 

# THERMOELASTIC DEGRADATION ON SHAPE MEMORY TI-NI SPRINGS DUE TO HEAT TREATMENT AND PLASTIC DEFORMATION

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***Abstract***. *This article studies changes observed on the martensitic transformation, due to heat treatments and plastic deformation on shape memory Ti-Ni springs with near-equiatomic composition. This study is develop by different heat treatments, X-ray diffraction, thermo-cycling and thermo-mechanical cycling under constant loading in shape memory springs. Two heat treatments were carried out to investigate the evolution of the R-phase transformation. The shape memory springs were obtained by these heat treatments and submitted to a training process. This training process was carry out in an apparatus by tensioning the springs under constant loading. This procedure allows the comparison of the thermoelastic effect on one step (B2→B19') and two-steps (B2→R→B19') martensitic transformations.*

**Keywords**: Heat treatments, R-phase transformation, Ti-Ni alloys, plastic deformation and Thermo-elastic properties.

## 1. INTRODUCTION

The development of smart actuators for industries is very often using the two-way shape memory spring. The main intention of this is the possibility to mix small size with large displacement. Ti-Ni alloys are an important class of memory alloys due to the shape memory effect and the superelastic effect. This material is been use to obtain actuators for mechanical industries applications and several other applications on science areas, as, medicine and robotics.

The already very study martensitic transformation on Ti-Ni alloys, still allows investigation on one-step and two-step transformation. This investigation is interesting due to the importance of knowing the actuators response to external stimulus. This stimulus such as temperature changes, electrical current density and stress may undergo the complete martensitic transformation (Corneliu et al, 2003).

Due to its small thermo-elastic deformation and reduce shape recovery, close to 0,5%, R-phase transformation is not very often use for actuator application. Its good fatigue behavior when compare to same other alloys based on Ti-Ni, allows investigation of the two-steps transformation by mechanical constant loading during heat and cooling cycles (Sittiner et al, 2006).

The main objective of this study is an investigation on the thermoelastic behavior by the training process developed on springs. Two different heat treatments were selected to obtain springs with one-step and two-steps martensitic transformation. A comparison of these two springs behavior is develop by means of shape memory effect degradation, temperature transformation, R-phase absent or precipitation.

As results, it is observed the phase's precipitations appliance with ageing, the martensite preferential orientation due to the thermo-mechanical process and the possibility to generate more dislocation by the martensitic transformation.

## 2. EXPERIMENTAL PROCEDURE

A cold-drawn binary near-equiatomic Ti-Ni alloy wire with diameter of 0.89 mm was used to manufacturer helical springs. The wire is mechanically conformed around a screw with 4,2 mm internal diameter. This set of wire mechanically conformed around the screw is submitted to a heat treatment to fix de spring shape. The shape memory springs obtained have 6.0 mm external diameter and 4.2 mm internal diameter and six coils, but only four active coils.

The heat treatment used to obtain the springs consist of homogenization at 400 and 500ºC for 24 hours followed by quench in water at 25ºC. After this heat treatment a little segment of the spring obtained is use to determine martensitic transformation temperatures (martensite start (Ms), martensite finish (Mf), austenite start (As), austenite finish (Af), rhombohedral start or R-phase start (Rs) and R-phase finish (Rf)). This procedure is developed by differential scanning calorimetric method (DSC) and also allows the temperature behavior investigation. Thermal cycles in DSC method were performed between -60 and 90°C at a constant rate 10°C·min-1.

X-ray diffraction is use to investigate precipitation of elements such as $Ti_3Ni_4$, $Ti_2Ni_3$ and $T_iNi_3$. These elements according to several studies seen to be involve with R-phase appearance. Elevate time of agein on elevate temperature may induce Ti-Ni alloys B2 phase decomposition.

Shape memory springs (SMS) was submitted to thermo-mechanical cycles in a mass-pulley-spring special apparatus described by Araujo et al, (2001) and Oliveira et al, (2007). This apparatus is constituted by a programmable silicon oil bath, linear variation displacement transducer (LVDT), thermocouple and a data acquisition system. In this apparatus, the SMS were submitted 50 thermal cycles under constant loads of 70, 105, 135 and 170 MPa and interval temperature between 25 and 140°C. The heat and cooling rate are estimated in 10 and 6ºC.min-1, respectively.

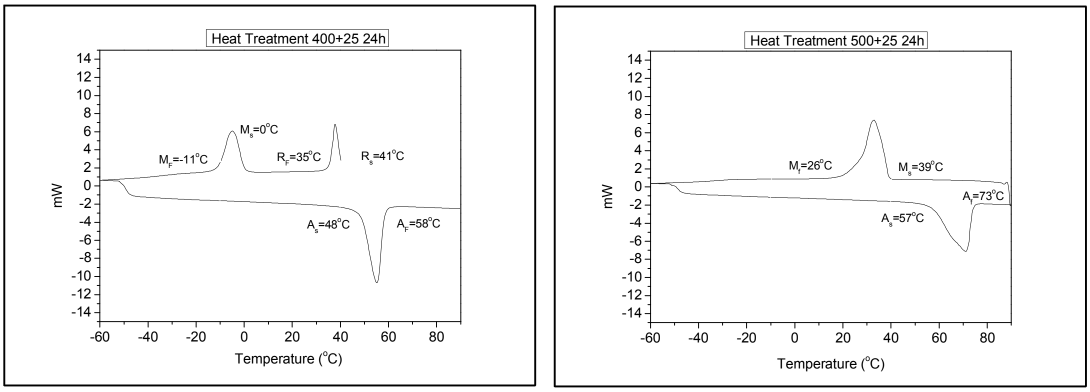
From a data acquisitions system, deformation versus temperature and temperature versus number of cycles curves were plotted. The shape memory effect thermo-elastic properties were determined. Using the tangent method performed by Oliveira et al, (2008) is possible to determine critical transformation temperatures under stress ($A_S$, $A_F$, $M_S$ and $M_F$), thermoelastic displacement, thermal hysteresis (Ht), and vertical displacement of hysteresis loops.

## 3. RESULTS

### 3.1. Calorimetrical Study and Phase Transformation

The main objective of this study is to compare the behavior and changes in two-way shape memory effect on Ti-Ni actuators obtained by heat treated at 400 (400T) and 500ºC (500T) with 24 hours of homogenization time followed by quench in water at 25ºC. These heat treatments wore already studied by Gonzalez et al. (2008). The one homogenized at 400ºC showed in DSC method two-steps sequence transformation (B2→R→B19') and the other at 500ºC show one-etep sequence transformation (B19'→B2).

Figure 1 show the calorimetrical curves obtained in DSC. Is possible to identify R-phase peak in the sample heat treated at 400ºC on cooling. In samples heat treated at 500ºC during cooling is only possible to identify martensite peak. During heat, inverse transformation occurs in one single step (B19'→B2) for both samples.




a) b)

Figure 1. Calorimetrical curves. a) Sample heat treated at 400ºC for 24 hours and b) Sample heat treated at 500ºC for 24 hour.

Literature Investigation have shown that changes in martensitic transformation, may be due to cold work, ageing and rich-Ni alloys (Khelfaoui, 2000, Ilczuk et al, 1996). The R-phase peak observed at 400T may be related to the saturation of precipitates such as $Ti_3Ni_4$, $Ti_2Ni_3$ and $TiNi_3$ in grain boundaries and in grain interior. The saturation of precipitates induces stress fields formation between parent phase (B2) and the precipitates. The ageing and elevated temperature reduce dislocation density and the R-phase formation star to be inhibited, as can be seen in figure 1.b (500T) (Huang et al, 2001; David et al, 2001).

### 3.2. X-Ray Diffraction

X-ray diffraction is developed in materials samples in tree condition: as-receive, heat treated at 400T and heat treated at 500T. Figure 2 show XRD analysis results for the tree condition specified. As can be see as-receive and heat treated at 400T samples show more intensity peaks. Literature comments say that ageing at elevate temperatures may results in TiNi decomposition to obtain precipitates likes $Ti_3Ni_4$, $Ti_2Ni_3$ and $TiNi_3$. As the annealed time is raised the decomposition results in more simples elements like $TiNi_3$ and TiNi (Otsuka et al, 2005; Melton, 1990). For low temperatures and short times decomposition riches $Ti_3Ni_4$ and more elevated temperatures decomposition riches $TiNi_3$. $Ti_3Ni_4$ are important because it can improve shape memory properties and like $TiNi_3$ it is involved with R-Phase formation, acting as nucleation center for R-phase formation.

Figure 2.a from samples as-receive show peaks of $TiNi_3$ and figure 2.b and 2.c show peaks of $TiNi_3$ and same peaks of $Ti_3Ni_4$. It is possible to compare this results with the one obtained by DSC methods. Samples Heat treated at 400T showed R-phase in DSC curves and the precipitates $Ti_3Ni_4$ and $TiNi_3$ involved with its formation. Samples heat treated at 500T already show one single peak in DSC methods during cooling, but with DRX results showed in figure 2.c is possible to identify same precipitates involved with R-phase formation. It is believe that maybe heat treatment at 500T still exhibits same part of R-phase elements.

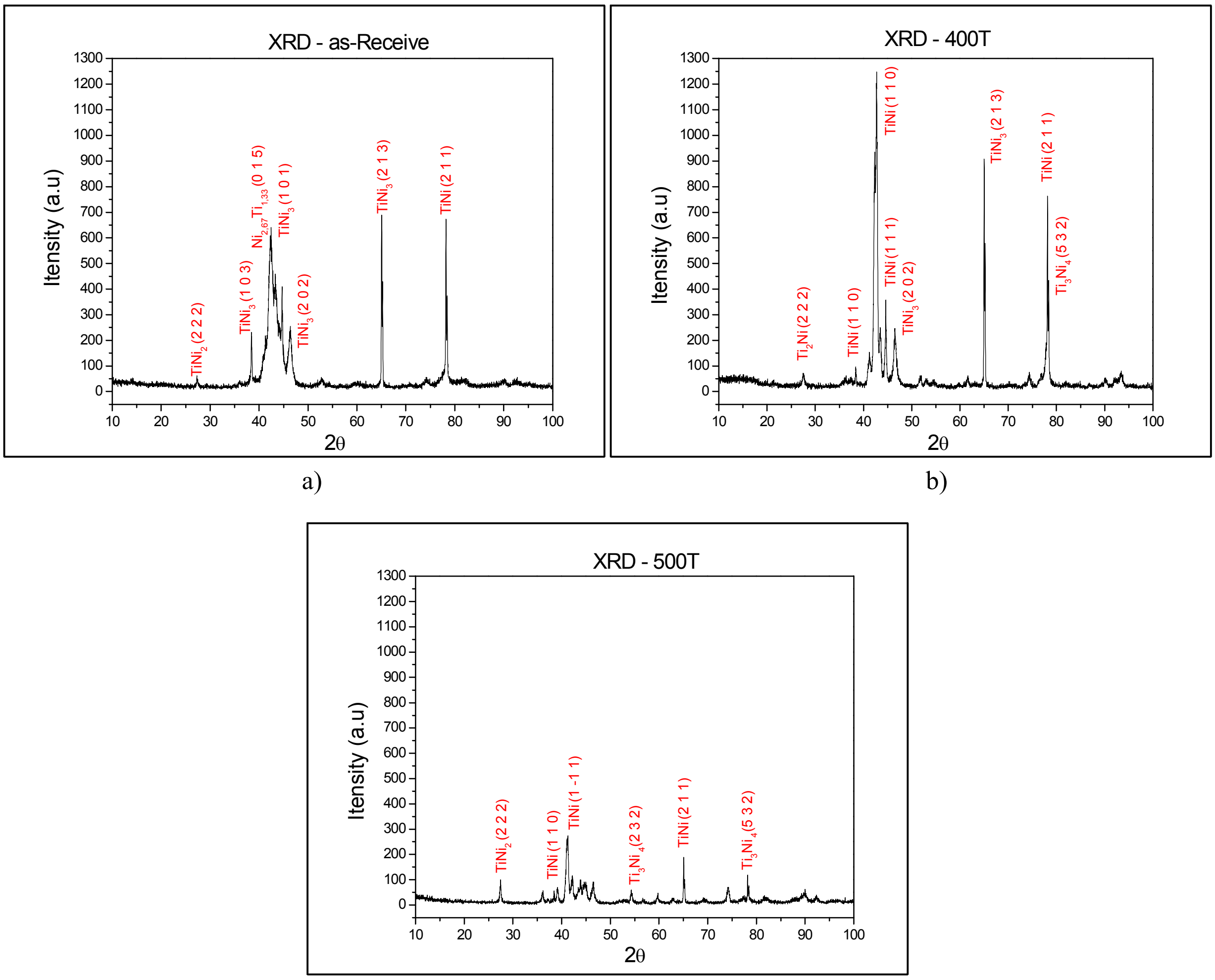
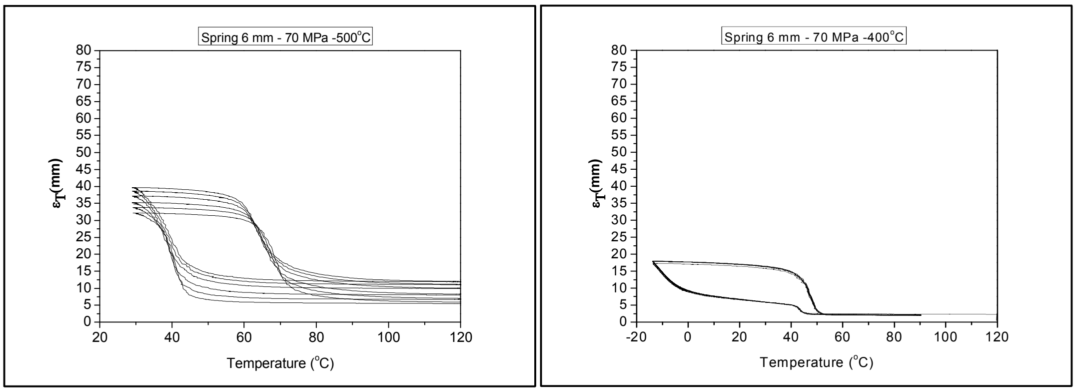



Figure 2. X-Ray diffraction results. a) as-receive sample b) heat treated at 400T and c) heat treated at 500T.

### 3.3. Thermomechanical Tests

Thermomechanical cycles were developed with shape memory springs (SMS) obtained by 400T and 500T to identify the thermoelastic properties of martensitic transformation under constant loads. Figure 3 compare displacement-temperature curves for SMS submitted to constant shear stress of 70 and 105 MPa for both heat treatment and figure 4 show this curves of 135 and 170 MPa for both heat treatment. These curves shown that critical temperatures increases gradually with load applied. This is closely in line with the Clausius–Clapeyron relationship, whem applied external stress increases so do the transformation temperatures. Hysteresis loops of the displacement - temperature curves develop changes to upward and to the right during cycling, principally initials cycles. These evolutions are due to variants reorientation process which easier martensitic transformation. Other characteristic in these curves is the presence of irrecoverable strain (degradation), which increase with load. The strain observed in springs obtained by 400T is reduce for the same shear stress of the one obtained by 500T, but the thermoelastic response to the thermo-stimulus is almost half of the one observed with 500T. A first factor is the relationship in the martensitic stabilization by stress induced (blockage martensite variants) and second is due to introduction of plastic deformation. R-phase transformation also involve more stress density and maybe the tensions in analysis is not enough to induce more variants dislocations during thermo-cycles, so 400T curves show in general way a small thermoelastic effect (Liu et al, 1997; Khalil et al 2004).

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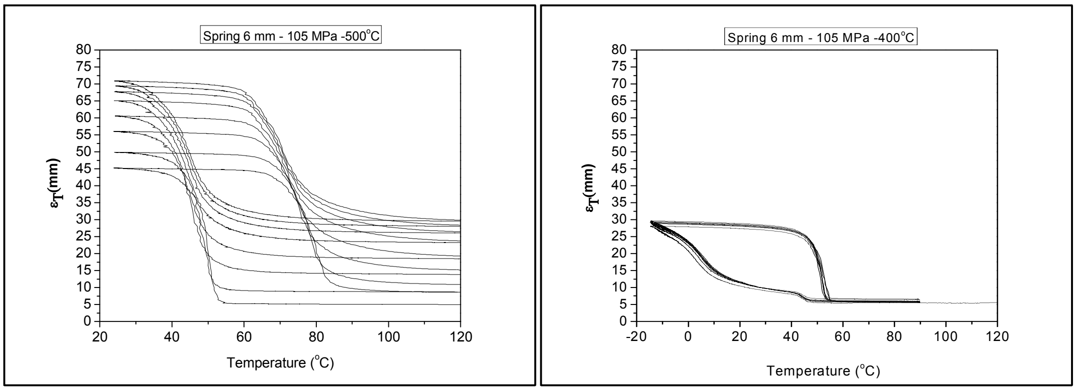
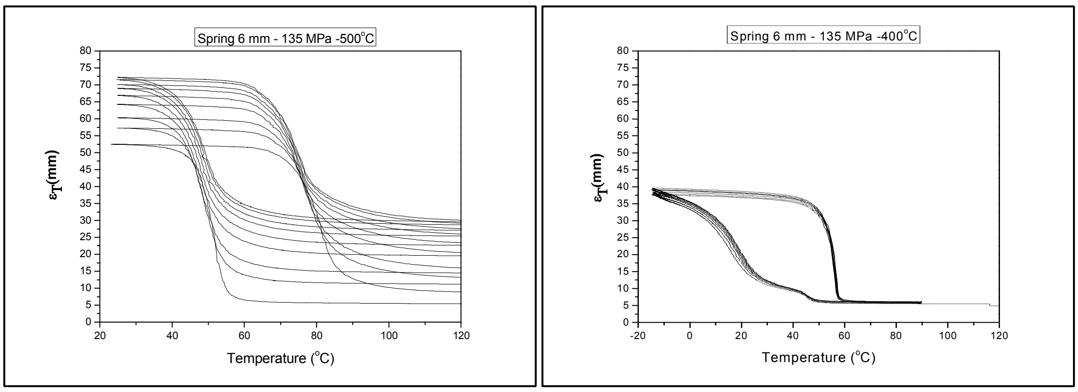



c) d)

Figure 3. Strain–temperature curves obtained during consecutive training cycles under tensile stress: a) and b) 70 MPa, c) and d) 105 MPa, (1, 2, 5, 10, 20 and 30 cycles).

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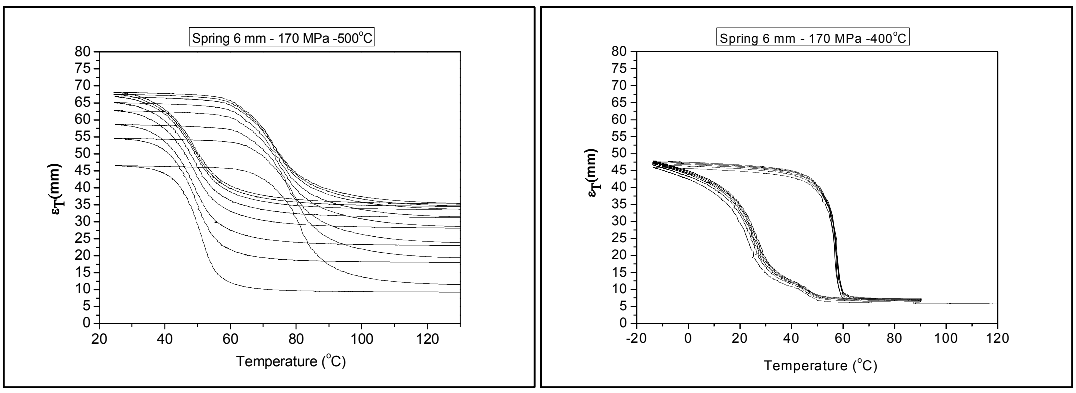
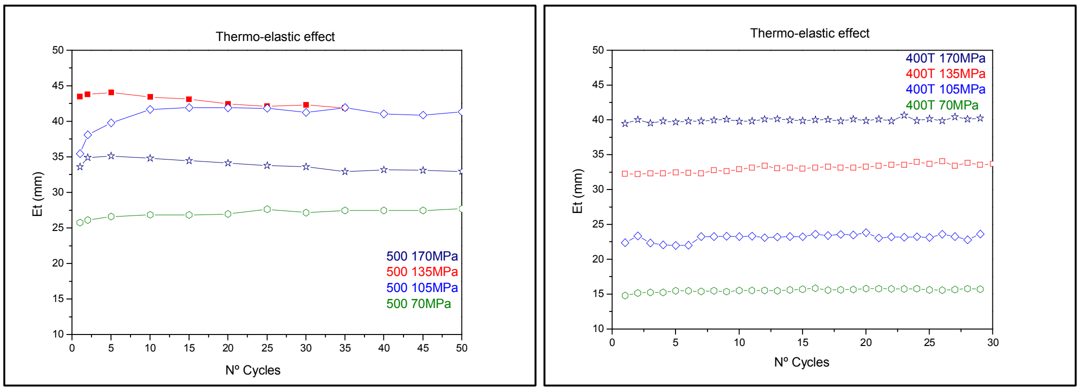



c) d)

Figure 4. Strain–temperature curves obtained during consecutive training cycles under tensile stress: a) and b) 135 MPa, c) and d) 170 MPa, (1, 2, 5, 10, 20 and 30 cycles).

The figure 5 show thermo-elastic strain behaviors during thermal cycles for each applied tensile stress in springs heat treated at 400T and 500T. Initially, thermo-elastic strain (Et) increases with the increase in the load applied, but their evolutions are different. For 70 and 105 MPa stresses present a gradual increase during training cycles until practically to stabilize strain in last cycles, whereas for 135 and 170 MPa stresses the thermo-elastic strain decrease continuously. For springs heat treated at 400T thermoelastic strain behavior is different from the ones heat treated at 500T, in most of cycles the thermo-elastic strain remains with the same grown tendency. The best thermo-elastic strain behavior is observed for 105 MPa at 500T with 41,0 mm as maximum value and 170 MPa at 400T with 40,0 mm as maximum value. Even showing in general reduces value of thermoelastic strain, the springs heat treated at 400T exhibits a better behavior. This behavior is possible to be related to R-phase presence in material. It is believe that stress field may be blocking martensite variants orientation during the training cycles and a higher tension is needed to improve the obtained thermoelastic strain. During training occurs a martensite variants reorientation process where internal stresses generated by dislocation fields favoring some martensitic crystallographic variants, according to stress direction.

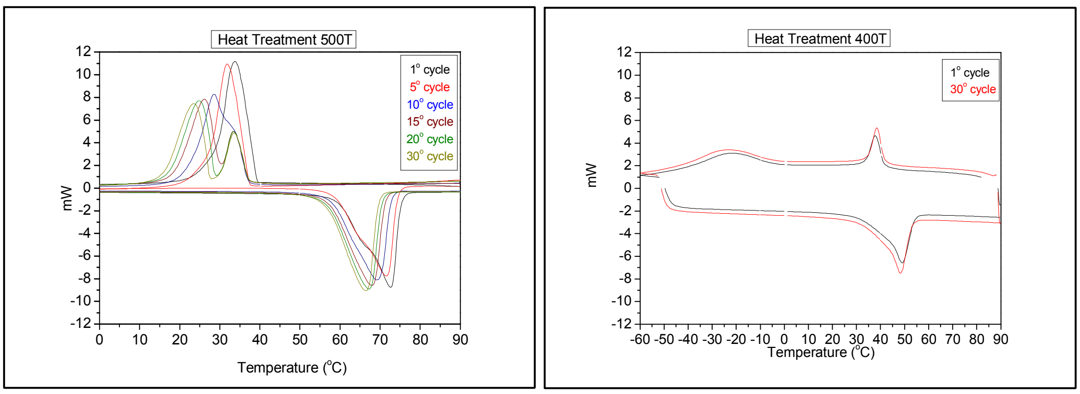



a) b)

Figure 5. Evolution of thermo-elastic strain with number of cycles for each tensile stress. a) heat treated at 500T b) heat treated at 400T.

### 3.4. Study Calorimetrical in as-Treated Samples

Calorimetric curve of sample heat treated at 400T show the R-phase characteristic peak and 500T don't present the R-phase characteristic peak. In all thermo-mechanical tests in the shape memory springs obtained with 500T there isn't macroscopic evidence of R-phase presence. In this section is presented a calorimetrical study in as-heat treated material. This study is developed because this technique is more sensible to identify the R-phase. In these tests, samples were thermically cycled thirty times in a DSC apparatus. Figure 7.a shows 1, 5, 10, 15, 20 and 30 calorimetrical curves for the as-heat treated sample at 500T and figure 7.b show 1 and 30 cycle. In the tenth thermal cycle present in figure 7.a is possible to distinguish the formation of the R-phase through a delay in the martensite peak. From tenth fifth cycle, martensitic transformation occurs in a two-step transformation (B2→R→B19'). It might be explained by the martensitic transformation that can induce defects in the lattice (Wu et al, 2000; Pelosin et al, 1998). The defect between the matrix and the precipitates allows the R-phase formation. Sample heat treated at 400T as showed in figure 7.b don't exhibits large difference between the first and the last cycle and all DSC curves show transformation in two steps. The temperature transformation involved in this experiment for samples heat treated at 400T don't show significant changes.




a) b)

Figure 6. Calorimetrical cycles for samples heat treated a) 500T b) 400T.

## 4. CONCLUSION

According to the obtained results can be concluded that:

a) Heat Treatments applied in the Ti-Ni commercial wire produce changes in the martensitic transformation thermo-elastic properties. Samples heat treated at 400T exhibits two-steps transformation (A - R - M) and samples heat treated at 500T exhibits one-step transformation for the same annealing period. Samples heat treated at 400T show a better efficiency in thermo-elastic behavior. This observation is due to the precipitates formed during heat treatment procedure. This precipitates form more stress fields in material. The random stress fields formed needs more elevated tension to induce martensite orientation and plastic deformation. 170 MPa still exhibits a good thermo-elastic behavior for samples heat treated at 400T, but is not so good for samples heat treated at 500T.
b) X-ray diffraction proves the existence of Ti-Ni precipitates in samples as-receive and heat treated. Heat treatment in elevated temperatures facilitates decomposition of precipitates as $Ti_3Ni_4$ and $Ti_2Ni_3$. This elements are very important in R-phase transformation because they modify the shape memory effect response to external stimulus.
c) Thermal cycling studies by DSC in the treated samples showed that R-phase is very sensitive to stress field formed during martensitic transformation. Samples treated at 500T show a gradually R-phase formation. The stress fields already present in material acquire a new level of density during the thermal-cycles and allows the R-phase transformation even after a long annealing period (Pelosin et al, 1998).

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