DYNAMIC MECHANICAL ANALYSIS OF A NiTi SHAPE MEMORY ALLOY: AN EXPERIMENTAL STUDY

Niédson José da Silva, niedsonjs@yahoo.com.br
Estephanie Nobre Dantas Grassi, end.grassi@hotmail.com
Jackson de Brito Simões, eng_jacksonsimoes@hotmail.com
Carlos José de Araújo, carlos@dem.ufcg.br

Multidisciplinary Laboratory of Active Materials and Structures
Department of Mechanical Engineering
Universidade Federal de Campina Grande
Caixa Postal: 10069, Cep: 58109-970
Campina Grande – PB, Brazil

Abstract. *Shape memory alloys (SMA) are smart materials that present potential applications in several fields due their property of recover a deformation by means of a simple heating. Moreover, these functional materials exhibit high damping capacity during phase transformation or in the martensitic state. In this work a* $Ni_{54.7}Ti_{45.3}$ *(% wt) SMA was produced using the plasma skull push-pull process to study the phase transformations and damping capacity in a single cantilever mode. Plate specimens were manufactured to accomplish the dynamic mechanical analysis. The studied NiTi presented the characteristic damping peak on phase transformation and increase of storage modulus after conversion of low temperature phase to high temperature phase.*

Keywords: Shape Memory Alloys, Smart Materials, Dynamic Mechanical Analysis, Damping Capacity

1. INTRODUCTION

The technological evolution in the materials science and engineering field in the last century and the demand for better and tailored properties have originated the active materials. These materials have the capacity of reaction to environmental impulses, such as temperature, light, tension and/or electrical current, among others (Culshaw, 1996). Shape Memory Alloys (SMA) are one of these advanced materials that present mechanical responses due to thermal or magnetic fields. The property of recovering a plastic deformation by means of a suitable heating is one of the reasons why SMA are widely applicable, besides the pseudoelasticity, impact absorption and vibration damping behavior (Lagoudas et al., 2008). The Shape Memory Effect (SME) occurs as a result of the phase transformations induced in the material. These diffusionless transformations are of the thermoelastic martensitic type and happen in the solid state, providing a reversible change in the crystalline structure of the material and, consequently, a change in their micro and macro-mechanical properties. Among all SMA, the NiTi alloy have been used to develop applications in some engineering fields as aerospace, biomedical, automotive and oil exploration, mainly as thermomechanical sensors and actuators.

In recent years, SMA has started to attract increasing attention due to their superior damping properties when compared to classical structural materials. These materials exhibit high damping capacity during phase transformation and in the low temperature martensitic state (Van Humbeeck, 2003). The best damping capacity of martensite is closely related to the movement of twin interfaces and dislocations induced through processing of the material (Cai et al., 2005). The damping capacity is interesting because it can lead to a better vibration control and improve the life time of mechanical systems. Moreover, these materials also present an increase in their storage modulus, which indicate an improvement of stiffness degree during phase transformation. The martensitic phase is related to low stiffness and higher damping capacity in comparison with the high temperature parent phase (austenite), which presents high values of stiffness. Some parameters can affect the phase transformation temperatures and change the absolute values of damping capacity and storage modulus. Among these parameters are heating rate, strain amplitude and frequency (Van Humbeeck, 2003). Recently, NiTiNbMo alloy has been presented as new high damping SMA (Chen et al., 2009).

The purpose of the present work is to manufacture a NiTi SMA by the Plasma Skull Push Pull (PSPP) method (De Araújo et al., 2009) and study the damping capacity and change of storage modulus in a single cantilever mode during phase transformation by using a commercial Dynamical Mechanical Analyzer (DMA). Some comparisons with damping in classical structural materials, like aluminum and stainless steel, is performed to demonstrate the high application potentiality of these materials in mechanical structures.

2. DYNAMIC MECHANICAL ANALYSIS (DMA) - FUNDAMENTALS

Dynamic mechanical analysis is a technique used to study materials behavior under dynamic loadings. Basically the method consists in applying an oscillating force to a sample and analyzing the material's response to that force (Menard, 1999). Since most material's applications involve dynamic forces, this test has the important advantage of analyzing a sample under conditions that are similar to the real operating ones.

DMA has been widely used for the investigation of viscoelastic material properties. Polymers, polymer solutions and dispersions, amorphous materials (organic and inorganic) are examples of these materials (Meyers and Chawla, 2009). Considering that metals show this behavior only in very high temperatures, DMA is not traditionally performed on them. For the study of SMA, DMA has been more and more used due to the similarity with the viscoelastic behavior. As pointed-out in Figure 1, the stress-strain load and unloading cycle curves for a viscoelastic material are not the same (Figure 1a) as in the purely elastic case (Figure 1b). In the viscoelastic case there is a hysteresis, showed as the shaded area inside the cycle in Figure 1(a). This stress-strain hysteresis represents the energy dissipated during the cycle, and therefore, the damping. In some cases, this behavior is also present in SMA.

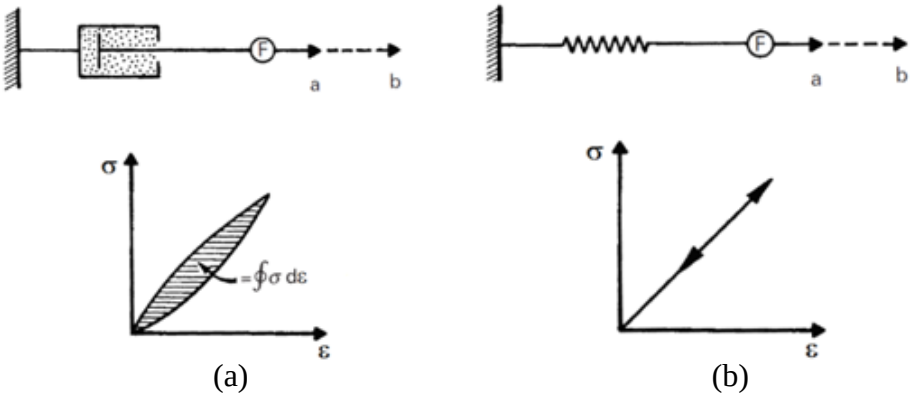

Figure 1. Stress–strain plots for (a) viscoelastic behavior (energy equal to the shaded area is lost in a load–unload cycle) and (b) elastic behavior (no energy is lost during a load–unload cycle) (Meyers and Chawla, 2009).

DMA works in the linear viscoelastic range of materials, what results that when a sinusoidal strain (or stress) is applied to a sample, a sinusoidal stress (or strain) will be measured. The two extreme cases are the purely elastic and the purely viscous. In the first, stress and strain are in phase, thus, there will be no phase lag between the curves. In the second case the curves are out of phase with a phase lag of 90 degrees. Figure 2 show that viscoelastic materials have an intermediate behavior between these two ideal cases, presenting a phase lag between zero and 90 degrees. The phase lag δ is then measured and from it we calculate the parcels of the two components in the material (elastic and viscoelastic).

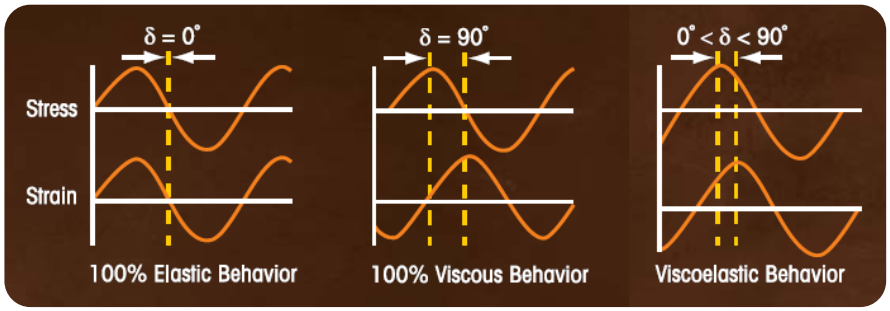

Figure 2. Difference in phase lag angle for the purely elastic case, purely viscous case and viscoelastic case (TA Instruments, 2008).

As demonstrated by Goertzen and Kessler (2006), the stress applied by DMA as a function of time at a given frequency, ω, is

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \tag{1}$$

where σ_0 is the maximum stress applied and δ is the phase lag angle present. The strain, which lags by the angle, δ, is given by

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t) \tag{2}$$

where ε_0 is the maximum strain amplitude. Through Hook's law, the input and the response are related by the dynamic modulus, *E*(ω)*,

$$\sigma(t) = E^*(\omega)\varepsilon(t). \tag{3}$$

The dynamic (or complex) modulus has in phase and out of phase components, and is given by

$$E^*(\omega) = E'(\omega) + iE''(\omega) \tag{4}$$

where the in phase, or real, portion and the out of phase, or imaginary, portion are, respectively

$$E'(\omega) = \left(\frac{\sigma_0}{\varepsilon_0}\right)\cos\delta \tag{5}$$

$$E''(\omega) = \left(\frac{\sigma_0}{\varepsilon_0}\right)\sin\delta. \tag{6}$$

The real portion of $E^*(\omega)$, E', is the storage modulus, and the imaginary portion, E'', is the loss modulus. The storage modulus represents the elastic component, related to the sample's stiffness. The loss modulus represents the viscous component, related to the ability to dissipate mechanical energy through mechanical motion (TA Instruments, 2008). The ratio of E'' and E' represents the damping, and is given mathematically by

$$\mathrm{Tan}\,\delta = \frac{E''}{E'} \tag{7}$$

Damping is a measure of how well the material can disperse energy. It lets us compare how well a material will absorb or loose energy (PerkinElmer, 2007). In Figure 3 a graphical representation of E^*, E', E'' and $\mathrm{Tan}\,\delta$ is showed. All of these parameters can be measured as a function of time, temperature, frequency and amplitude (of strain or stress) depending on the application. These different moduli allow a deeper characterization of the material, because we can now examine its ability to return or store energy, to lose energy and its damping capacity (Menard, 1999). Besides these, many others dynamic properties can be obtained as complex shear modulus, complex viscosity and complex compliance.

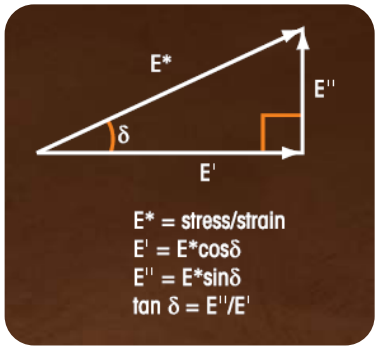

Figure 3. Complex modulus (*E**) and its components: storage modulus (*E'*) and loss modulus (*E''*) (TA Instruments, 2008).

A dynamic mechanical test can be run in many ways, depending on the kind of applied load. DMA analyzers can be free or forced resonance, strain or stress controlled and works in axial or torsional way. In each case a number of fixtures are available (Menard, 1999).

3. EXPERIMENTAL PROCEDURE

The nominal chemical composition 54.7Ni-45.3Ti (% weight) was selected on the basis of a commercial SMA used for actuator applications. The raw materials used to produce this Ni-Ti SMA were commercial pure nickel (> 99.9%)

and the ASTM F67-00 (grade 2) biomedical titanium. The SMA was produced by the Plasma Skull Push Pull (PSPP) process (de Araújo et al, 2009), which provides a prismatic bar with about 25 grams. This bar was cut off and hot-rolled to achieve plate specimens with dimensions around of 17 mm x 5 mm x 0.4 mm. For DMA tests two specimens were utilized: one in the as-fabricated state and another annealed at 450 ºC for 15 min followed by water quench at room temperature to achieve martensitic structure. The dynamic mechanical analysis was performed using a commercial equipment from TA Instruments (DMA Q800) that was used to measure damping capacity of the designed specimens. Several tests were performed varying frequency, amplitude of strain and heating rate. Moreover, some comparative tests were performed using aluminum and stainless steel specimens to demonstrate the high damping capacity of Ni-Ti SMA with regard to classic materials. Figure 4 shows the DMA Q800 model used for the dynamic tests. The clamp used for the tests in single cantilever mode is shown in Fig. 5.

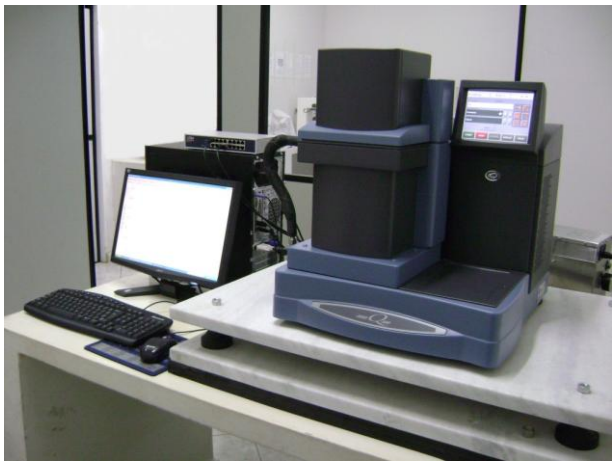

Figure 4. Dynamic Mechanical Analyzer (DMA) Q800 model from TA Instruments.

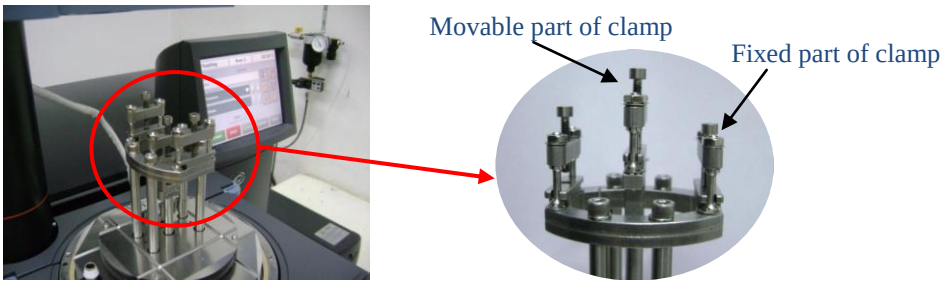

Figure 5. Single cantilever clamp.

The phase transformation temperatures of the NiTi SMA specimens were determined by electrical resistance as a function of temperature (ERT) using an apparatus specially designed for this task by Reis et al (2006). For the as-fabricated specimen these temperatures were R_s = 313.5 K (40.5 °C), M_s = 305.5 K (32.5 °C), M_f = 287.5 K (14.5 °C), A_f = 325.0 K (52.0 °C). In the case of the annealed specimen, the measured transformation temperatures were R_s = 314.6 K (41.6 °C), M_s = 308.2 K (35.2 °C), M_f = 294.3 K (21.3 °C), A_f = 332.1 K (59.1 °C). Therefore, before DMA tests the plate specimens are cooled to 243 K (- 30 °C) to assure that the NiTi SMA specimens are in the low stiffness martensitic state.

4. RESULTS AND DISCUSSIONS

4.1. Optimization of the dynamic tests parameters

The annealed NiTi specimen was employed to perform a parametric analysis in DMA. The first parameter analyzed was the frequency of excitation with values from 1 to 10 Hz. Figure 6 shows the behavior of damping (Tan δ) for a tip deflection amplitude of 5 μm and heating rate of 5 °C/min. Qualitatively there are observed three regions. The first, between 25 and 60 °C gives a medium Tan δ of 0.007 and corresponds to the damping produced by the movement of the interfaces of martensite variants. In the second region, between 60 and 90 °C, there is an important increase in damping due to the phase transformation of martensite into austenite in the solid state. In the third region, above 90 °C the material is completely transformed in the austenitic phase and the damping tends to zero (100% elastic case, Fig. 2). In terms of sensitivity to frequency, it is observed that the more pronounced damping peaks during the phase transformation occurs for values less than or equal to 2 Hz. Excitation frequencies as higher as 5 to 10 Hz, tend to

inhibit the Tan δ peak so that the damping remains almost constant until the transformation, where falls abruptly and tends to zero.

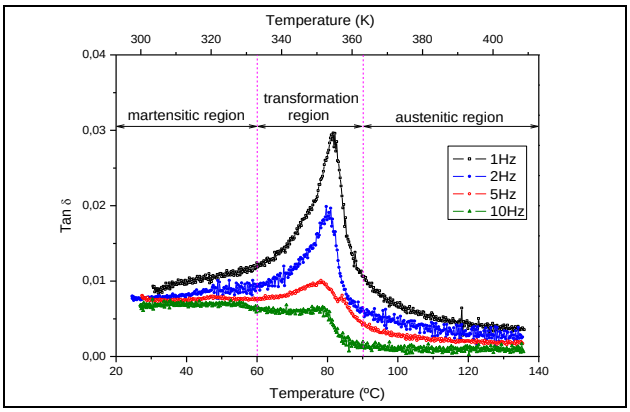

Figure 6. Frequency dependence of damping for the studied NiTi SMA.

Regarding the sensitivity of the damping with respect to heating rate, Fig 7 shows the obtained results for rates ranging between 2 and 20 °C/min. For these tests were used an excitation frequency of 1 Hz and tip deflection amplitude of 5 μm. It is observed that the increase in heating rate leads to a shift of damping peaks for regions of higher temperatures. It appears that for heating rates less than 10 °C/min this displacement does not cause change in the value of damping, which remains unchanged at around 0.035. Above 10 °C/min, the Tan δ peak becomes more pronounced with a more noisy response. This behavior can be attributed to the fact that for high heating rates, above 5 °C/min, cannot be a good uniformity of temperature throughout the volume of the sample at every time. Thus, the sample may provide regions with different structures combined between martensite, austenite and a mixture of both. According to literature, the Tan δ values of the transformation peaks decrease with decreasing the heating rate (Chang and Wu, 2008). Therefore, the heating rate of 5 ºC/min leads to a relatively fast test and a recognizable characteristic damping curve.

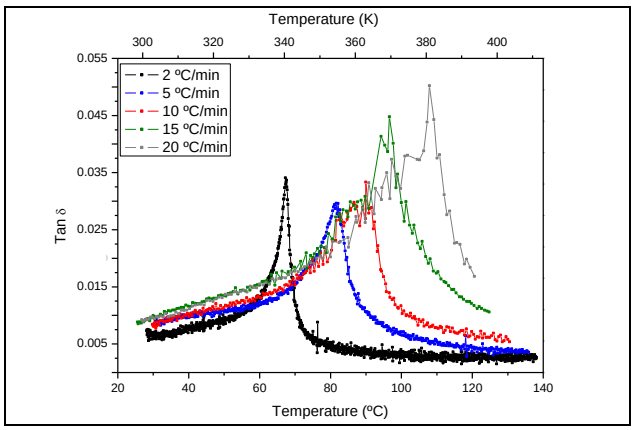

Figure 7. Heating rate dependence of damping for the studied NiTi SMA.

It was also verified the influence of oscillation amplitude (tip deflection) on the dynamic tests. Figure 8 show the obtained results for the tip deflection varying between 2 and 20 μm with a frequency of 1 Hz and a heating rate of 5 ºC/min. Amplitudes so lower present a noisy response signal, which provide hesitating values of damping capacity like the peak value observed in the obtained curve using amplitude of 2 μm. For amplitudes equal or superior to 5 μm, the response is established already, being not necessary input more force on the material, minimizing its fatigue.

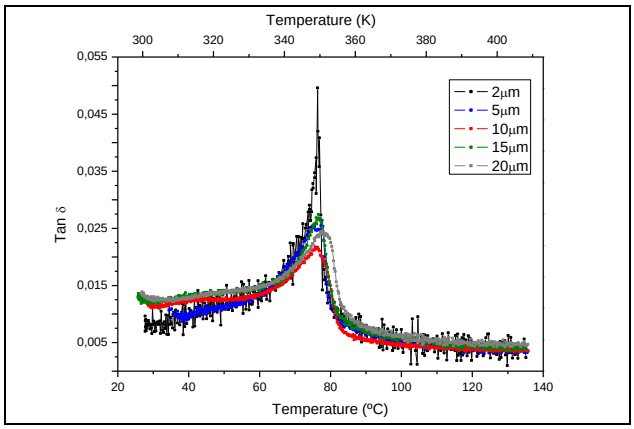

Figure 8. Oscillation amplitude dependence of damping for the studied NiTi SMA.

From the results of Figs 6, 7 and 8, the optimal parameters for evaluating the damping capacity of NiTi SMA seem correspond to a frequency of 1 Hz with displacement amplitude of 5 μm and maximum heating rate of 5 °C/min. These parameters are recommended by literature, aiming the minimum influence of them on the results (Van Humbeeck, 2003).

4.2. Damping behavior of SMA NiTi specimens

Figure 9 shows the damping capacity as a function of temperature for the annealed and as-fabricated NiTi SMA specimens. As can be observed, the SMA presents a peak of damping capacity during its phase transformation. The peak of damping is related to the movement of twin interfaces and dislocations into SMA, so that can be associated to martensitic transformation (Cai et al., 2005). It can be also verified that annealed specimen presents higher damping capacity in comparison with the as-fabricated one. This behavior can be due to the higher quantity of defects found in the last sample, which are rearranged or eliminated during the heat treatment. The annealed specimen presents higher damping capacity in low temperatures (martensitic region in Figure 6), when compared to the as-fabricated. However, the damping capacity values at austenite state (high temperatures) are almost the same for both specimens.

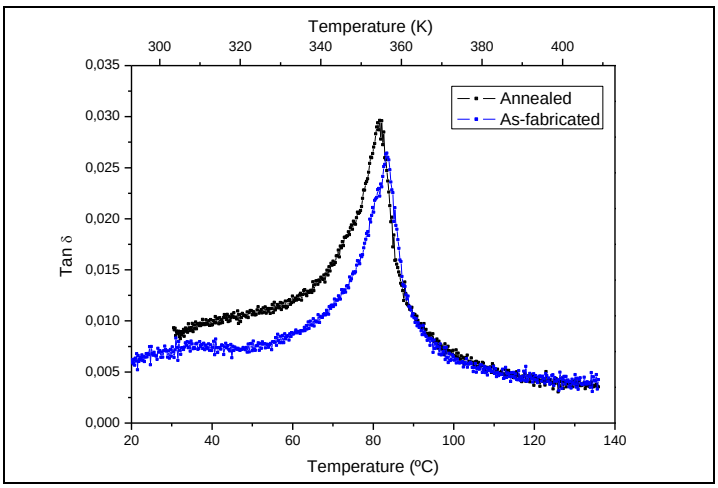

Figure 9. Damping capacity as a function of temperature for the as-fabricated and annealed NiTi SMA specimens.

Figure 10 shows the storage modulus as a function of temperature for the studied NiTi SMA specimens. It can be noted the increase of storage modulus, that indicate improvement of material's stiffness. The change that storage modulus undergo during the phase transformation process has the same reasons of damping capacity, associated to inner movement of material structure, increasing while temperature increases, which demonstrate inferior stiffness in martensitic phase whether compared with the parent phase as reported in literature (Otsuka and Wayman, 1998). Concerning transformation temperatures, there is a difference between the values obtained by ERT and DMA during heating. This occurs due to the difference of stabilization in relation to temperature between the mechanical properties captured by dynamic test and martensitic transformation instantaneously observed by electrical resistance variation (Batalu et al., 2006). Through DMA test the start of reverse transformation (A_s) can be perceived by the inflection of the modulus curve. For instance, the ERT results for annealed specimen show that the phase transformation is completed at about 332.1 K (59.1 °C) (A_f – reverse martensitic transformation finish temperature), while according to DMA results,

the mechanical properties start to stabilize at around 357.16 K (84.16 ºC). This difference becomes insignificant when the heating rate approaches zero, as established by Chang and Wu (2008). This observation is very important for practical applications involving dynamical loads or mechanical vibrations.

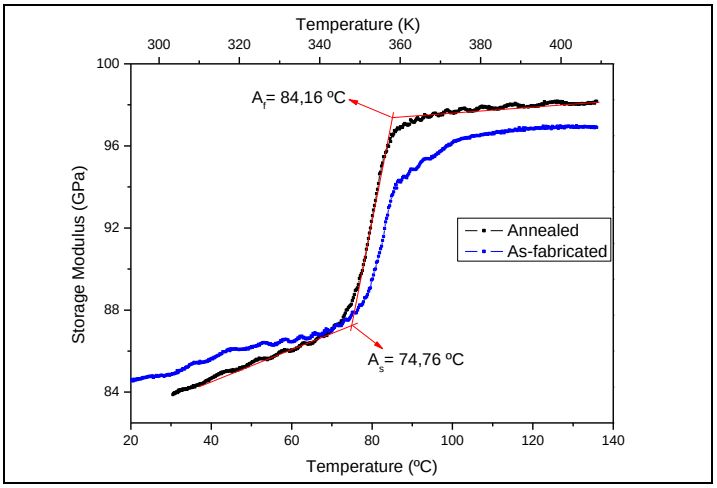

Figure 10. Storage modulus as a function of temperature for the as-fabricated and annealed NiTi SMA specimens.

Another type of test carried out with the NiTi SMA specimens was the frequency sweep between 0.1 and 10 Hz at room temperature (martensitic state) and 5 μm of tip deflection amplitude. Figure 11 show the damping behavior as a function of frequency. It can be verified that the damping capacity decreases rapidly at the beginning, between 0.1 and 1 Hz, and then decreases more slightly when the vibration frequency becomes larger than 1 Hz. These results are in according with the literature for this type of materials (Cai et al., 2005; Van Humbeek, 2003).

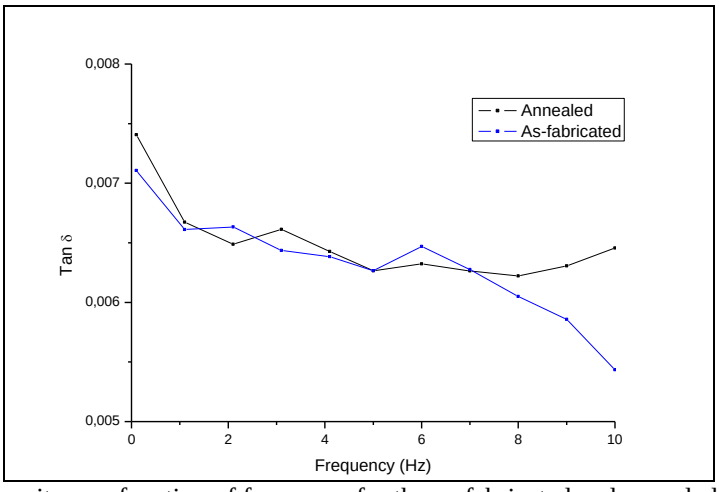

Figure 11. Damping capacity as a function of frequency for the as-fabricated and annealed NiTi SMA specimens.

4.3. Comparative DMA analysis: NiTi SMA versus classic structural materials

A comparative analysis between the studied NiTi SMA and some conventional materials was performed to verify their dynamic properties. Figure 12 shows the damping capacity behavior of NiTi SMA, aluminum and stainless steel under a temperature ramp of 5 ^{o}C/min in an optimized dynamic test (1 Hz and 5 μm of tip deflection). As can be observed, the damping capacity of NiTi SMA is much higher than classic materials at median (80 ^{o}C) and room temperature. During heating, there is a perceptive increasing of damping capacity in the classic materials, being smooth increase for stainless steel. The damping capacity of aluminum specimen also increases, but more sharply than stainless steel. At high temperatures, NiTi SMA presents a reduction of damping capacity due to its parent phase (austenite) to absorb less mechanical energy, while the aluminum demonstrate a higher damping capacity. Thus, the aluminum presents more mechanical energy absorption than SMA and stainless steel at high temperatures (above 100 ^{o}C).

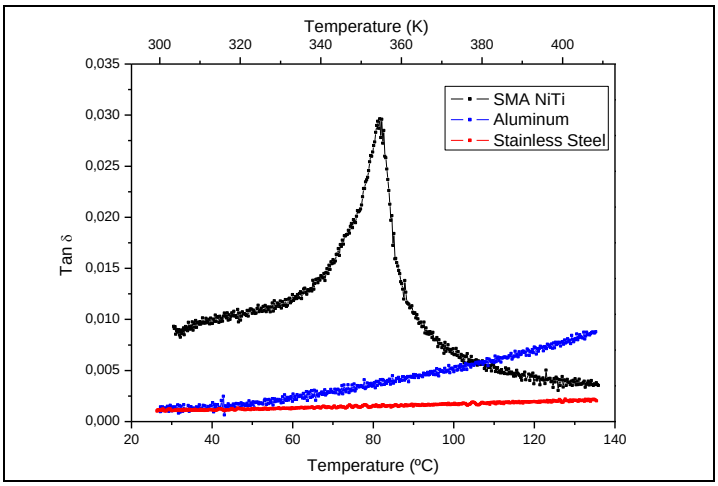

Figure 12. Damping capacity versus temperature for NiTi SMA, aluminum and stainless steel specimens.

Figure 13 shows the behavior of storage modulus for the above mentioned materials. It is verified that the stainless steel presents a larger storage modulus than another materials, which result in a higher stiffness too. The values of modulus at room temperature in Fig. 13(a) are compatible with results found in the literature (Callister Jr, 2001). Both, stainless steel and aluminum, present reduction of storage modulus when temperature increases. The NiTi SMA present completely opposite behavior, because demonstrate an increase of modulus during phase transformation. So, at high temperatures (austenitic state) the NiTi SMA specimen holds higher storage modulus and, consequently, higher stiffness than at low temperatures (martensitic state). In Figure 13(b), it can be seen that the classic structural materials presented a decrease of about 5 % in storage modulus for the temperature range studied, while SMA increase modulus in 16% due to phase transformation. This modulus improvement in SMA is a behavior well known from literature (Otsuka and Wayman, 1998; Lagoudas et al, 2008).

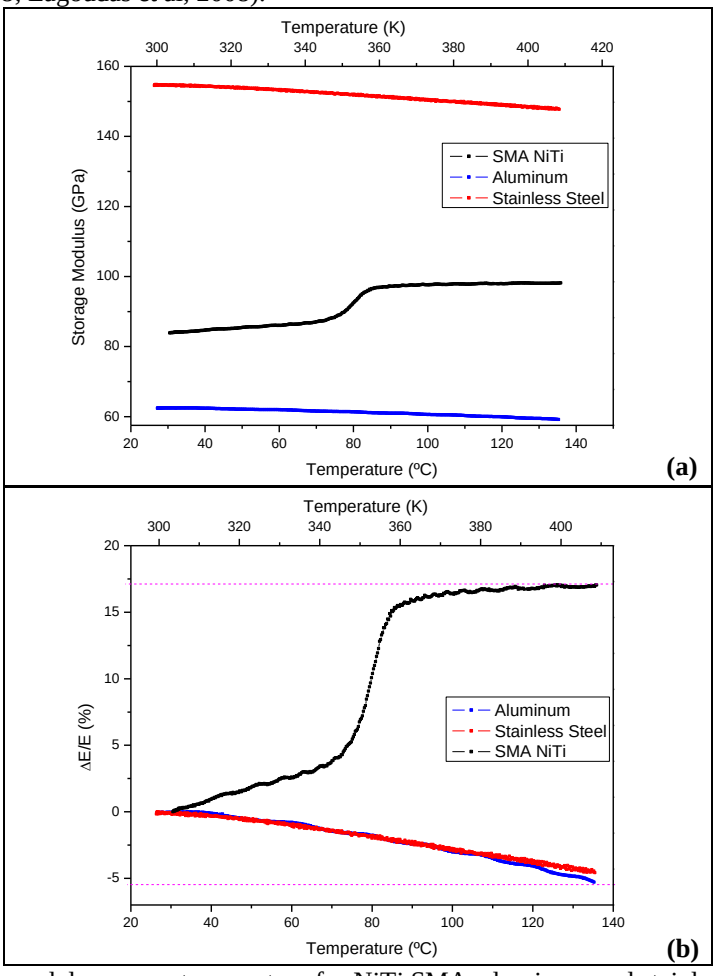

Figure 13. Storage modulus versus temperature for NiTi SMA, aluminum and stainless steel specimens. (a) Absolute values. (b) Relative change.

5. CONCLUSIONS

The casting by Plasma Skull Push Pull was performed successful obtaining a prismatic bar of the designed NiTi SMA, which was hot-rolled to obtain plate specimens for ERT and dynamic tests. On the whole, the dynamic mechanical analysis of NiTi SMA, stainless steel and aluminum can be summarized as follows:

- The suitable parameters for realization of dynamic tests were analyzed and found to be frequency of 1 Hz, heating rate of 5 ºC/min and 5 μm of oscillation amplitude as best parameters for optimum results;
- Upon heating, the annealed and as-fabricated NiTi SMA specimens present the same qualitative behavior of damping capacity. The annealed specimen demonstrated higher values of damping capacity due to a fewer density of defects into structure after heat treatment. Then, an annealing treatment for NiTi SMA can apparently enhance the damping capacity during phase transformation. The high damping capacity of NiTi SMA specimens is closely related to the movement of twin interfaces and dislocations during transformation;
- For devices based on shape memory effect, the difference between phase transformation temperatures indicated by ERT and DMA tests, and the stabilization temperature of mechanical properties should be considered. Moreover, this difference becomes insignificant when the heating rate approaches zero;
- All absolute values for damping capacity and storage modulus are in agreement with literature, as well as the behavior before, during and after martensitic phase transformation;
- The results of frequency sweep at room temperature on the NiTi SMA specimens is also reported in literature, presenting a decrease of damping capacity from 0.1 to 10 Hz;
- The comparative study between conventional materials and NiTi SMA using dynamic analysis has shown the high damping properties that SMA present, what confers to it several possibilities of applications in engineering. The classic materials present an almost linear behavior of damping capacity and storage modulus while increasing temperature, in opposition with SMA, which presents a high damping capacity peak and increase of storage modulus during phase transformation.

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