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# ANALYSIS OF THE EFFECT OF HEAT TREATMENTS IN NITINOL SHAPE MEMORY ALLOYS

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**Abstract.** *Shape memory alloys (SMAs) are smart materials that are capable to recover strain when heated above their transformation temperature. The Nitinol alloy has stood out because of the high forces and large displacements that it can be submitted. A thermomechanical process is needed to shape it to the configuration for the desired application. The thermomechanical behavior of Nitinol SMAs suffers significant change due to material processing such as the introduction of microstructure defects with cold working and  $Ni_3Ti_4$  precipitates generated with aging process. This study aims to analyse the effect of heat treatments in thermomechanical behavior of SMAs wires. Several heat treatments are applied on nitinol wires, and their behaviour are evaluated with a quasi-static tensile cyclic tests and Differential Scanning Calorimetry (DSC) tests. Quasi-static tensile tests are used to determinate the critical transformation stresses and characterize the mechanical behaviour of the alloy at room temperature (Shape Memory Effect or Pseudoelastic). DSC tests are used to obtain the phase transformation temperatures, the latent heat of transformation and establish witch phase is stable at room temperature.*

**Keywords:** *Shape Memory Alloys, Heat Treatments, Thermomechanical behavior*

## 1. INTRODUCTION

Near equiatomic NiTi shape memory alloys (SMAs) can consist, due to the thermomechanical conditions, of two phases: martensite (B19') or austenite (B2) (Wang, et al., 2015) (Otsuka & Ren, 2005) (Otsuka & Wayman, 1998). The martensitic transformations between these phases produce strain recovery up to 10% (Mahmud, 2009) (Duarte, et al., 2017) (Lester, et al., 2015) (Lagoudas & Miller, 2001), which is associated to the shape memory effect and pseudoelastic effect.

The material processing used to conform a SMA element in a geometric configuration as a spring for a specific application, can change the stability of the phases modifying thermomechanical characteristics as transformations temperatures and the critical stresses. For instance, cold working tends to decrease the transformations temperatures, inducing the presence of the pseudoelastic effect (Mahmud, 2009) (Khaleghi, et al., 2013). A subsequent annealing, usually done between 350 and 700° C, minimizes the cold work effect, so the two process can be used to control the transformations temperatures, (Otsuka & Ren, 2005) (Otsuka & Wayman, 1998) (Mahmud, 2009) (Khaleghi, et al., 2013) (Karimzadeh, et al., 2015). Another important heat treatment for the SMAs is the aging, done between 200 and 600° C (Wang, et al., 2015), that promotes  $Ni_3Ti_4$  precipitates in the matrix. The introduction of these precipitates can generate an intermediary martensitic transformation R-phase, depending on its shape and size (Nishida, et al., 2014). The precipitates also reduce the Ni concentration on the matrix, increasing the transformation temperatures (Otsuka & Ren, 2005) (Nishida, et al., 2014).

In this work tensile quasi-static cyclic tests and Differential Scanning Calorimetry (DSC) tests are used to analyze the influence of heat treatments on the thermomechanical behavior of NiTi SMA wires.

## 2. EXPERIMENTAL PROCEDURE

The specimens used in the experimental procedure are made from a NiTi wire, with 0.9mm diameter, provided by Sandinox. According to the manufacture the alloy is Ni 50.90 at.-%-Ti.

Firstly, DSC tests are developed to characterize the material in as received condition. Figure 1 shows the DSC results indicating the phase transformation temperatures. Frenzel *et al* (2010) shown that the chemical composition can be determined by de value of  $M_s$  on the solutionized sample. Through this method the alloy is calculated to be Ni 50.88 as%-Ti, which agrees with the data provided by de manufacture.

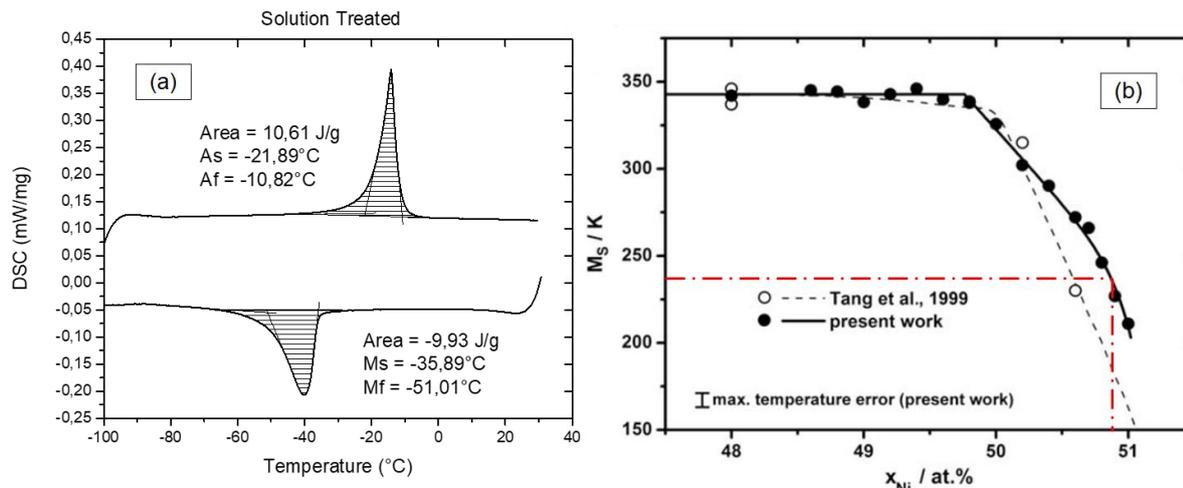


Figure 1 - (a) DSC results of the solution treated specimen and (b) results found by Frenzel et al. (2010), in red the solution treated specimen.

To study the effects of heat treatments on the SMA wires, three parameters are defined: heat treatment temperature, heat treatment duration and the cooling method applied. Three temperatures, two durations and three cooling methods are considered, giving a total of 18 heat treatments, as shown in Tab. 1.

Table 1. Heat Treatments applied on the specimens

Temperature		Duration		Cooling Method	
465° C					Water
490° C		30 min			Air
540° C		60 min		Furnace	

Each heat treatment was applied to two wires. So, considering the as received condition, a total of 38 specimens were studied.

The specimens used for the tensile tests have 100 mm length and are shown in Fig. 2. For the DSC tests, 2 samples were removed from all the wire specimens, one from each end to ensure homogeneity of the specimen. The samples were removed using a metallographic precision cutter to avoid heating and deformations during the cutting process that may interfere with the results.



Figure 2 – Example of the specimen, marked where the DSC samples were removed

The two removed samples of each wire were tested in a NETZSCH DSC 200 F3 machine (Figure 3a) and cycled from  $-120^{\circ}\text{C}$  to  $50^{\circ}\text{C}$  on a 10 K/min rate. The DSC results shows the transformation temperatures, the latent heat and if the R-phase appeared, indicated by a second transformation peak on the graphics.

A INSTRON 5982 universal testing machine shown in Fig. 3b is used to perform the tensile cyclic tests. The specimens are submitted to a tensile cycles with controlled temperature. The cycles range from 0 to 600 MPa at a rate of 1% strain per minute. The performed tests consist of the following stages: 1) application of 10 tensile cycles to the specimen; 2) heating the specimen above the transformation temperature  $A_f$ ; and 3) application of 3 additional tensile cycles. These last 3 tensile cycles are used to analyze the mechanical behavior of the wires.



(a)

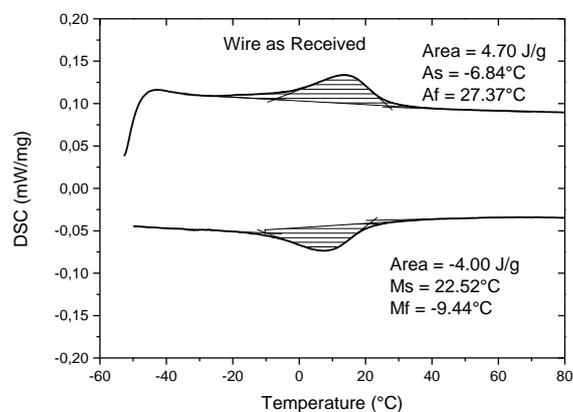


(b)

Figure 3. (a) NETZSCH DSC 200 F3 and (b) INSTRON 5982 universal testing machine.

### 3. RESULTS AND DISCUSSION

The DSC tests provide the values of the transformation temperatures  $A_s$ ,  $A_f$ ,  $M_s$ , and  $M_f$ , the latent heat of transformation, and permits to verify the presence of the R-phase. The comparison of the results obtained for the heat treated specimens with the ones in the condition as received is used to determine the influence of each heat treatment on the observed parameters. The DSC results for the as received wire and for the different heat treatments applied is shown on Fig. 4. The hatch areas are used to obtain the latent heat of transformation



(a)

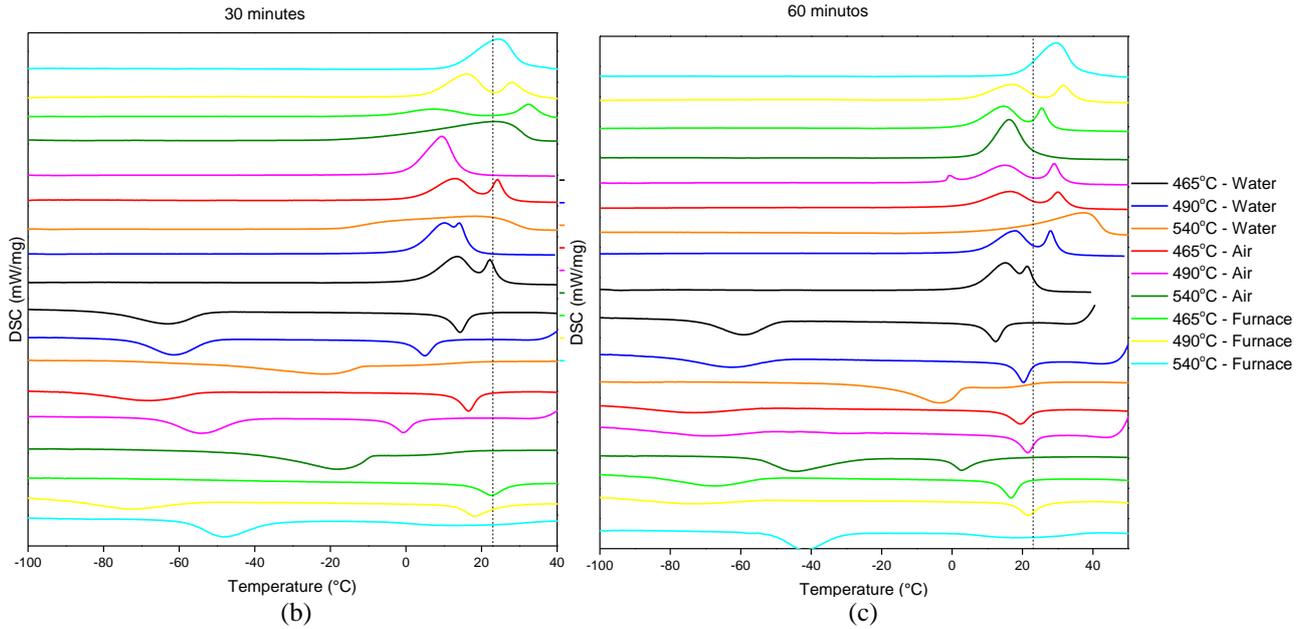
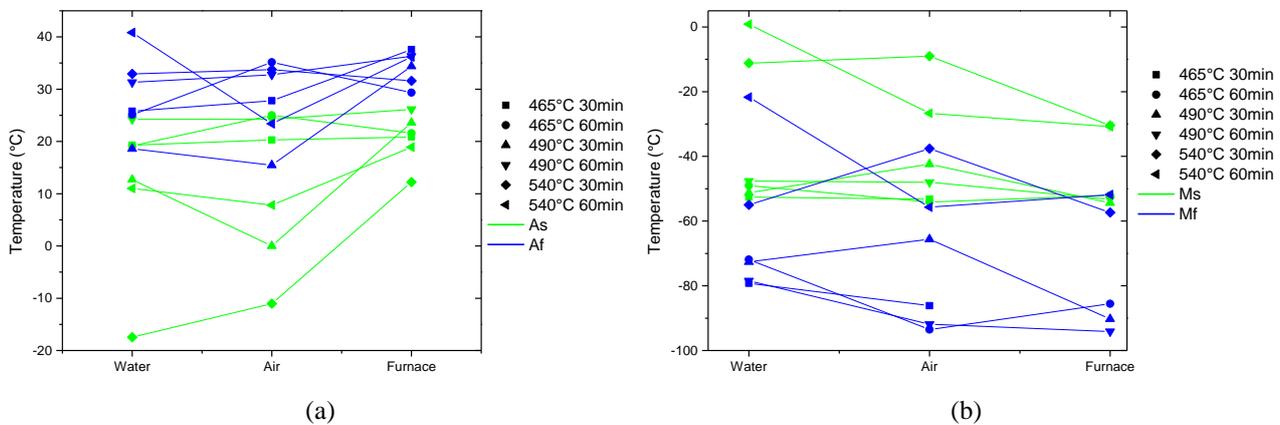


Figure 4. DSC results for the: (a) as received condition, (b) heat treated for 30 min and (c) heat treated for 60 min

Figure 4 shows that the heat treatments as a significant impact on the transformation temperatures and latent heat of transformation. They also can introduce a second transformation called R-phase, observed on heating and cooling stages for some heat treatments and only on the cooling stage for the others. The vertical lines on Figs. 4b and 4c represent the temperature used on the tensile tests. For the 30 min treatments, the 490° C treatments had lower transformations temperatures on the reverse transformation when compared to the 465° C, but when looking at the 60 min results they had higher transformations temperatures. This behavior indicates that for the 30 min treatments the annealing was more influential (Mahmud, 2009; Otsuka & Ren, 2005), and for the 60 minutes treatments the precipitation growth surpassed, increasing the transformation temperatures (Nishida, et al., 2014).

To better investigate the effects, the following figures will group the DSC results and focus on the transformation temperatures for each heat treatment parameter.

Figure 5a and 5b shows the main transformation temperatures as a function of the cooling method, for the reverse transformation and forward transformation, respectively. Figures 5c and 5d shows DSC curves for the 490° C as a visualization of the parameter influence. The results shows that the 30 minutes furnace cooled specimen had similar results as the 60 minutes air cooled, indicating that the slower cooling method probably increased the precipitate size, dissipating the second forward transformation (Otsuka & Ren, 2005). In most cases the slower cooling methods increased the  $A_s$  and  $A_f$  temperatures and decreased the  $R_s$  on the reverse transformation.



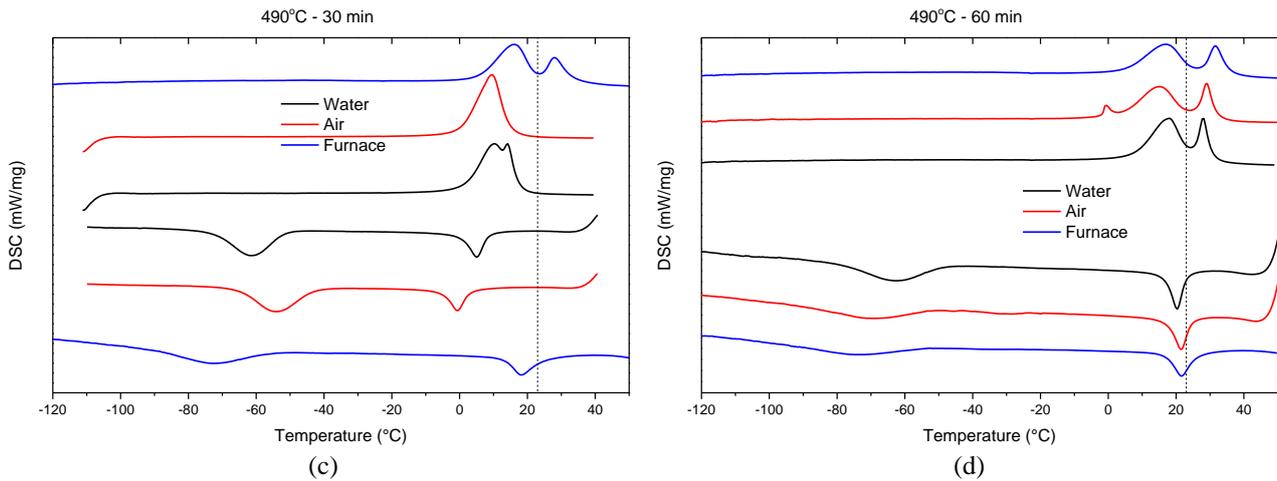
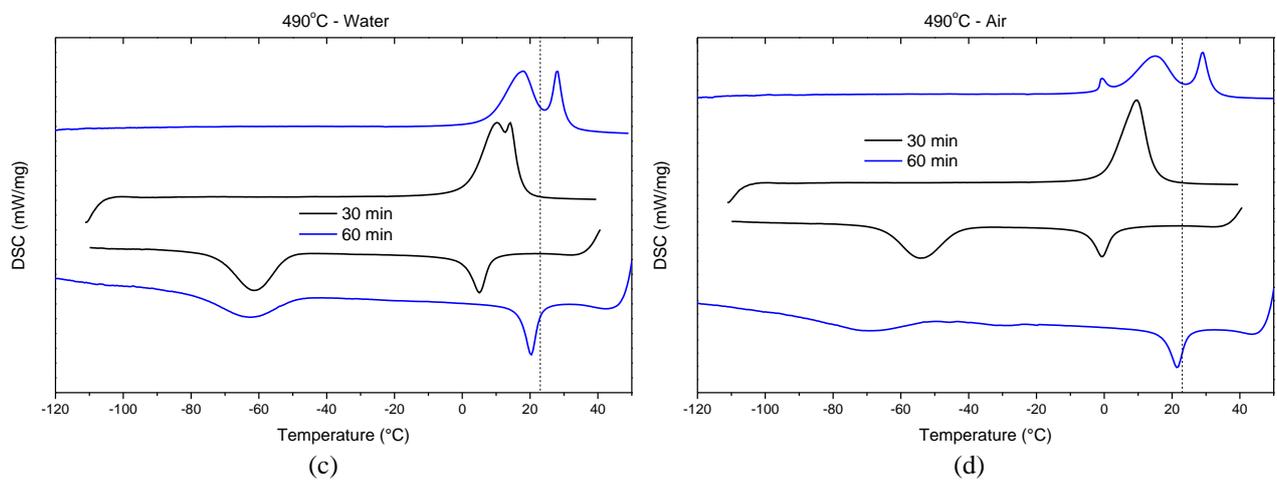
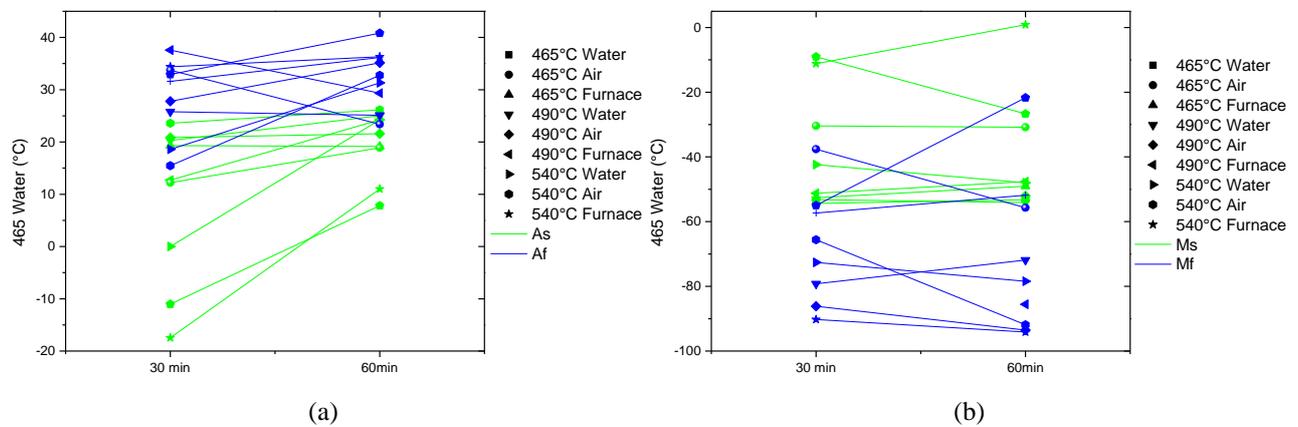


Figure 5. Effect of cooling method on transformation temperature: (a) reverse transformation, (b) forward transformation. DSC results for cooling methods treated at: (c) 490° C for 30 min and (d) 490° C for 60 min.

Figure 6a and 6b shows the main transformation temperatures as a function of the heat treatment duration, for the reverse transformation and forward transformation, respectively. Figures 6c, 6d and 6e shows DSC curves for the 490° C as a visualization of the parameter influence. The results shows that for longer heat treatments the reverse transformations temperatures increases, as there is a larger time for the precipitation to occur, reducing the Ni concentration in the matrix (Frenzel, et al., 2010; Nishida, et al., 2014; Otsuka & Ren, 2005). The same is not found in the furnace cooled ones, as the slower process results in a larger time for the precipitation. It is also seen that the two forward transformations tend to separate further, with  $R_s$  and  $R_f$  increasing and  $M_s$  and  $M_f$  decreasing



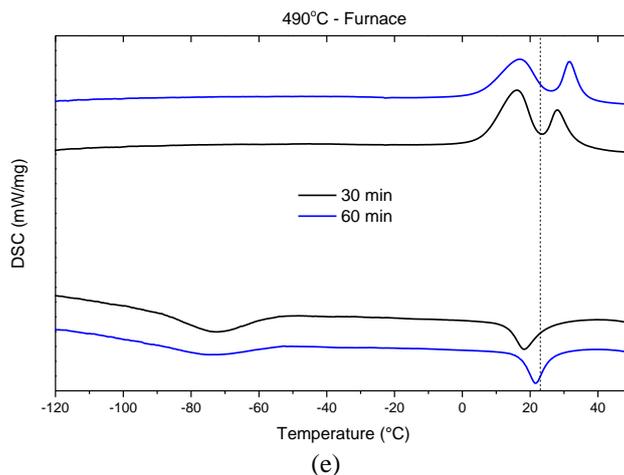


Figure 6. Effect of heat treatment duration on transformation temperature: (a) reverse transformation, (b) forward transformation. DSC results for heat treatment duration treated at: (c) 490° C water cooled, (d) 490° C air cooled and (e) 490° C furnace cooled,

Figure 7a and 7b shows the transformation temperatures as a function of the heat treatment temperature, for the reverse transformation and forward transformation, respectively. This parameter presents the larger impact on the transformation temperatures for the cases considered in this study, having great influence on the  $M_s$  and  $M_f$  temperatures on the forward transformation. Mahmud (2009) claims that the  $B19' \rightarrow R \rightarrow B2$  transformation appear with the aging treatments at lower temperatures, and tends to disappear, returning to  $B19' \rightarrow B2$ , with higher temperatures, that can also be observed on Figs. 4b and 7a

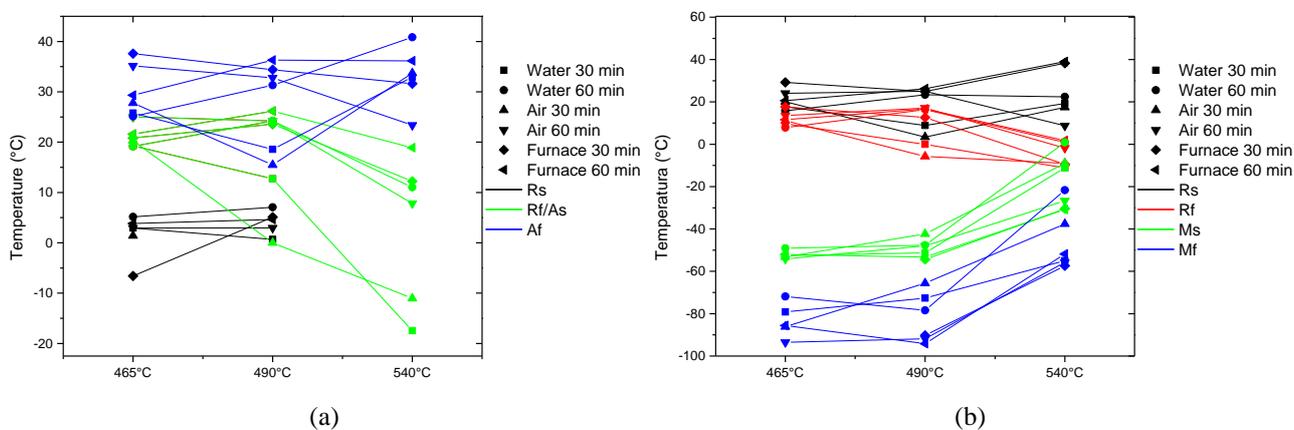


Figure 7. Effect of heat treatment temperature on the transformation temperature: (a) reverse transformation, (b) forward transformation

The tensile tests permits the identifications of the following mechanical parameters: phase transformation critical stresses  $\sigma_{A_s}$ ,  $\sigma_{A_f}$ ,  $\sigma_{M_s}$  and  $\sigma_{M_f}$ , Young's Modulus before and after the phase transformation process and the maximum strain. Comparing the results with the as received condition will determinate how the heat treatments affect the mechanical macroscopic behaviour of the specimen wires. Figure 8a shows the last 3 cycles on the as received condition, tested at room temperature (23° C), indicating that the applied cycling loading results in a stabilize condition. Figure 8b shows the first and last cycle for the specimen heat treated at 465°C for 30 min and water-cooled. Figure 8c shows the first and last cycle on the heat treated specimen wires. The arrows direction indicate higher temperatures and faster cooling methods.

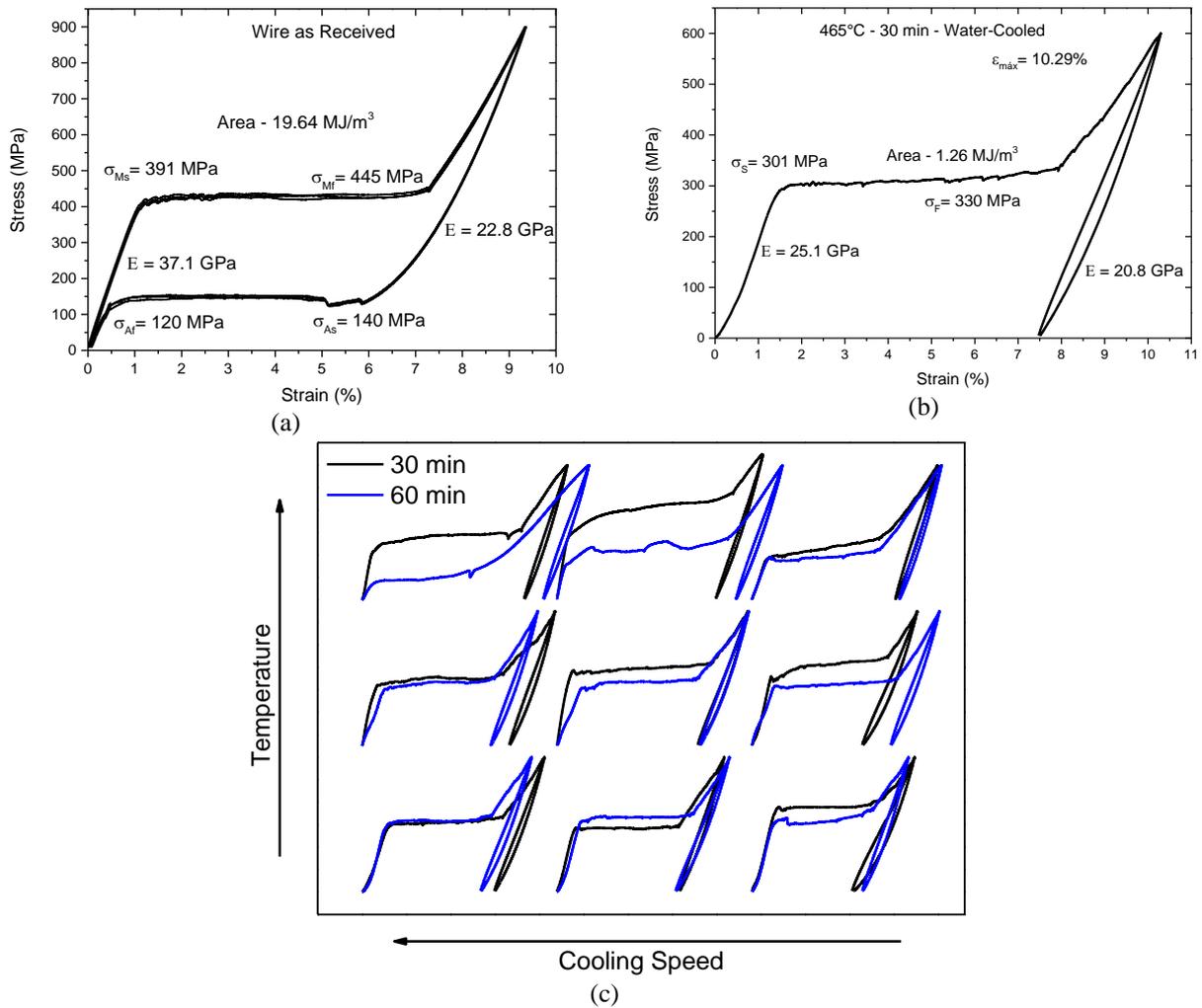


Figure 8. Tensile cyclic tests. (a) Last cycles on the as received condition, (b) first and last cycle for the specimen heat treated at 465°C for 30 min and water-cooled and (c) comparison of all heat treated specimens.

Tables 2 to 6 resumes the values for the transformation critical tensions, Young's Modulus and maximum strain found for each specimen, the largest values are highlighted with a darker background. The longer heat treatments with higher temperatures, result in specimens wires that can withstand larger strains but with diminished values for  $\sigma_s$  and  $\sigma_f$ .

Table 2 –  $\sigma_s$  Values

$\sigma_s$ (MPa) – 30 min				$\sigma_s$ (MPa) – 60 min			
	Water	Air	Furnace		Water	Air	Furnace
465°C	301	287	374	465°C	306	316	314
490°C	270	337	311	490°C	261	278	261
540°C	246	288	194	540°C	86	160	191

Table 3 –  $\sigma_f$  Values

$\sigma_f$ (MPa) – 30 min				$\sigma_f$ (MPa) – 60 min			
	Water	Air	Furnace		Water	Air	Furnace
465°C	330	295	394	465°C	343	344	349
490°C	324	372	399	490°C	350	301	297
540°C	306	471	280	540°C	147	268	222

Table 4 –  $E_s$  Values

$E_s$ (GPa) – 30 min				$E_s$ (GPa) – 60 min			
	Water	Air	Furnace		Water	Air	Furnace
465°C	25,1	32,8	33,8	465°C	31,9	30,6	32,3
490°C	34,7	46,9	36,4	490°C	25,1	20,8	24,2
540°C	43,1	47,4	24,7	540°C	22,5	32,4	21,2

Table 5 –  $E_f$  Values

$E_f$ (GPa) – 30 min				$E_f$ (GPa) – 60 min			
	Water	Air	Furnace		Water	Air	Furnace
465°C	20,8	23,2	16,4	465°C	20,3	19,3	22,5
490°C	22,7	20,8	18,9	490°C	22,2	21,3	21,3
540°C	24,2	23,7	24,6	540°C	15,2	22,3	24,8

Table 6 –  $\epsilon_{m\acute{a}x}$  Values

$\epsilon_{m\acute{a}x}$ (%) – 30 min				$\epsilon_{m\acute{a}x}$ (%) – 60 min			
	Water	Air	Furnace		Water	Air	Furnace
465°C	10,29	9,44	9,19	465°C	9,57	9,74	8,83
490°C	10,90	10,77	9,34	490°C	9,92	10,83	10,58
540°C	11,57	11,61	10,47	540°C	12,80	12,72	10,69

Analyzing Fig. 8c and the tables it is observed that the parameters of heat treatments has a significant influence on the mechanical behavior, with substantial variations, the  $\sigma_s$  up to 334.9%;  $\sigma_f$  up to 220.4%;  $\epsilon_{max}$  up to 44.9%. The Young's module had greater changes on the initial values (127.9%). That is because the wires was heated to 90°C and then cooled to room temperature (23°C), so the specimen initial conditions was a mixture of the B2, B19' and R phases, as seen on Fig.4b and 4c. The proportion of the phases causes the higher variation on the initial Young's module. The final Young's module ( $E_f$ ) had 63.2% of variation, because it was only a mixture of B19' and R phases, that have similar Young's module.

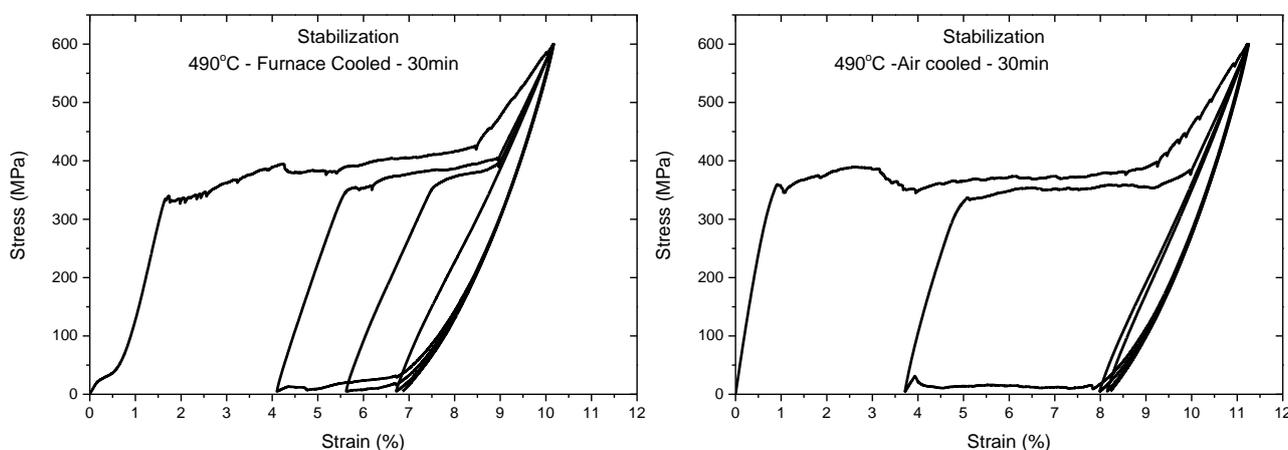


Figure 9 – Stabilization cycles of expected pseudoelastic behavior

It was expected that some wires to have a pseudoelastic behavior, such as the wire heat treated at 490°C for 30 minutes and air cooled, that his  $A_f$  temperature was below the room temperature used on the tensile tests. But as observed on Fig. 8c, they all had shape memory effect. That occurred because the stabilization cycles on the specimen changed slightly the transformation curves, modifying the wires behavior. The stabilization of two wires expected to have pseudoelastic behavior can be seen on Fig. 9.

#### 4. CONCLUSION

An experimental procedure was established to study the influence of heat treatments on of Ni 50.90 at.%-Ti shape memory alloys wires. Three parameters are considered: heat treatment temperature, heat treatment duration and the cooling method applied. Differential Scanning Calorimetry (DSC) and tensile cyclic tests were performed.

DSC tests showed that the temperature of the heat treatment was the most influential, having great influence on the transformation temperatures and the appearance of R-phase. Being in accordance with previous studies. The cooling method and heat treatment duration also changed the thermomechanical behavior and can be used to fine tune for the desired output.

Tensile cyclic tests showed that the heat treatments can heavily influence the Young`s modulus, with changes of 127%, and the phase transformation critical stress, reaching 334.9%. Also have a impact on the strain the wires can sustain for a given stress, with variation up to 44.9%. This results showed that the heat treatment can be defined to obtain the desired thermomechanical characteristics for the SMA wire

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