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INFLUENCE OF HEAT TREATMENT ON PHASE TRANSFORMATION OF PSEUDOELASTIC NITI ALLOY

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Abstract. *Shape memory alloys (SMA's) are a group of metallic materials that are able to retrieve their original geometry (or develop considerable restitution forces when restrict their recovery) through a field of temperature and/or stress, due to martensitic phase transformations. The pseudoelasticity (PE) and shape memory effect (SME) are the two main behaviors presented by these alloys and are associated respectively to mechanical and thermally induced martensitic transformations. The aim of this work is to study the effects of heat treatment temperature on the microstructure and phase transformation temperatures of the NiTi alloy (57% Ni-43% Ti). The study of the phases present and their transformation temperatures were conducted by differential scanning calorimetry (DSC). The samples were heat treated at 350°C and 600°C for 30 minutes and then water cooled to room temperature. After the DSC analysis, was observed that the sample "as received" presents austenite and R phases during heating, and a martensite and R phases on cooling. At 600°C the R phase was solubilized and the offset of the Af, As, Ms and Mf temperatures were changed. Hardness testing, metallographic and micro hardness were also performed.*

Keywords: *NiTi pseudoelastic, phase transformation, heat treatment.*

1. INTRODUCTION

Shape memory alloys (SMA) are such that have a distinct property of pseudoelasticity and/or shape memory. Both of these properties are directly associated to the martensite - austenite phase transformation. There are many alloys that have these properties (CuZnAl, CuAlNi, AuCd, NiTiNb and others), but the NiTi alloy exhibits excellent mechanical properties that have been used and studied for decades (Ostuka, 1998).

The shape memory effect and superelasticity are based on a diffusionless martensitic phase transformation. In the shape memory effect the alloy presents a martensite phase at room temperature and upon loading, at temperature that is under the austenite start (A_s), can be deformed, recovering its initial form upon heating above the final austenitic transformation temperature (A_f). The effect of pseudoelasticity works similar to the shape memory effect, but the temperature that the loading occurs must be above the A_f. After unloading the alloy it will recover its original state without the need of heating (Moringa, 1992). It is important to know that NiTi alloys can recover a deformation that reach as far as 10% (Gil, 1998). The pseudoelastic property is important to increase the damping capacity of the material, since it increases the energy dissipation of the alloy.

The heat treatment is used on many alloys and can change the properties on the SMA. In the case of a NiTi alloy the type of heat treatment chosen can change the austenite and martensite transformation temperatures and the thermal hysteresis that is part of this range of temperatures (Magela *et al.*, 2009). Another important characteristic of this kind of treatment is that you can solubilize the R phase present on most of the NiTi alloys. The R phase occurs because of the presence of Ti_3Ni_4 precipitate on the rich Ni alloy and can increase the size of the thermal hysteresis on the transformations temperature and the alloy hardness (Otsuka, 2005; Santos, 2006).

This works focuses on the 350°C and 600°C heat treatments with water quenching and their effect linked to it on the mechanical properties of the alloy.

2. EXPERIMENTAL PROCEDURES

For the present study a bar with a diameter of 8mm was used, composed of NiTi with a nominal range of 54.5% to 57% of Ti. The x-ray fluorescence procedure was performed by EDX-720 to obtain the chemical composition of the as received material.

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As aforementioned, different types of heat treatments were performed to compare their effect on transformation temperatures. To perform these treatments a Nabertherm GmbH LHT 04/17 oven was used. The samples are heat treated at 350°C and at 600°C for 30 minutes, using a 7°C/min heating rate to reach the desired temperature and then all samples were water quenched at room temperature. In the Tab. 1 are showed the acronym for each sample.

Table 1 - Samples acronym

Samples	
Acronym	**Treatment**
AR	As Received
HT350	Heat treated at 350°C
HT600	Heat treated at 600°C

The samples were cut in smaller sizes using a Struers Secotom 15 precision cut-off. To prevent any undesirable transformation or deformation, all the cutting procedures were done using a coolant and performed at a slow displacement of 0,005mm/min. To prepare the samples for the metallography process, the procedures described in the ASTM E-384 were used, and the procedures on ASTM E3 were selected in order to prepare them for the microhardness (HV0,5) tests. Every sample was flattened, grinded and polished according to its own normative process. The Rockwell C (HRC) hardness tests and the microhardness (HV0,5) were performed on an Identec Zwick/roell durometer.

The samples were etched using a solution of acetic acid, nitric acid and hydrofluoric acid. Later the microstructure was analyzed by scanning electron microscope using a JSM-7001F Scanning Electron Microscope, under a vacuum atmosphere of $3.6x10^{-4}$ Pa.

The microstructures of the specimens are observed by scanning electric microscope. In order to obtain the phase transformation temperatures, the differential scanning calorimetry (DSC) method was used. The heating rate and cooling rate were of 10°C/min, going from the initial temperature of -100°C to the final temperature of 100°C. To establish a precise reading of the results, two cycles were used: the first one starting at the ambient temperature and the second one from the -100°C temperature. To perform the differential scanning calorimetry a Netzsch 200 F3 Maia was used.

3. RESULTS

3.1 X-ray Fluorescence

Since the alloy composition is really important, the x-ray fluorescence was used to obtain the chemical composition of the as received material (table 2).

Table 2 – Chemical composition of as received NiTi alloy.

	Component Elements (w.t.%)
Element	**XFR**
Ni	57.446
Ti	42.235
Ca	0.159
Fe	0.1
Ac	0.059

As can be seen on the Tab. 2, this alloy presents around 57% w.t. Ni. In the NiTi alloys the Ni element tends to stabilize the austenitic phase and that way increasing the pseudoelastic property of this material.

3.2 Hardness and Microhardness

The hardness and microhardness tests on the alloy as received (AR) and after heat treatments (HT350 and HT600), were performed.

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Table 3 – HRC values to the CR, HT350 and HT600 samples

HRC		
CR	**HT350**	**HT600**
43.5 ± 0.7	47.3 ± 0.5	39.5 ± 0.7

Table 4 – HV0,5 values to the CR, HT350 and HT600 samples

HV0,5		
CR	**HT350**	**HT600**
468 ± 16	337 ± 14	234 ± 8

As seen on Tab. 3 and Tab. 4, the heat treatment altered the hardness of the samples. The increased hardness found on the HT350 is due to the increased amount of precipitate Ti_3Ni_4 found in this alloy (Villamarin, 2013). The higher temperature used on the heat treatment of the HT600 sample increases the solubilization of the precipitates, thus decreasing the hardness.

3.3 Scanning Electron Microscope (SEM)

As can be seen comparing Fig. 1 and Fig. 2 there was a grain growth after heat treatment at 350°C.

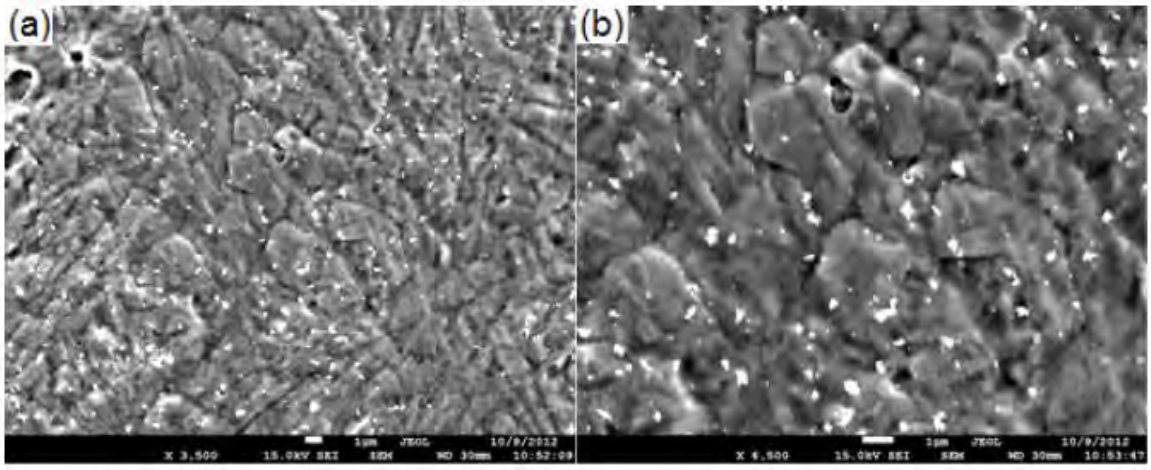

Figure 1 - SEM of the sample as received.

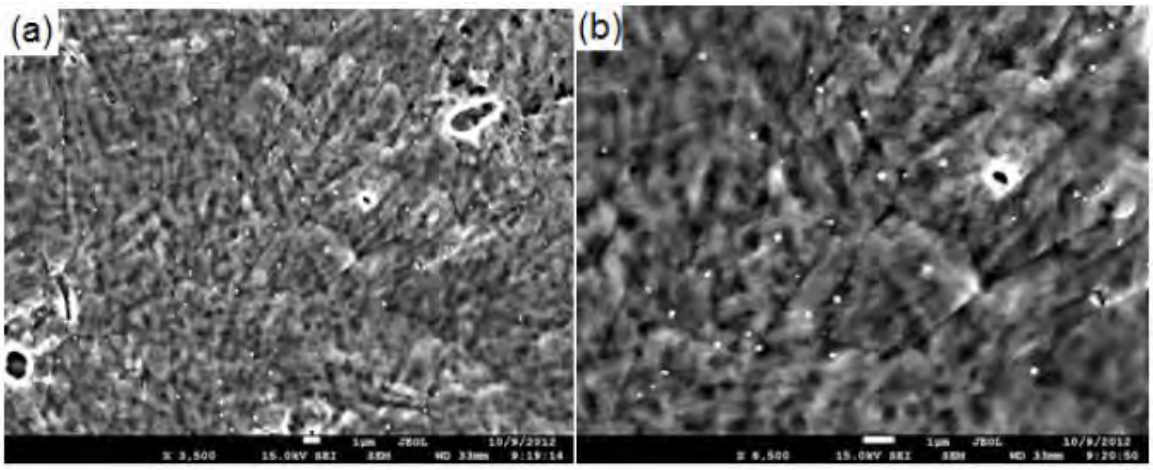

Figure 2 - SEM of the sample HT350.

Comparing Fig. 1 and Fig. 3 a smaller grain size can be observed. This is due to the recrystallization of the material structure during the heat treatment (Padilha, 1996).

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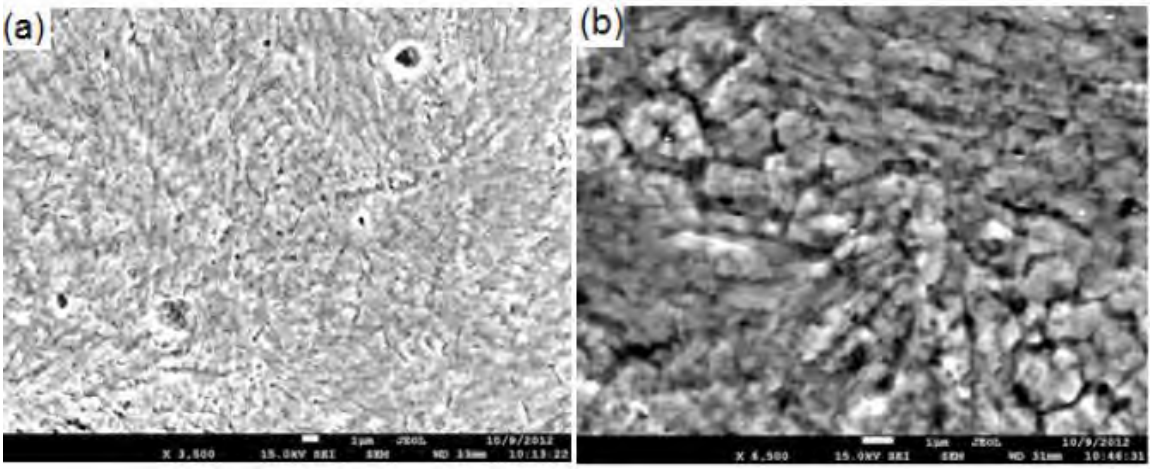

Figure 3 - SEM of the sample HT600.

3.4 Differential Scanning Calorimetry (DSC)

The DSC analyses were done using the heating and cooling curve as shown on Fig. 4.

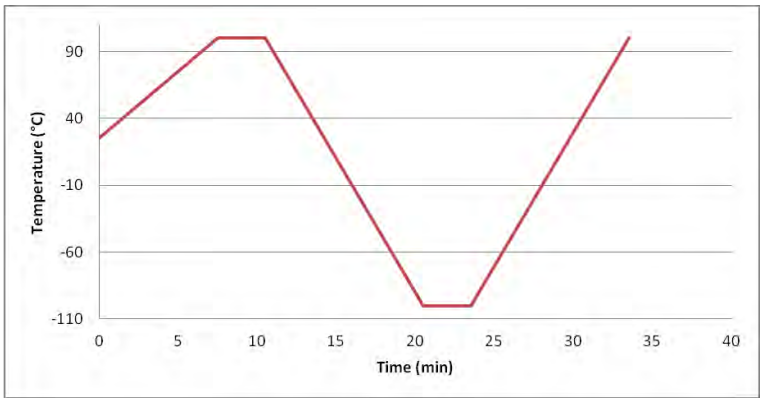

Figure 4 - DSC Heating and cooling curves

Figure 5 shows the transformation temperatures of the sample as received. On the heating step there are two exothermic peaks between the temperature of As (-41.2°C) and Af (-6.6°C). These peaks could be from the transformation from the phase B19 (martensite) to phase R and from phase R to the final phase B2 (austenite). Upon cooling there are also two peaks, in this case endothermic peaks, the bigger one is has the martensite start (-74.7°C) and martensite end (-98°C) and the smaller peak is the R phase that starts at 11.5°C and ends at -60.2°C. So, looking the temperature of phase transformations, figure 5, is possible to confirm that the as received material is fully austenitic at room temperature.

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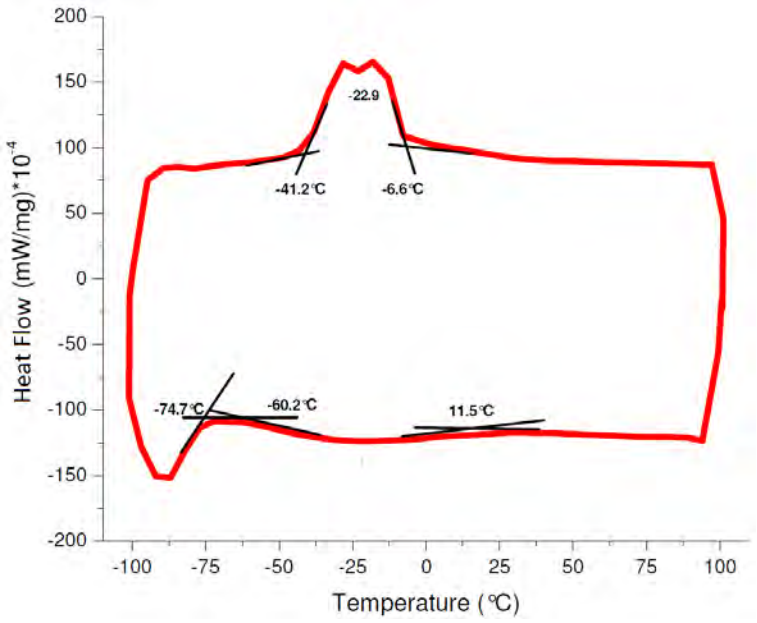

Figure 5 - Sample as received DSC

Figure 6 shows the transformation temperatures of the HT350 sample. In this case two peaks again compose the total austenitic and martensitic transformations, so, the transformation occurs in two steps. The austenite transformation goes from a martensitic phase to an R phase and later to an austenite phase, and the reverse transformation goes from an austenite phase to an R phase and later to a martensitic phase. On the heating the phase R transformation starts at 5.6°C and the Af is at 49.53°C; on the cooling the transformation from austenite to the R phase starts at 42.35°C and ends at 23.75°C, and later the martensite transformation starts at -44.95°C and ends at -83.73°C. So, the HT350 sample presents an austenite and R phases at room temperature.

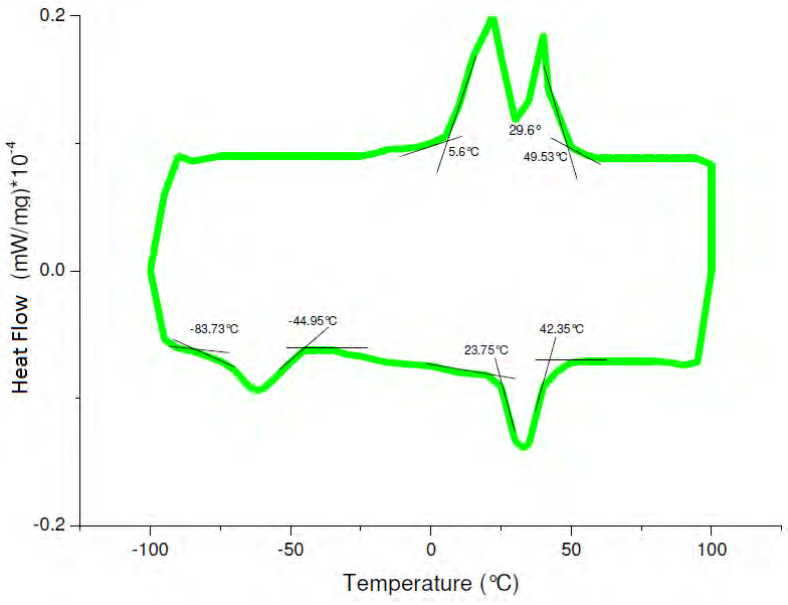

Figure 6 - HT350 sample DSC

Figure 7 shows the martensite to austenite transformation in a single stage for the HT600 sample. So, the R phase was probably solubilized during heat treatment. From the DSC curve it is possible to find the As (-39.5°C) and Af (-0.9°C) temperature during the heating and the martensite start (-35.4°C) and end (-79.4°C) temperature during the cooling.

In aged rich Ni alloys the appearance of Ti_3Ni_4 precipitate (Santos, 2006) seems common. The phase R transformation appears due the Ti_3Ni_4 precipitate formed on the B2 phase. Using this information and the curves from

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the DSC, it is possible to conclude that the HT350 samples had an increased amount of precipitate and the HT600 samples had most of these precipitates solubilized resulting in a microstructure fully austenite at room temperature.

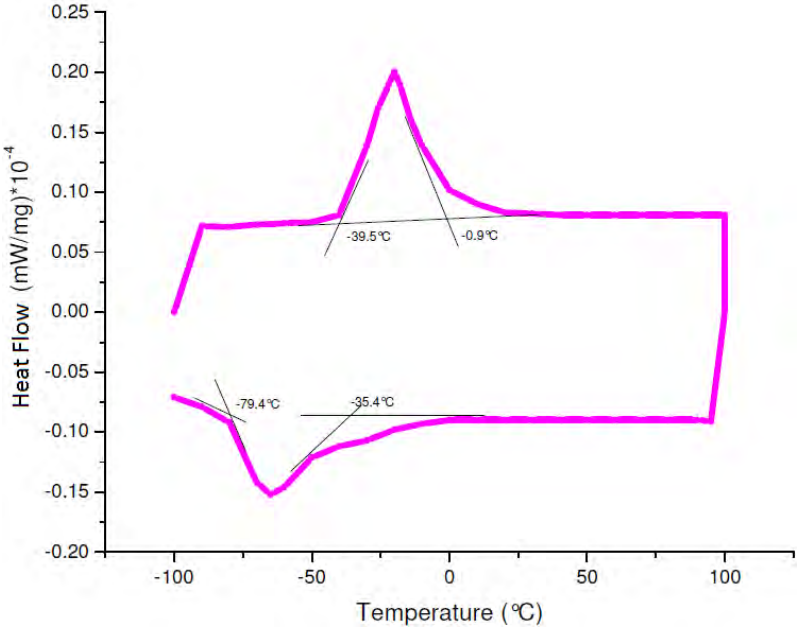

Figure 7 - HT600 sample DSC

The phase transformation occurs not in a single temperature, but at a temperature range. To analyze this temperature range a thermal hysteresis was calculated for each sample, shown in Fig. 8. The thermal hysteresis is obtained calculating the distance between the medium point of the Af and As and the medium point of the Ms and Mf. A lower thermal hysteresis means that the difference between the martensitic transformation and the austenitic transformation is smaller and therefore the transformation from one phase to another phase will occur faster. The samples HT600 showed the lowest thermal hysteresis.

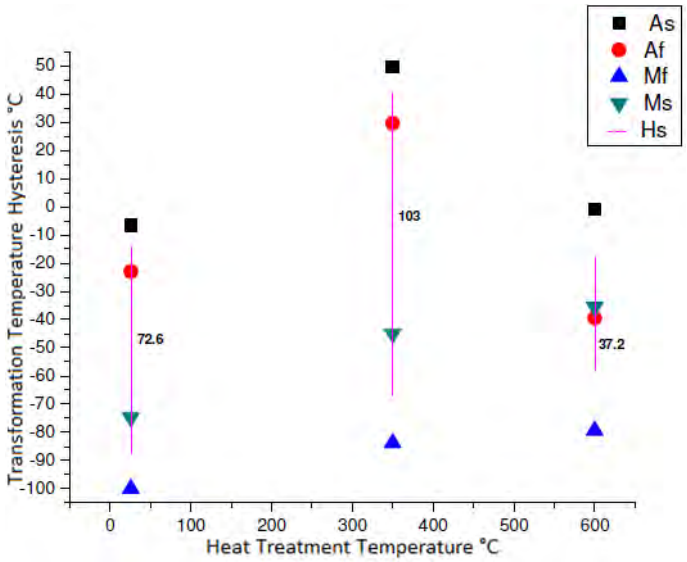

Figure 8 - Transformation temperatures hysteresis for tested samples

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4. CONCLUSIONS

From the analysis presented in this study is possible to realize that different types of thermal treatment can be applied to the NiTi alloy and each of these treatments will give a peculiar parameter on the alloys physical characteristic.

The DSC curves showed that variation on heat treatment temperature cause different phase transformation temperatures and different thermal hysteresis range. The heat treatment at 600°C didn't present an R phase and had a lower thermal hysteresis when compared to the samples as received and heat-treated at 350°C. The DSC also proved the difference found in the hardness tests, showing that the R phase is present on the samples with probably more Ti_3Ni_4 precipitates.

Through this study can be seen that these three samples shall differ in the dynamic and static mechanical behavior, since the hardness and the presence of precipitates can directly affect the hysteresis range and damping capacity of NiTi alloy.

5. ACKNOWLEDGEMENTS

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7. RESPONSIBILITY NOTICE

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