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INFLUENCE OF DEEP CRYOGENIC TREATMENT ON THE CYCLIC BEHAVIOR OF A PSEUDOELASTIC $NI_{57}TI_{43}$ ALLOY

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Abstract. *This work investigates the influence of Deep Cryogenic Treatment (DCT) on the cyclic behavior of a pseudoelastic $Ni_{57}Ti_{43}$ Shape Memory Alloy. The studied material is a $Ni_{57}Ti_{43}$ drawn wire of 3.81 mm diameter that presents an A_f of 3.31 ºC, therefore a pseudoelastic behavior is expected at room temperature. The test specimens were machined accordingly to ASTM E-466-15 for force controlled fatigue testing in metallic materials and half were submitted to cryogenic immersion of 24 hours. Both treated and non treated specimens were submitted to a cyclic tension testing. To define the stress levels at the fatigue testing, tensile tests were taken adopting the methodology covered in the ASTM F-2516-06. The fatigue tests were conducted on a MTS 647 Hydraulic Wedge Grip. The initial, intermediate and final pseudoelastic curves of treated materials were compared to the ones obtained from the cycling of non treated materials. The results show an increase of the maximum strain, residual strain and hysteresis area for the specimens submitted to the DCT.*

Keywords: NiTi, Pseudoelastic Effect, Deep Cryogenic Treatment, Fatigue Testing, Microstructure

1. INTRODUCTION

Shape Memory Alloys - SMA - are a subgroup of the smart materials group. Leo (2007) defines smart materials as a group of materials with the ability of coupling distinct physical domains. This domain is characterized by two state variables that describe a transition between these domains. In the case of the SMA, the transition between the mechanical domain (having stress and strain as variables) and the thermal domain (characterized by temperature and entropy) gives the SMA the ability to sense an external stimuli and react with a change in its properties as a response, that can be physical or mechanical (Leo, 2007; Rao et al., 2015).

The domain transition in the SMA is based on the martensitic phase transformation, which is a phase transformation that presents an atomic coordinated reordering of the material without diffusion. The SMA are characterized by two phases: the austenite high temperature phase, that presents an ordered *B2* cubic crystalline structure, in the case of NiTi alloys, and the martensite low temperature phase, that presents the *B19′* structure, also in the case of NiTi alloys (Otsuka and Wayman, 1998; Rao et al., 2015). The martensitic phase can have either tetragonal, orthorhombic or monoclinic structures. There is an intermediate phase called *R-phase* because of its rhombohedral crystal structure, but it generally vanishes with heat treatments at elevated temperatures (Lagoudas, 2008).

The SMA present two thermomechanical phenomena: the Shape Memory Effect (SME) and the Pseudoelasticity (PE). The SME is observed when the material is in the martensitic phase. Under certain level of load the material undergoes large strains that are fully recovered upon heating. The Pseudoelasticity, also known as superelasticity, is observed in the austenitic phase. As the material is mechanically loaded, it presents a linear elastic zone until reaches a plateau of stress, when the material begins to deform without relevant increase in the stress levels but with a large deformation. This plateau represents the beginning of the martensitic transformation induced by tension, when the martensite percentage starts to rise, until the transformation is complete. Then, the material presents another linear elastic zone for the *martensite* phase. During the unloading process, the material recovers its original form passing by a different path between the relation of stress and strain. This effect gives the material the ability to recover large strains, such as 8 % for NiTi alloys (Funakubo, 1987; Otsuka & Wayman, 1998; Lagoudas, 2008; Rao et al., 2015; Elahinia, 2015).

The near equiatomic NiTi alloys are widely explored in medical and industrial applications not only due to its phenomenology, but also by its good corrosion resistance and biocompatibility because of the passive TiO_2 layer (Lagoudas, 2008; Rao et al., 2015). Normally, NiTi alloys are applied in actuators and dampers, i.e, devices that, when submitted to mechanical or thermal loads, present a unique behavior (Barcelos, 2018; Mahtabi, 2016; Barbero, 2004). More than 90 % of all commercial shape memory applications are NiTi, NiTiCu or NiTiNb alloys (Elahinia, 2015).

Systems that uses the SMA rarely are designed for a strain greater than 6 % (Rao et al., 2015). Some examples of applications are: smart concrete structure (Rao et al., 2015), Active Hatch vent (Elahinia, 2015), Smart Wings in the aircraft industry (Barbarino et al., 2014), artificial muscles and superelastic braces (Jani et al., 2014).

Structural fatigue is responsible for 50 to 90 % of the mechanical failures in materials (Stephens et al., 2001; Elahinia, 2015). This kind of failure represents the change in the material's properties until the fracture occurs (Bathias and Pineau, 2010). When it comes to the SMA, there is also the functional fatigue (Eggeler, 2004). This kind of fatigue can be divided into three groups: i) the mechanical cycling with constant temperature and varying stresses, ii) the thermal cycling with no stress and varying temperatures and iii) thermomechanical cycling with constant stress and varying temperatures. The functional fatigue is characterized by the degradation of mechanical properties from a smart alloy. It causes loss of material functionality, therefore the material will no longer present its interesting properties. (Castilho, 2017; Mammano, 2017). For the same number of load cycles, NiTi alloys can tolerate strain amplitude ranging from 4 % to 12 %, while most of other metals tolerates a total strain of usually around 1 % (Elahinia, 2015). Therefore, mathematical models and standard methodologies for fatigue analysis cannot be applied to SMAs (Maletta, 2012).

The Deep Cryogenic Treatment (DCT) has demonstrated that low temperature treatments can bring many benefits to metals such as increasing hardness, wear and corrosion resistance (Huang et. al, 2003). The DCT is a technique that consists in the total immersion of the material in liquid Nitrogen (-196 ºC) and its maintenance for a specific period of time. Then the material is slowly heated in order to avoid abrupt temperature changes (Wuzbach and Defelice, 2004). Recent studies showed some alterations of the SMA's properties that were cryogenically treated, the alterations observed on mechanical properties are: increase of the damping characteristics (dissipated energy) and decrease of Young's modulus and hardness. (Castilho, 2017; Cruz Filho, 2017).

Knowing that the pseudoelastic NiTi devices (dampers or actuators) are constantly submitted to cyclic loads, the study of how the DCT influences its fatigue life becomes interesting and important for those applications. This work intends to investigate what are the consequences from the microstructural point of view of the DCT in the functional fatigue of this alloy.

2.   MATERIALS AND EXPERIMENTAL METHODS

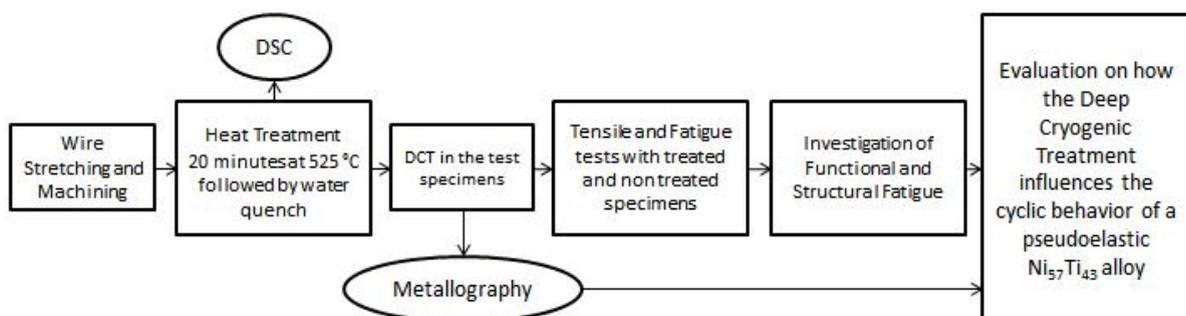In Figure 1 a flow chart of the main tasks in the work is shown.

Figure 1. Flow chart of the study.

The material is a NiTi drawn coiled wire of 3.81 mm diameter. Initially the wire has to be cut, stretched and machined accordingly to ASTM E-466-15. A sample of the material was reserved to analyze the chemical composition using XRF/EDX. After the process of machining, the material is heat treated. The test specimens can be seen in Fig. 2a. A couple of samples were taken in order to analyze the transformation temperatures using Differential Scanning Calorimetry (DSC). Then, half of the test specimens were cryogenically treated in a 24 hour period using the nitrogen tank Dewar YDS 20-50, as shown in Fig. 2b.

Figure 2a. Test specimens.

Figure 2b. Nitrogen tank Dewar YDS 20-50.

To investigate if the DCT influences the material from a microstructural point of view, two samples, a treated and non treated, were analyzed. Both samples were cold mounted in polyester resin, grinded with 120, 220, 400, 600, 800, 1000, 2000, and 2500 grit SiC, polished with a 1 to 0,3 µm Alumina suspension and cleaned in a 10 minute alcohol bath in a QUIMIS Q335D ultrasonic cleaner.

According to ASTM E407-99, the chemical etchant and procedure utilized to reveal the general structure of the two samples of NiTi was a 70 second swab made by HF + HNO_3 + H_2O (1:4:5). After the chemical etching, the microstructure was analyzed utilizing the LEXT OLS 4100 Confocal Microscope.

In order to know the stress levels of the material, two tensile tests are going to be done: one in a DCT treated and another in a non treated test specimen following the procedure of ASTM F-2516, specifically for pseudoelastic NiTi alloys. So, after the tensile tests, stress levels are going to be defined and the fatigue tests are going to initiate. From the results, the evaluation of the Functional and Structural Fatigue will depend on the analysis of the curves, plotted with the data that was collected in tests executed on an MTS 647 Hydraulic Wedge Grip. In Figure 3 is shown how the fatigue experiments were conducted.

Figure 3. MTS 647 Hydraulic Wedge Grip used on fatigue tests.

3.   RESULTS AND DISCUSSIONS

To discover the chemical composition of the NiTi alloy, a sample of the material was sent to a Dispersive Energy X-Ray Fluorescence Spectrometer (XRF/EDX) after an ultrasonic bath. The alloy presents a chemical composition of: 57.4 % Ni, 42.4 % Ti and 0.2 % Fe.

After the Heat Treatment, a DSC test was made in order to investigate the transformation temperatures of the material, shown in Tab. 1, to assure that the alloy presented the pseudoelasticity, i.e, the A_f (*Austenite* Finish) temperature has to be lower than the temperature room.

Table 1. Transformation Temperatures.

Transformation	Temperature (ºC)
As	-7.41
Af	3.31
Ms	-39.40
Mf	-61.07

The first step of the study was to determine the stress parameters for the cyclic tensile test. The tension testing was conducted for each specimen, as received and cryogenically treated, following the method designated in ASTM F2516-06. This standard test method is specific for superelastic materials. The hysteresis loops are shown in Fig.4a and Fig.4b.
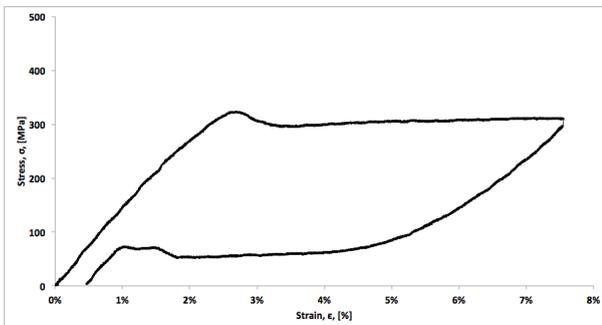

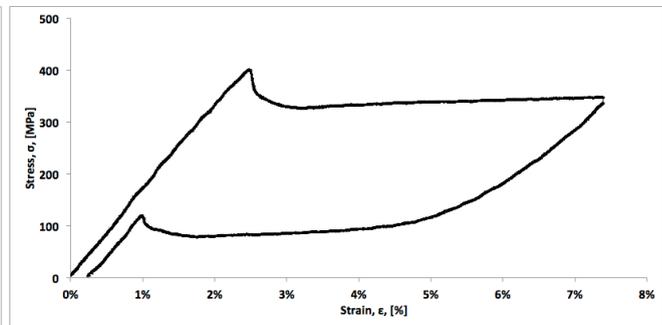Figure 4a. Hysteresis loop of non-treated sample   Figure 4b. Hysteresis loop of treated sample

To cover different spots of the material's hysteresis loop, it was chosen four peak stresses for the fatigue tests. One of them is situated in the austenite elastic region, two in *plateau* region, and one in martensite region. The peak stresses selected were: 400 MPa, 450 MPa, 500 Mpa and 550 Mpa. The Table 2 shows the relevant properties obtained during this test for the determination of the peak stresses in the fatigue tests.

Table 2. Experimental results for tension testing of $Ni_{57}Ti_{43}$ of specimens as received and after cryogenic treatment

Properties	As Received	Cryogenically treated
Upper Plateau Strength (MPa)[1]	300	330
Lower Plateau Strength (MPa)[1]	55	85
Residual Elongation	0.45 %	0.25 %
Hysteresis Area (MJ/m³)	12.60	12.79

[1] measured at 24 °C

The stress test results showed an improvement of the properties alloy after it receives a cryogenic treatment. Both Upper Plateau and Lower Plateau Strength were dislocated by 30 MPa, meaning 10 % and 54.5 % of increase respectively. Also, the residual elongation was decreased by 44.4 % and the hysteresis area increased by 1.5 %.

The next step of the experiment was to compare the hysteresis curves obtained with the data collected in the fatigue tests. The hysteresis area is responsible for the dissipated energy of SMAs (Maletta et al., 2014). The evolution of the pseudoelastic behavior for a stress peak of 400 MPa, 450 MPa, 500 MPa and 550 MPa can be verified in Fig. 5, Fig. 6, Fig. 7 and Fig. 8, respectively.
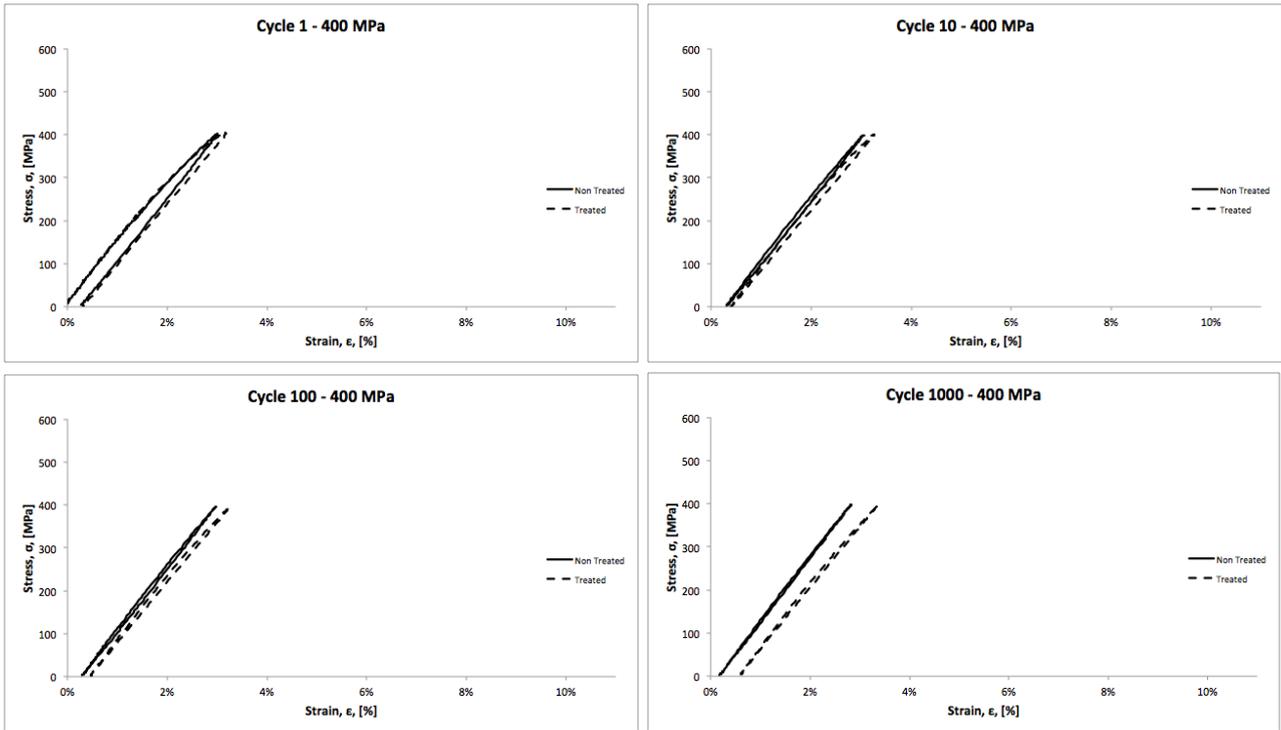

Figure 5: Evolution of the pseudoelastic behavior for a peak stress of 400 MPa.
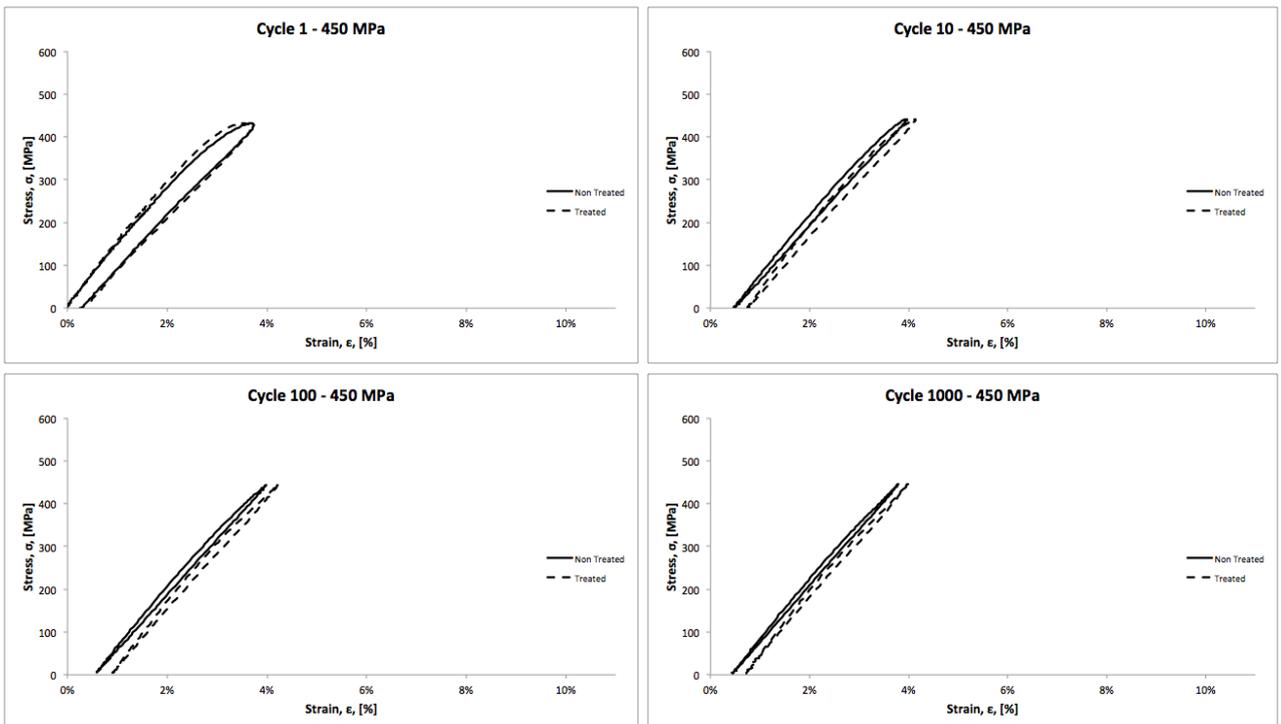
Figure 6: Evolution of the pseudoelastic behavior for a peak stress of 450 MPa.
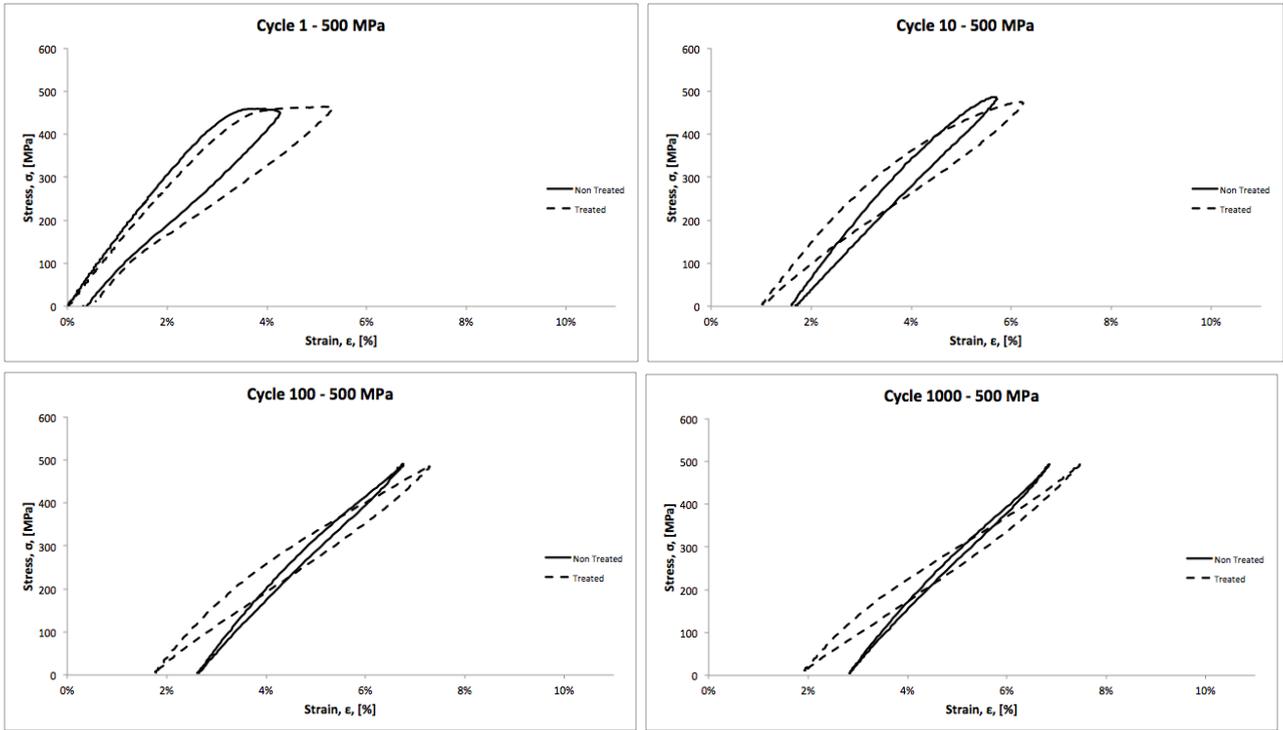

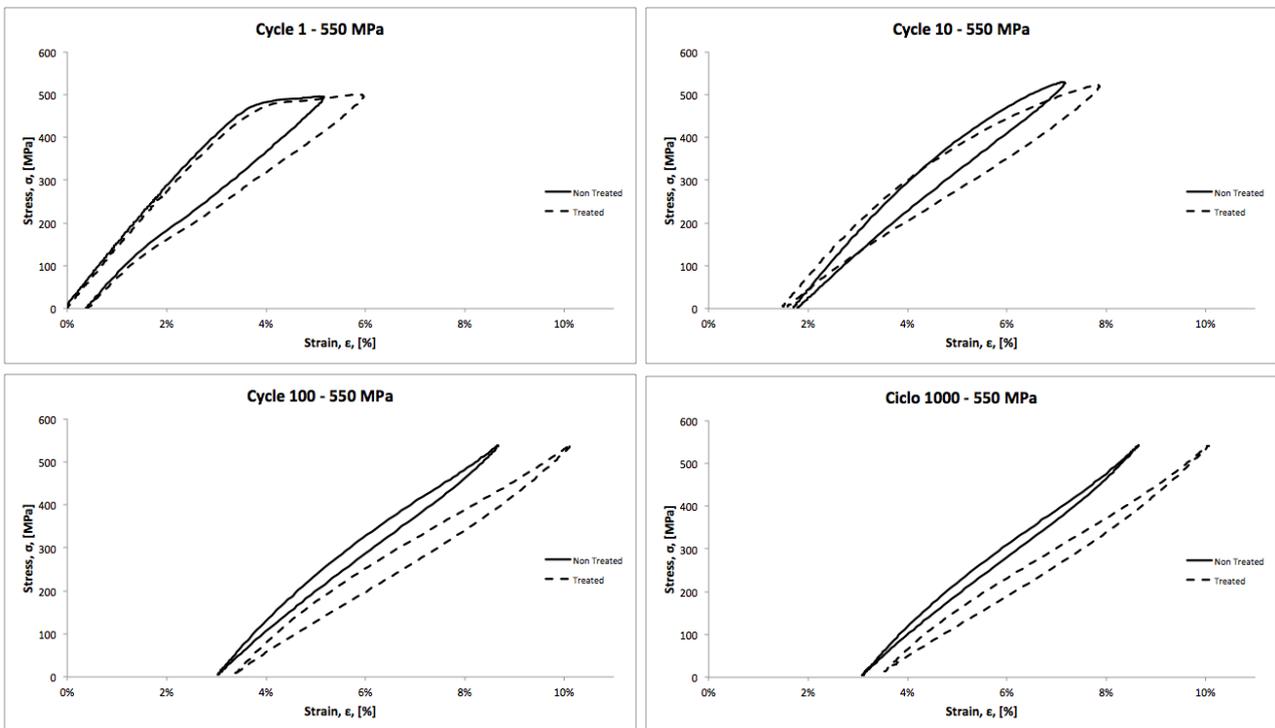Figure 7: Evolution of the pseudoelastic behavior for a peak stress of 500 MPa.

Figure 8: Evolution of the pseudoelastic behavior for a peak stress of 550 MPa.

It is possible to observe a ratcheting, accumulation of irreversible strain, at the end of each loading cycle for the treated and non-treated specimens (Rao et al., 2015). The treated samples presented a larger residual strain compared to

the non-treated ones, except the peak stress of 500 MPa. Also, the hysteresis area for each cycle was increased with the DCT, which matches the results obtained by Castilho (2017) and Cruz Filho (2017) that indicated an increase in the dissipated energy.

Both microstructures are shown in Fig. 9 with a 200X magnification.
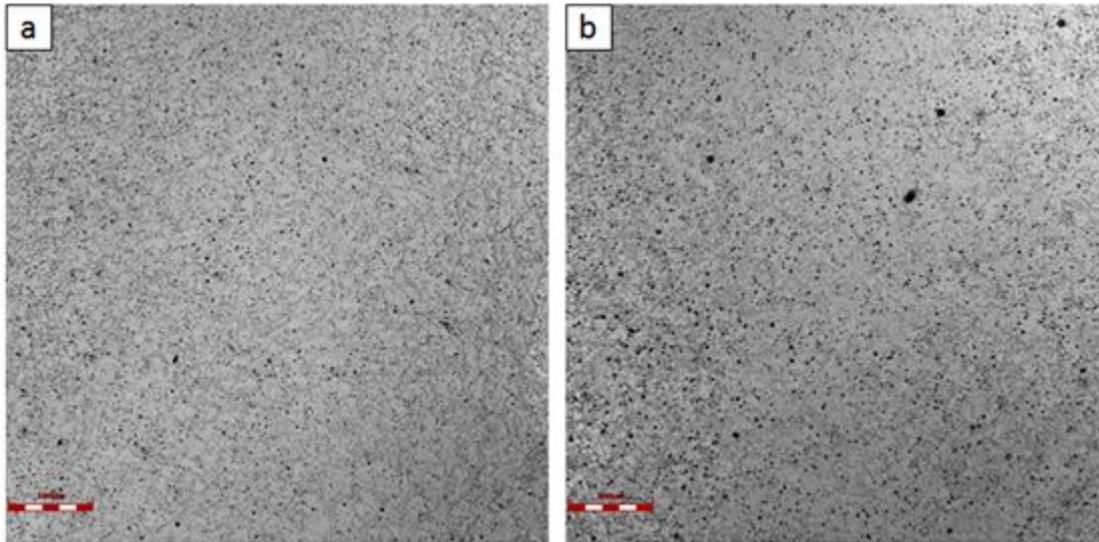

Figure 9. Microstructure of a cryogenically non treated (a) and treated (b) specimen.

It is clear that when it comes to general structure and its morphology, the cryogenically treated specimen did not show great variation when compared with the sample of the non treated material. The difference in the samples are mainly due to the presence of some black spots in the treated specimen. Castilho (2017) worked with a similar material and made EDS-SEM tests focusing on resembling precipitates of a $Ni_{57}Ti_{43}$ austenitic alloy, which were identified being a Ti_4Ni_2O. Those kind of precipitates are commonly generated at the fabrication process of NiTi alloys (Saburi, 1998; Otubo, 2006).

4. CONCLUSION

The DCT increases the dissipated energy, indicating an improvement of an important property for applications evolving seismic systems. Meanwhile, the influence of a larger residual strain should be evaluated according to the design. Future studies will investigate if those factors are correlated with the increase of precipitates. The pseudoelastic behavior of both treated and non-treated specimens was stabilized around 100 cycles. The results observed rose a hypothesis that the DCT increases the martensite retained percentage when compared to a non treated specimen.

5. ACKNOWLEDGEMENT

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