2.2 (0.3)	1.5(0.2) ; 0.2(0.4)	6.4(0.8)
HT575		1.023 (0.001)	156 (16)	2.1 (0.2)	1.2(0.2) ; 0.2(0.4)	6.4(0.8)
HT600		1.024 (0.001)	191 (20)	2.4 (0.3)	1.7(0.2); 0.2(0.3)	8.2(0.8)
HT650		1.030 (0.001)	206 (23)	2.3 (0.2)	1.4(0.1); 0.2(0.9)	12.7(2.0)

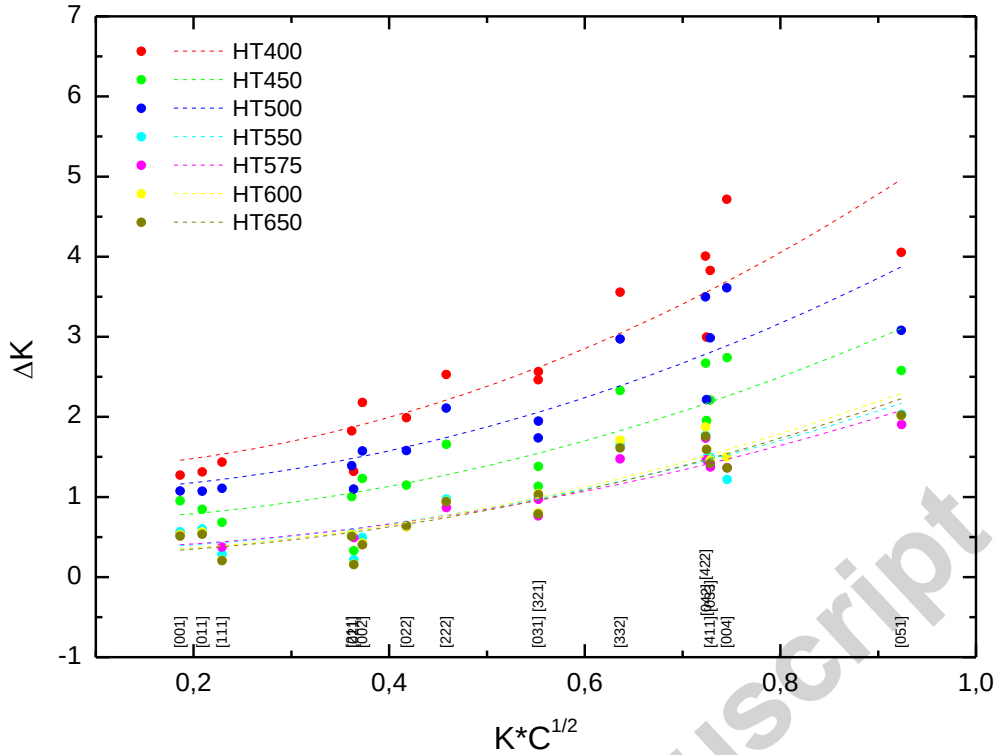


Figure 8. Modified Williamson-Hall plot (dots) of the NiTi-austenite peaks measured at 120°C for different temperatures of training: peak width (ΔK) v. peak position corrected by the average diffraction contrast factor ($K\bar{C}^{1/2}$). Dashed lines: fitted function in Eq. 7 from the dots. The Miller indexes (hkl) for each peak are indicated.

As the temperature of the heat treatment is increased, the precipitate nucleation rate seems to stabilize. But if the temperature gets higher (600 and 650°C) the growth rate of existing precipitates increases, which is a consequence of accelerated diffusion [59]. A lower number of coarser precipitates are therefore present in the matrix and this coarsening may produce a loss of precipitate/matrix interface coherency [39], this being the reason for the observed strength reduction in the HT650 sample [33]. As the material is titanium-rich the expected phase would be Ti_2Ni , but given the ternary Cu addition, this is likely to become $Ti_2(Ni,Cu)$. Moreover, crystallite size in the B19' phase is also found to change in HT600 and HT650, which means that changes in crystallite size can interact with the Ti_2Ni precipitates that are also being modified by the HT. These changes seem to be coherent with the hypothesis of a change from a coherent convalence (factor 4A) to an incoherent convalence between the matrix and the Ti_2Ni precipitates (factor 4B).

The results from SXRD confirm the points raised in the discussion section based on the other techniques studied. Factors F1 and F2 can be appreciated from the reduction in texture and microstrain (density of dislocations) shown in Table 4. Factor F3 can be detected from the crystallite size (D). Despite the fact that crystallite size has only been evaluated in the B19' phase, the absence of big differences in mechanical properties (tensile test and microhardness measurements) has shown that factor F3 does not really play an important role. Factors F4A and F4B are correlated to the presence (wt%) of Ti_2Ni precipitates. The increase in the presence of Ti_2Ni precipitates with increasing HT temperature together with the increment in crystallite size in HT600 and HT650 specimens supports the hypothesis of the incoherency of precipitate/matrix being the cause of most of the effects observed in the HT600 and HT650 specimens in

contrast with the others. Finally, the general decrease in thermomechanical properties from HT550 onward can also be attributed to the fact that the amount of retained martensite increases at high HT temperatures. In short, the SXRD results contribute to the conclusions of this work while at the same time enabling a better understanding of the effects of heat treatment temperature on the microstructure.

In order to clearly present the different mechanisms that modify the microstructure and govern the thermomechanical properties, a scheme of the tendencies of the properties measured and the hypothesis taken into account are shown in Figure 9.

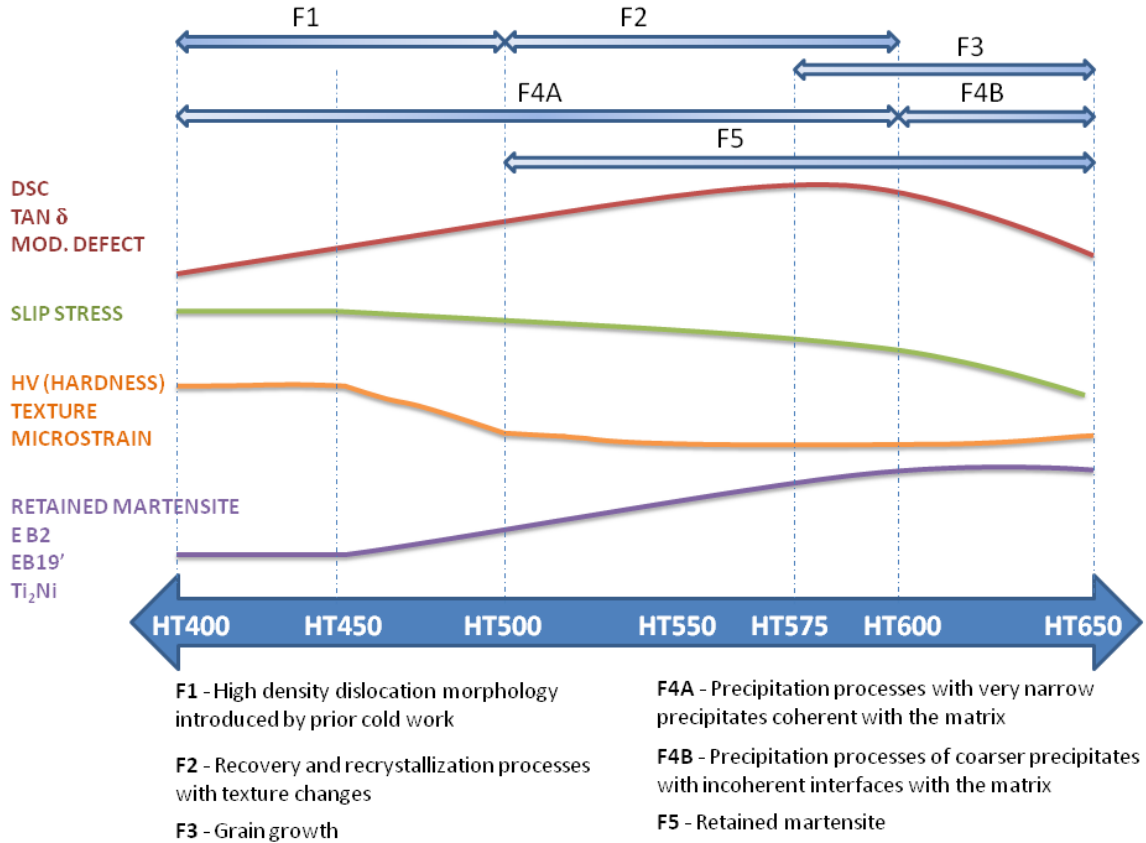


Figure 9. Scheme of the properties' tendencies measured as a function of HT temperature

Figure 9 shows a scheme of the tendencies of the different properties measured as a function of the HT temperatures. In order to identify the temperature range of each microstructural factor that governs the changes in microstructure, the different factors are displayed in the upper part of Figure 9. Although this figure is a scheme and for the sake of clarity the vertical axis is not scaled, it is still useful for giving an overall perspective of the tendencies of all the variables measured along with the links between factors. The main changes due to factor F1 can be seen in microhardness, texture and microstrain. The effects from factor F2 can be observed in all variables. Factor F3 does not play a big role because the results from tensile tests and microhardness tests showed no evidence of grain growth. Nevertheless, grain growth was identified through crystallite size. Factors F4A and F2 are together responsible for improving the thermomechanical properties of the NiTiCu alloy. The DMA results ($\tan \delta$ and modulus defect) clearly show the evolution from a textured and microstrained microstructure to an incoherent microstructure with coarser precipitates and large amounts of retained martensite (Factors 4B and 5) that diminishes the thermomechanical properties of the NiTiCu alloy. Because of this, the maximum values of $\tan \delta$ (HT575) do not correlate with the best thermomechanical performance (HT450). Factor 4B can be observed in the change of properties in HT600 and HT650 in comparison with all other HT temperatures. Factor 5 correlates with slip stress and can also be attributed to the lower thermomechanical properties identified at high HT temperatures.

Conclusions

The results presented in this study have shown that DMA analysis at a specific frequency and strain amplitude is a suitable tool for studying the effects of HT temperature on the microstructure of the Ti50Ni45Cu5 alloy. The DMA results ($\tan \delta$ and modulus defect) clearly show the evolution from a textured and microstrained microstructure to an incoherent microstructure with coarser precipitates and large amounts of retained martensite (Factors 4B and 5) that diminishes the thermomechanical properties of the NiTiCu alloy.

The effects of HT temperature on the microstructure have been contrasted with additional characterization techniques, and it can be stated that the DMA results have contributed to a better understanding of the internal mechanisms that govern the effects of HT on the microstructure.

These effects have been attributed to different factors that have been separately identified: (F1) high density dislocation morphology introduced by prior cold work; (F2) recovery and recrystallization processes with texture changes; (F3) grain growth; (F4A) precipitation processes with very narrow precipitates coherent with the matrix or (F4B) precipitation processes of coarser precipitates with incoherent interfaces with the matrix; and (F5) wt(%) of retained martensite.

Judging by the DMA and DSC results, $\tan \delta$ and ΔH present the same tendency as the temperature of the HT increases, leading to the identification of three regions that can be attributed to factors F1 and F2.

At low temperatures (HT400 and HT450), the low values of $\tan \delta$ and ΔH have been attributed to low twin boundary mobility due to high dislocation density caused by the cold work. From HT500 to HT600 a competition between the reduction in dislocations and a recovery and recrystallization process causes a stabilization of the $\tan \delta$ and ΔH . At high temperatures (beyond recrystallization temperature HT650), the decrease in $\tan \delta$ and ΔH cannot be explained only by DSC and DMA and need further experimental results.

The DMA and DSC results show a correlation with the mechanical tests (stress-strain and hardness). From the stress-strain results, it can be shown that while UTS and critical stress are more stable except for the HT650 specimen, slip stress shows a constantly decreasing rate as the HT temperature increases. Hence the mechanical tests (break tensile and hardness) also show the influence of factors F1 and F2, while at the same time confirming that factor F3 plays no significant role. The SXRD results confirm factors F1 and F2 on the basis of the reduction in microstructure and microstrain. Factor F3 was also contrasted with the crystallite size parameter measured on the diffractograms. At the same time, SXRD results prove the existence of Ti_2Ni precipitates and also support the hypothesis regarding the incoherency of the precipitate/matrix which causes most of the effects observed in the HT650 specimen in contrast to the others.

The best SMA properties are found between 400 and 575°C. Low temperatures (400 and 450°C) are not high enough to eliminate the effects of the cold work and produce decent mechanical properties and lower transformation temperatures. Medium temperatures (500 to 575) lead to higher transformation temperatures and the maximum martensitic transformation capacity (ΔH and $\tan \delta$) because of the recovery and recrystallization process from the HT temperature, but they also show a reduction in mechanical properties (slip stress). High temperatures (600 and 650) are not suitable because they bring about a reduction in transformation capacity and a huge decrease in mechanical properties (slip stress and UTS). As a result, HT450 is the best annealing temperature from a mechanical performance point of view and HT575 is the best annealing temperature for a maximum martensitic transformation capacity in terms of calorific energy and damping capacity.

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