Heat Treatments and Thermomechanical Cycling Influences on the R-Phase in Ti-Ni Shape Memory Alloys

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This article studies changes observed on the R-phase thermoelastic behavior in a near-equiatomic Ti-Ni shape memory alloy. Three kinds of procedures have been performed: different treatments, thermomechanical cycling under constant loading in shape memory helical springs and thermal cycling in as-treated and trained samples. Several heat treatments were carried out to investigate evolution of the R-phase by differential scanning calorimetry (DSC). A heat treatment was chosen on which R-phase is absent. Shape memory springs were produced and submitted to a training process in an apparatus by tensioning the springs under constant loading. Thermal cycling in DSC was realized in as-treated and trained samples. Several aspects of one-step (B2→B19') and two-steps (B2→R→B19') martensitic transformations and R-phase formation and their evolution during tests were observed and discussed.

Keywords: *shape memory spring, heat treatments, R-phase, ti-ni alloys and thermoelastic properties*

1. Introduction

Mechanical properties of Ti-Ni alloys are very interesting for the development of smart actuators manufactured from this special kind of non-conventional material. In many technical applications these actuators need to generate forces and to avoid the degradation of the shape memory effect caused by the martensitic stabilization processes[1-3]. These characteristics allow its utilization in various domains of knowledge, for example: space reduction (miniaturization), human movement simulation (robot), medical applications and others. In the smart sensor/actuators, helical spring shapes are more interesting because of their deflection and the possibility of forces generation, as for example in endoscope activated by a shape memory spring that makes the surgery with less or minimum evasion to the patient[2,3].

Several heat treatments were investigated in order to modify the transformation temperatures of alloys object of this study. The objectives went to dislocate the critical temperatures for near room temperature and to avoid the R-phase formation, very common in Ti-Ni alloys submitted to cold work. Despite the several studies of understanding about the R-phase formation in the Ti-Ni alloys, there are yet few applications that could use the narrow ranges of shape recovery presented by this phase. Several research indicate that the presence of the R-phase during martensitic transformation (two-steps, B2→R→B19', where B2 and B19` represent crystalline structures of the austenitic and martensitic phases, respectively) because matrix phase hardened, hindering the generation of the stress fields associated to dislocation reconfiguration process that facilitate the two-way shape memory effect. The main advantage of suppressing the R-phase formation is to the attain an uniformity in the stress fields, proportioning a better efficiency of the shape memory effect[4,5]. Thermoelastic studies on the sma-springs allows to study the R-phase behavior (R) and martensitic phases (M), during thermal cycles with and without tensile loads application.

This study was developed in a wire with 0.89 mm in diameter of a near-equiatomic Ti-Ni alloy. Samples of this wire were submitted for three tests: different heat treatments by calorimetry, thermomechanical cycling under constant loading in shape memory helical springs and thermal cycling by calorimetry in the as-treated and trained samples. Wire was drawn to manufacture helical springs with 6 mm in diameter and four active coils.

2. Experimental Procedure

A cold-drawn shape memory alloy wire of Ti-Ni with near-equiatomic composition and diameter of 0.89 mm was used to manufacturer helical springs. Procedure is demonstrated in the references 1 and 6. Shape memory springs have 6.0 mm external diameter and 4.2 mm internal diameter and four active coils.

Initially, a study were realized in as-received specimens by differential scanning calorimetric method (DSC) to determine martensitic transformation temperatures (martensite start-M_s, martensite finish-M_f, austenite start-A_s, austenite finish-A_f, rhombohedral start or R-phase start-R_s and R-phase finish-R_f after, samples was submitted for several heat treatments to verify the behavior of the critical temperatures. Thermal cycles in DSC method were performed in a range between –60 and 90 °C at a rate constant of 10 °C/min. Specimens was homogenized at 400, 500 and 600 °C followed by quench in water at 25 °C and the ageing times applied were 1, 2, 4, 8, 12 and 24 hours. The treatment chosen for subsequent tests (cases: spring samples and thermal cycling without loading samples) was homogenization at 500 °C for 24 hours followed by quench in water at 30 °C. In this treatments, the transformation temperatures were above room temperature and the R-phase seems to have been suppressed.

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Shape memory springs (SMS) was submitted to thermomechanical cycles in a mass-pulley special apparatus described in the references 6 and 7. 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, 170 and 200 MPa and temperature interval between 25 and 140 °C. The heating and cooling rate are estimated in 10 and 6 °C/min, respectively.

From data acquisitions, deformation vs. temperature and temperature vs. number of cycles curves were plotted, and shape memory effect thermoelastic properties were determined. Figure 1 shows a typical curve and the procedure to determine critical transformation temperatures under stress (A_s, A_F, M_s and M_F) using the tangent method, thermoelastic strain (ε_t = difference between the strain at low and high temperatures), thermal hysteresis (Ht), and vertical displacement of hysteresis loops (X)[6].
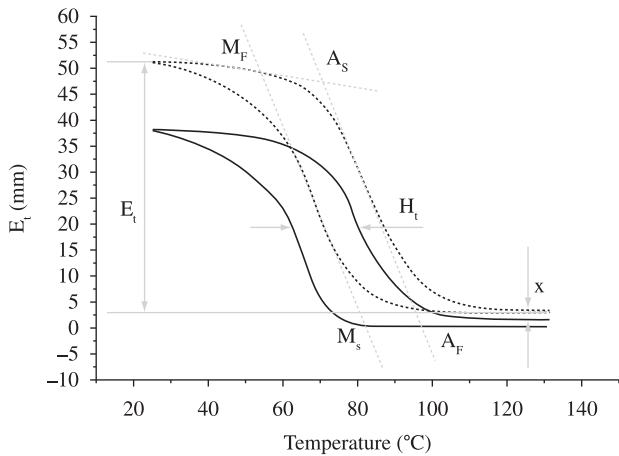

Figure 1. Characteristic parameters of the shape memory effect in a strain vs. temperature curve.

3. Results

3.1. Study calorimetrical of heat treatments influences in phase transformations

The objective of this investigation is to observe the changes in transformation temperatures and enthalpies obtained from heat treatments procedures. Samples were heat treated at 400, 500 and 600 °C with homogenization times of 1, 2, 4, 8, 12 and 24 hours and followed by quench in water at 25 °C. For all samples heat treatment at 400 °C has showed the normal sequence of phase transformation in the near-equiatomic Ti-Ni wire: B2→R→B19'. This result is presented in Figure 2a. During heating, the inverse transformation to occurs in an alone step (B19'→B2). The sum of enthalpies of exothermic heat flow peaks (R and martensitic phases, $\Delta H_C = 19.25$ J.g^{-1}) is very closed for enthalpy of endothermic heat flow peak (austenitic phase, $\Delta H_H = 21.03$ J.g^{-1}). In the samples heat treated at 600 °C haven't showed R-phase, transformation's enthalpies are of about 20.64 J.g^{-1}, as shown in Figure 2b. Other observation for this treatment is stabilization of critical transformation temperatures and enthalpies values independently of ageing time.

Figure 3 show calorimetrical curves for samples heat treated at 500 °C during six homogenization times. This figure shows evolution of the R and martensitic phases where peaks tend to approach. From 12 hours of heat treatment theses peaks form practically one alone peak, but with a much larger hysteresis. Changes presented in the calorimetrical curves have been investigated in the literature and two principal causes are appointed. Near-equiatomic Ti-Ni shape memory alloys but lightly rich in nickel can during heat treatment at elevated temperatures to form precipitates such as Ti_3Ni_4, Ti_2Ni_3 and $TiNi_3$[8-10]. These precipitates make martensitic transformation more easier (increase of M_s in Figure 3) because they act as preferential sites for nucleation of reaction, inhibiting and/or suppressing the appearance of the R-phase. Precipitations occur from diffusional processes which involve changes in chemical composition, modifying transformation temperatures of such a way that increase critical temperatures, in case of the Ni-rich alloys[5, 11-13].
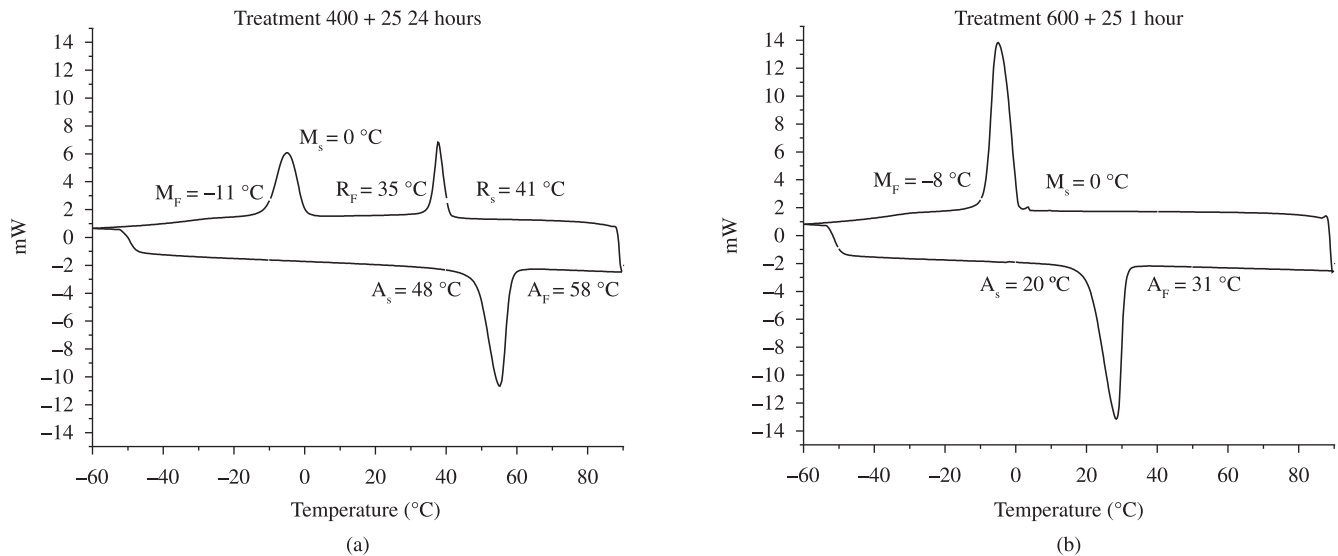

(a)

(b)

Figure 2. Calorimetrical curves: a) Sample heat treated at 400 °C for 24 hours and b) Sample heat treated at 600 °C for 1 hour.
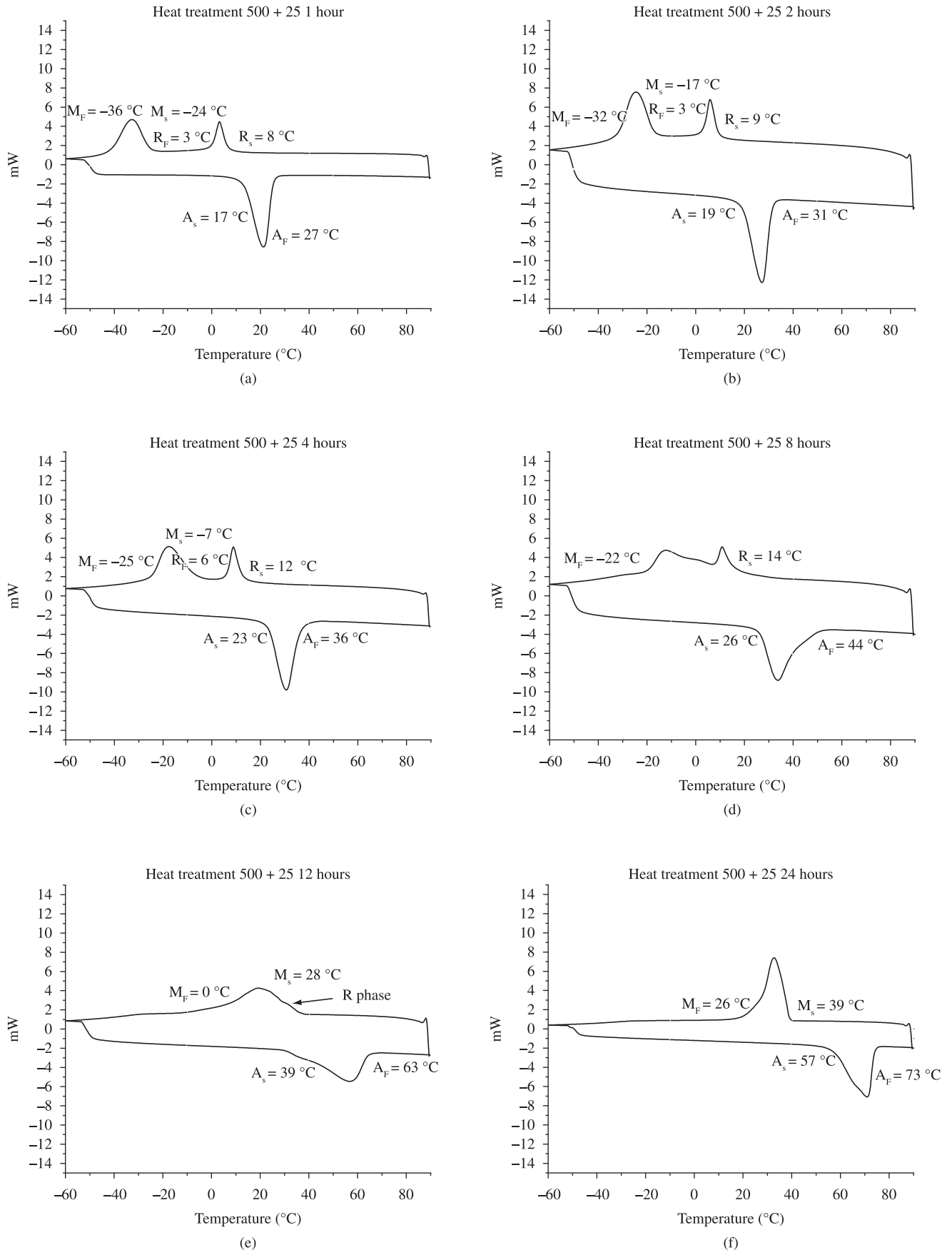
Figure 3. Calorimetrical curves for samples heat treated at 500 °C: a) 1 hour; b) 2 hours; c) 4 hours; d) 8 hours; e) 12 hours; and f) 24 hours.

A second important factor is about deformation stage or dislocation density configurations. This factor depends of the fabrication process, thermomechanical treatments and others. Normally alloys with high dislocation densities present two peaks that correspond to R and martensitic phases[8, 12]. Wires utilized in this work were obtained by cold-drawn process, resulting in a material with high dislocation density.

From curves of Figure 3 is observed during cooling the appearance of multiple peaks or a two-step transformation (Austenite →R-phase→Martensite). Increasing anneal time, this two-step transformation changes gradually. The R-phase peak temperatures and enthalpies remain practically unchangeable, but martensitic phase peak temperatures increase and hysteresis present a widening. In a first moment, precipitation reactions must to be responsible by the critical temperatures increase due to modifications localized in the chemical compositions. On the other hand, recuperation and recrystallization processes (variation of dislocation density and grain growth) leads changes in the calorimeter curves,

showing a decrease in hysteresis and an apparent elimination of the R-phase, In this case the martensitic transformation consisted in a single-step (Austenitie→Martensite)[5, 7, 14, 15].

Samples heat treated at 600 °C present an one-step transformation. However, shape memory springs produced using this treatment are more rigid than those treated at 500 °C. Apparently, the presence of precipitates difficult the movement of the martensite variants. This behavior appears to be similar when the increase of precipitates are blocking the dislocations, producing hardening of material. Thus, treatment at 500 °C for 24 hours was chosen for thermomechanical tests.

3.2. Thermomechanical tests

Thermomechanical cycles were realized in the SMS to determinate thermoelastic properties of martensitic transformation under constant traction loads. Figure 4 show strain-temperature curves for SMS submitted to constant shear stress at 70, 105, 170 and 200 MPa. These curves shown that critical temperatures
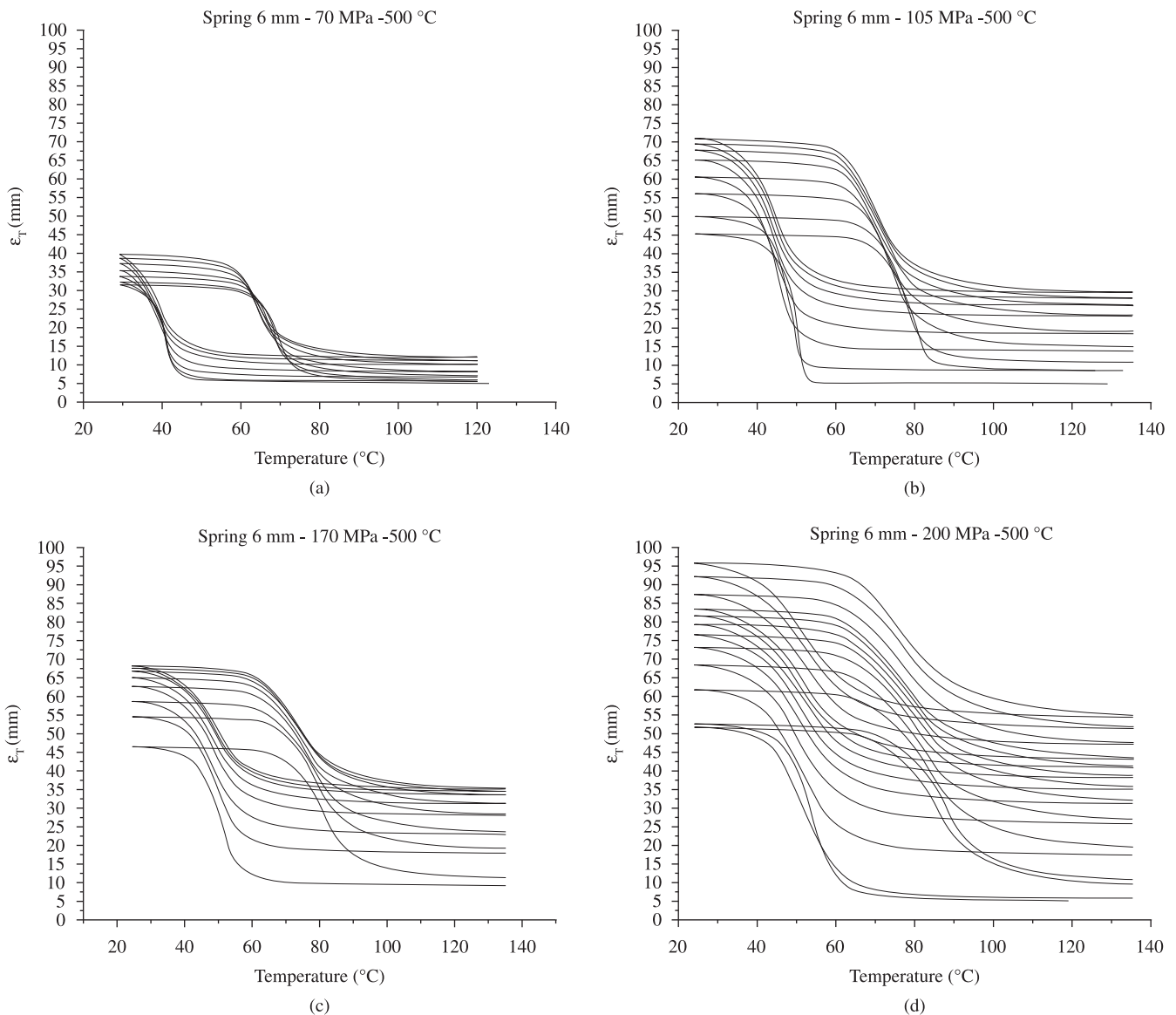

Figure 4. Strain vs. temperature curves obtained during training cycles under tensile stress: a) 70 MPa; b) 105 MPa; c) 170 MPa; and d) 200 MPa (1, 2, 5, 10, 20, 30, 40 and 50th cycles).

increases proportionally with load applied. This is very close to the Clausius–Clapeyron relationship, on which the applied external stress increases the critical transformation temperatures[16]. Hysteresis loops of the strain vs. temperature curves developed changes to right and upward during thermal cycling, principally in the first five cycles. These evolutions are due to variants orientation process, facilitating the direct and reverse martensitic transformation (increase Ms and decrease As), therefore it's necessary less energy for transformation. Other characteristic in these curves is the presence of irrecoverable strain, which increase with applied load. A first factor is martensitic stabilization process by the excess of load that quickly and widely modifies the dislocations stress fields resulting in pinning or blocking of martensite variants. The second factor is due to introduction of microplastic deformation[16, 17].
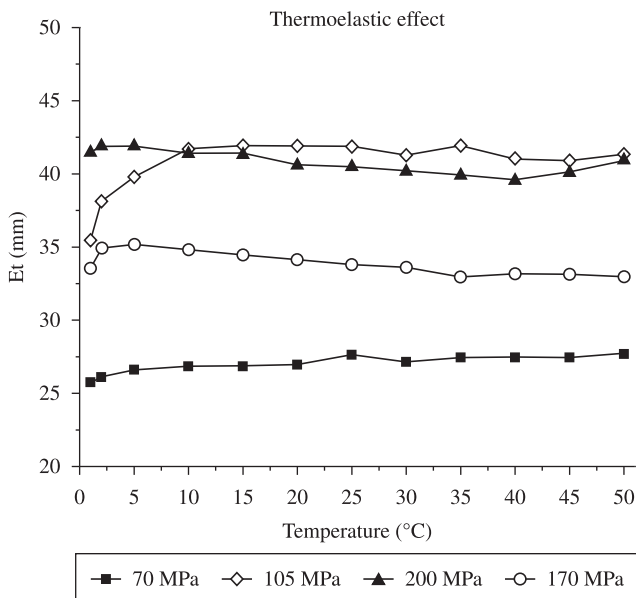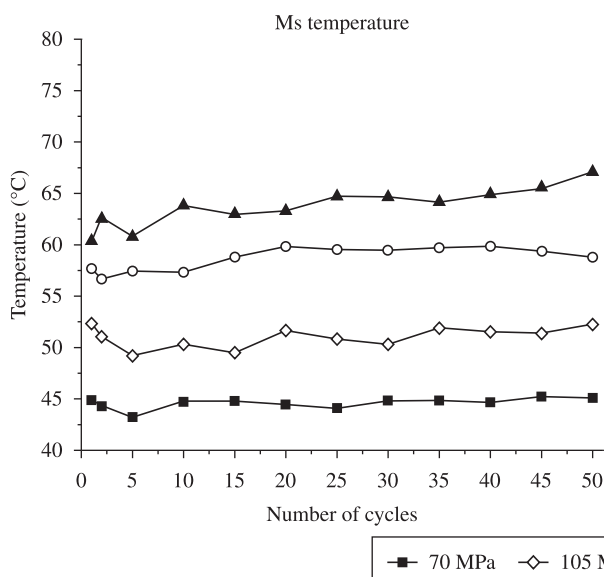
Figure 5 present the evolution of thermoelastic strain during thermal cycles for each applied tensile stress. Initially, the thermoelastic strains obtained increase with the load applied, but their evolutions during thermal cycles are different. For 70 and 105 MPa stresses present a gradual increase during training cycles until practically to stabilize strain in the last cycles. For 170 and 200 MPa stresses, the thermoelastic strain decrease continuously, after the two first initial cycles. During training occurs a martensite variants reorientation process where internal stresses generated by the dislocation fields becoming preferential some martensitic crystallographic variants, according to stress direction. For low and intermediate stresses, internal stress fields are formed gradually in each cycle, increasing thermoelastic strain during thermal cycling. In this sense, 105 MPa stress presents best results, whereas 170 and 200 MPa stresses produce a decrease of the thermoelastic strain because the internal stress fields (dislocation configuration) were saturated rapidly, inducing the martensitic stabilization. These behaviors were observed in cooper based shape memory alloy springs[7].

Evolution of the M_s and A_s critical temperatures are presented in the Figure 6. The M_s temperatures increase during thermal cycles due to martensite variants reorientation process. For this same reason, the A_s temperatures decrease because reverse transformation is much easier, resulting in a thermal hysteresis small. For both evolutions, the temperatures become practically constant from twenty fifth cycle.

3.3. Calorimetrical study in as-treated and training samples

Calorimetric curve of sample heat treated at 500 °C for 24 hours, here in this section identified of as-treated sample, doesn't present the characteristic R-phase peak (Figure 3f). Also in the thermomechanical tests of the shape memory springs there isn't evidence of presence of the R-phase. In this section is presented a calorimetrical study in as-heat treated and training samples because this technique is more sensible to identify the R-phase. The second sample was obtained from memory spring training.

In the calorimetric tests, the samples were thermally cycled thirty times in a DSC apparatus, utilizing a temperature interval of 0 and 90 °C at a constant rate of 10 °C/min. Figure 7 shows 1, 5, 10, 15, 20 and 30 calorimetrical curves for the as-treated sample. In the
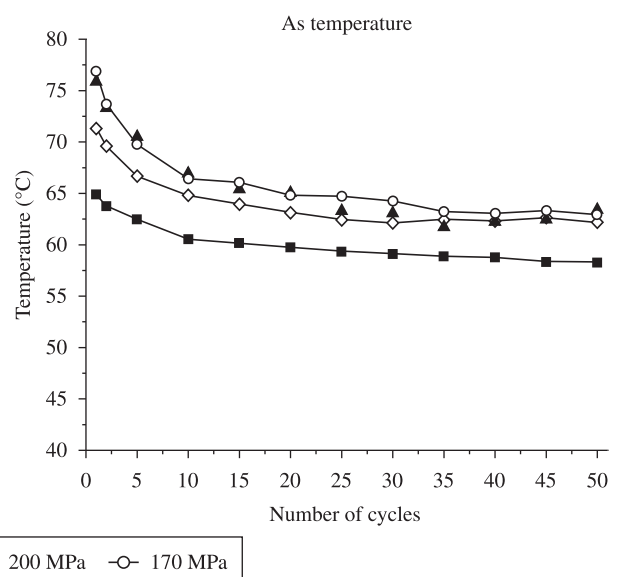

Figure 5. Evolution of thermoelastic strain with number of cycles for each tensile stress.

Figure 6. Temperature vs. number of cycle curves: a) Ms temperature and b) As temperature.
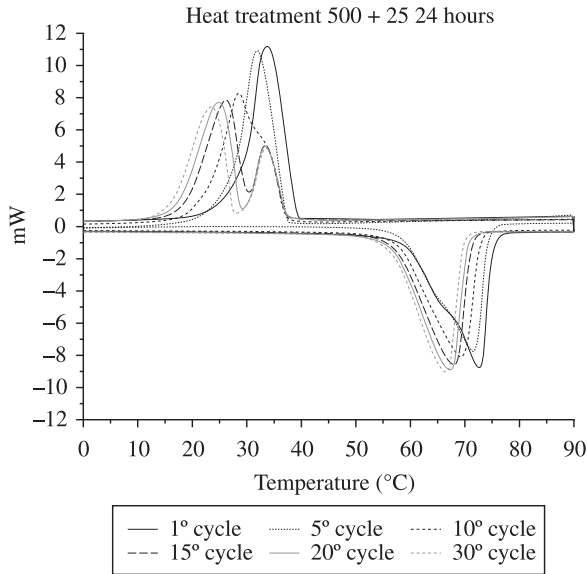
Figure 7. Calorimetrical cycles for the as-treated sample (500 °C / 24 hours). Cycles: 1, 5, 10, 15, 20 and 30º.
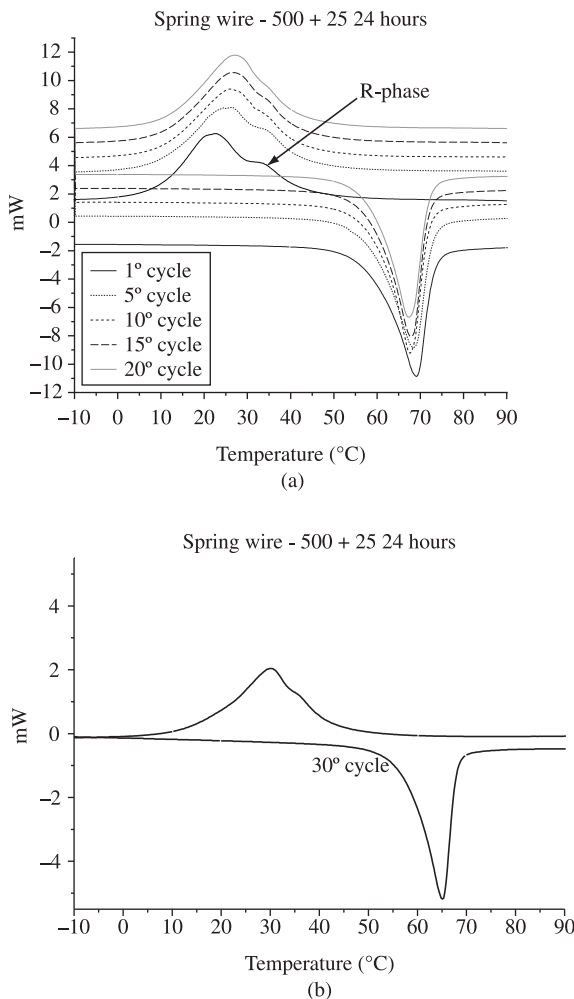

Figure 8. Calorimetrical cycles for training sample (135 MPa). a) Cycles: 1, 5, 10, 15, 20 and b) 30º.

tenth thermal cycle is possible to distinguish the formation of the R-phase through a delay in the martensite peak (width peak increases). From tenth fifth cycle, martensitic transformation occurs clearly in a two-step transformation (B2→R→B19').

A DSC sample was prepared from a Ti-Ni spring utilized in the thermomechanical test at 135 MPa (training sample). Figure 8 shows calorimetrical cycles in this sample. On the first cycles, the martensite phase is formed thought two-step transformation, undetectable in the thermomechanical tests, showing a large thermal hysteresis (M_s – M_f = 50 °C).

In the case of the as-treat sample, precipitates were generated during heat treatment of 24 hours (Ti_3Ni_4 precipitates). The interfacial strain energy stored among matrix phase (Ti-Ni) and precipitates benefits or induces the nucleation of martensite. This energy tends to decrease of intensity during thermal cycling due to accommodation or dissipation of these internal stresses.

Thus, the B19´ martensitic transformation needs more free energy, resulting in decrease of transformation temperatures (Ms and Mf – Figure 7). As this energy is very large in comparison to R-phase transformation, environ two order of magnitude, B19' peak gradually leave of R-phase peak[17, 18]. These differences among phase formation energies explain the passage for two-step transformation[19].

Trained sample calorimetrical curves show the presence quasi two-step transformation during initial thermal cycles (Figure 8 – curves 1 and 5). The handing in the occasion of manufacturing of the sample introduces some small deformation, resulting in appearance of R-phase. Preferential martensite variants orientation process occurs during thermomechanical test in the training sample. This process produced a configuration practically stable, even after the removal of load. After initial cycles, the transformation occurs in one step and general characteristics of transformation becomes unchangeable (temperatures, hysteresis and enthalpies), showing the efficacy of the training process under stress.

4. Conclusions

According to the obtained results can be concluded that:
- Heat Treatments applied in the Ti-Ni commercial wire produce important changes in the martensitic transformation thermoelastic properties. Samples treated at 400 °C always presented two-steps transformation (A - R - M), same after aged 24 hours. For samples treated at 600 °C always became transformation in an only step (A - M), independently of time. Samples treated at 500 °C showed an increase of the transformation critical temperatures, and after 12 hours, the R-phase was suppressed. These samples are also more ductile in comparison the samples treated at 600ºC, due probably the large presence of precipitates.
- During thermomechanical tests in the Ti-Ni springs showed evolutions of the critical transformation temperatures but becomes stabilized from 25° thermal cycle. Stress applied of better efficiency was at 105 MPa, presenting a thermoelastic strain of about 40 mm.
- Thermal cycling studies by DSC in the treated (500 °C/24 hours) and trained samples showed that the R-phase is very sensitive the thermomechanical history of alloy. The first sample doesn't show the R-phase initially, but during thermal cycling this phase reappears. In the second case, the R-phase is inhibited due to stresses fields create during thermomechanical test, indicating to be the best method to avoid the presence of this phase.

Acknowledgments

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