

Thermal Cycling Influence on the Transformation Characteristics of a Ni₅₀Ti₄₈Nb₂ Shape Memory Alloy

IOANA ARINA GHERGHESCU¹, SORIN CIUCA¹, GABRIELA LILIANA JICMON², RUXANDRA ELENA DUMITRESCU¹, MIHAI BRANZEI*

¹ Politehnica University of Bucharest, Materials Science and Engineering Faculty, Department of Materials Science and Physical Metallurgy, 313 Splaiul Independentei, 060042, Bucharest, Romania

² Carol I Technical High School, 52 Porumbacu Str., 060366, Bucharest, Romania

The alloy was chosen in order to obtain a shape memory alloy having a wider hysteresis than equiatomic NiTi, that involves a better thermo-mechanical stability. Two samples investigated by differential scanning calorimetry (DSC) were previously annealed at 800°C/12 h and, respectively, 900 °C/12 h followed by furnace cooling. These were afterwards submitted to thermal cycling. The thermal cycling of a Ni₅₀Ti₄₈Nb₂ alloy sample previously annealed at 900 °C/12 h results in lower critical points and higher hysteresis values as compared to those of the sample annealed at 800°C/12h, also submitted to thermal cycling. Thus, annealing a metallic part made of such an alloy at 900 °C/12 h followed by thermal cycling prior to putting it into service enhances its reliability.

Key words: NiTiNb shape memory alloy, thermal cycling, wide hysteresis, differential scanning calorimetry (DSC)

A proper conservation of the integrity of a NiTi shape memory coupling needs that the part remains austenitic throughout its service life. When the part microstructure becomes martensitic, the recovery stresses will be lowered to the martensitic yield stress or even leading the joint to physically separate because of the two – way shape memory effect.

Such a required feature is ensured by an alloy having a wider hysteresis than equiatomic NiTi and also lower transformation temperatures. The Ni-Ti-Nb - based alloys are mainly advantageous for pipe-joint couplings, due to their wide hysteresis [1].

The transformation temperatures (also known as critical points) in a shape memory alloy are: austenite start temperature (A_s), austenite finish temperature (A_f), martensite start temperature (M_s) and martensite finish temperature (M_f). They describe a complete thermal cycle and also allow the calculation of the thermal hysteresis. This set of four temperatures are the main feature that assigns a shape memory alloy to a specific application.

NiTiNb alloys are typically used in shape memory nickel titanium coupling devices that need to have cryogenic martensite transformation temperatures (thus very low) but also need room temperature storage capability.

As for the hysteresis, the addition of niobium as a third element results in doubling or more the thermal hysteresis in comparison to that of a NiTi equiatomic alloy. M_s must be as far as possible separated from A_s , because M_s controls the stress decay process and A_s imposes the maximum storage temperature [1]. This feature is useful in NiTi pipe joints not to lose the joint tightness upon unanticipated lowering of temperature. On a contrary, when considering other elements, for instance the addition of copper replacing nickel, this allows us to reduce the thermal hysteresis from 40 to 10 degrees when copper content exceeds 10%. This feature is needed when using NiTiCu alloys in actuators and orthodontic wires [2].

A coupling material must have some different shape memory alloy properties as against an actuator material. The alloy must exhibit a minimal change when an important drop of temperature takes place. This may be

accomplished by alloying a binary NiTi with Nb, resulting in a larger hysteresis. A wide hysteresis Ni₄₇Ti₄₄Nb₉ alloy has already been studied as for its microstructure, deformation behavior, thermal hysteresis [1,3,4]. Such alloys are needed for applications where room temperature lies above the transformation temperatures and consequently the hysteresis. This allows the material to be deformed at low temperatures and be safely put in final form at room temperatures.

The Ni₄₇Ti₄₄Nb₉ alloy has a thermal hysteresis of 72.5 degrees as against equiatomic NiTi alloy having roughly a 30 degrees one [1].

An interest may arise in identifying the transformation temperatures and the thermal hysteresis of a NiTiNb alloy containing less than 9 at% Nb, the latter being an expensive metal with a big specific weight.

Therefore, a shape memory Ni₅₀Ti₄₈Nb₂ alloy was chosen in order to check its critical points and hysteresis width. A method of widening this latter feature is also aimed to be established; that will involve a better thermo-mechanical stability, therefore a higher reliability.

Experimental part

The raw materials employed in order to obtain NiTiNb alloys were the following: Ti (Ugine) refined in vacuum (99.99%), electrolytic (99.98%) Ni (INCO) and master alloy TiNb, containing 44 wt% titanium. All three were grinded and then etched in a 1/3 HF + 2/3 HNO₃ solution. The metals were melted in a high induction furnace (0.5 MHz) having 25 kW maximum power. This furnace allows the making of the alloy in neutral atmosphere, in a cavity made in a copper pipe, continuously cooled by water. A satisfactory homogeneousness is obtained thanks to the electromagnetic induction and the quick final cooling allows segregation reduction.

The resulting ingot had a cylindrical shape of 6 mm radius and 50 mm length. Its mass was of 40 g.

Prior to all deformation, a homogenizing annealing was applied at 900°C/48 h.

The subsequent hot rolling was performed at 850°C, until 40 mm² of the ingot section, followed by cold rolling.

* email: mihai.branzei@upb.ro; Phone: +40745189310

Two $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ samples investigated by differential scanning calorimetry (DSC) were previously annealed at $800^\circ\text{C}/12\text{ h}$ and respectively, $900^\circ\text{C}/12\text{ h}$ followed by furnace cooling. These will be referred to as S1 and respectively S2 along the paper.

Tests were performed on a METTLER TA 4000 differential scanning calorimeter, equipped with a DSC30 cell with automatic temperature control, operating under nitrogen flow. The temperature range of the calorimeter is -170°C to 600°C , results reproducibility being of $\pm 0.2^\circ\text{C}$.

After rising the temperature up to 50°C in order to assure a complete austenitic structure of the material, several alternating cooling and heating cycles were applied on both samples.

Each further DSC test was made when the sample reached room temperature after the previous test; thus both samples were submitted to a double number of heating and cooling cycles. Tests are completely covering the transformation temperatures range of the alloy, the interval being established by preliminary testing. The test scanning rate was of $5^\circ\text{C}/\text{min}$.

Results and discussions

DSC diagrams for both $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ samples are found in figures 1-5 that show different overlapped heating and cooling cycles for both samples S1 and S2 in order to ease observations on these transformations, and the first two cooling cycles of both samples, also overlapped.

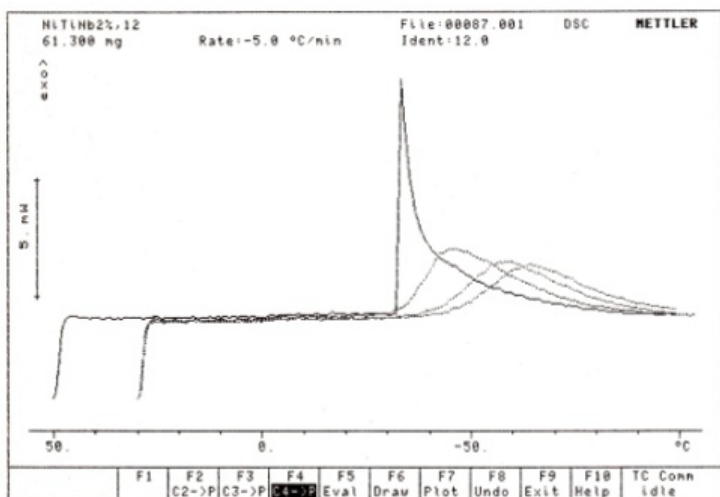


Fig.1. Overlapped first four cooling cycles for sample S1, previously annealed at $800^\circ\text{C}/12\text{ h}$

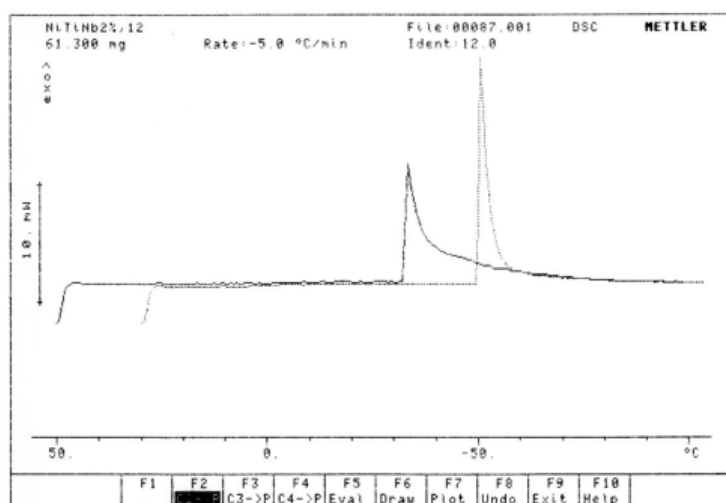


Fig.2. Overlapped first cooling cycles for samples S1 and S2

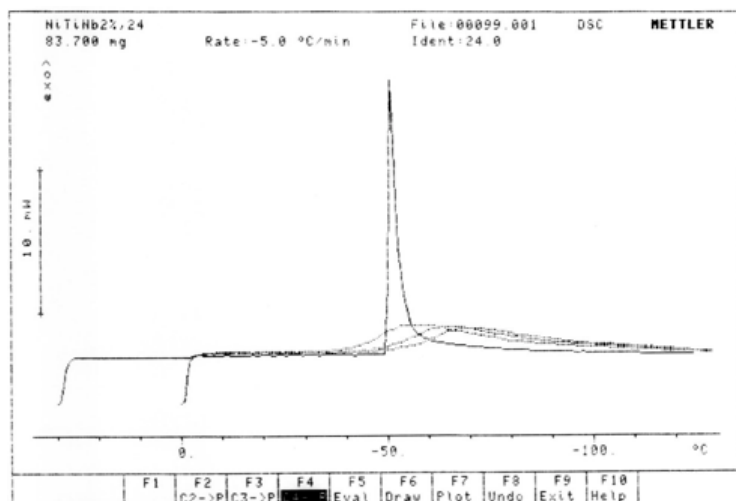


Fig.3. Overlapped first four cooling cycles for sample S2, previously annealed at $900^\circ\text{C}/12\text{ h}$

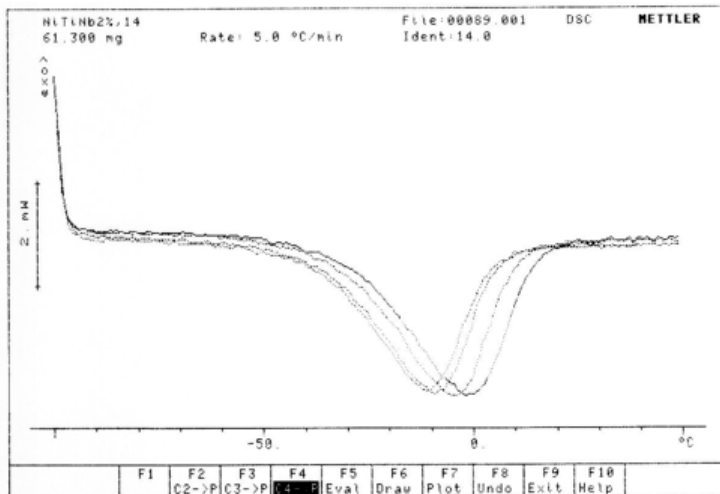


Fig.4. Overlapped first four heating cycles for sample S1, previously annealed at 800 °C/12 h

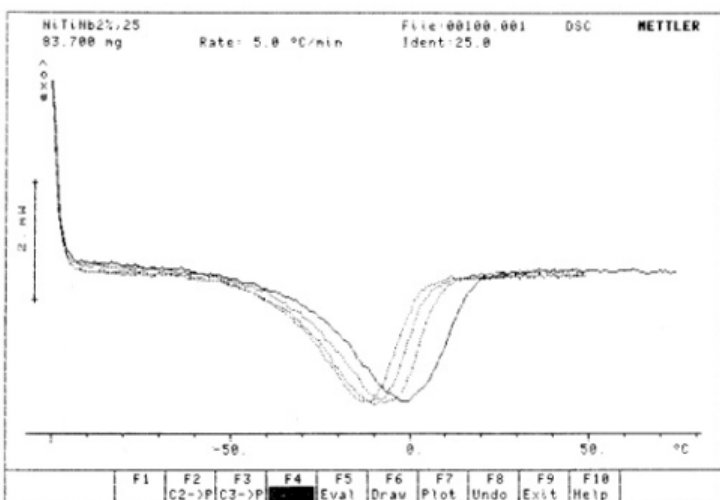


Fig.5. Overlapped first four heating cycles for sample S2, previously annealed at 900 °C/12 h

Tables 1 and 2 show the transformation temperatures for each cycle, the enthalpy values for each transformation and also the hysteresis values.

Prior to all results interpretation on $Ni_{50}Ti_{48}Nb_2$ alloy, several aspects of the behavior of the Nb - richer $Ni_{47}Ti_{44}Nb_9$ have to be mentioned.

The $Ni_{47}Ti_{44}Nb_9$ alloy microstructure, which was the subject of earlier research [1,3,4] reveals the presence of niobium-rich compounds in the matrix solid solution of equiatomic NiTi composition. These particles are insoluble on heating up to 1100 °C. For higher holding times, the compounds grow [4]. These are therefore compound particles formed at high temperatures, probably during

solidification, also known as primary solid solution particles. The particles have a chemical composition very close to that of the β phase in the NbTi system, containing ~ 80 %Nb.

The deformation behaviour of this soft near - β phase on martensitic transformation and reverse was found to be responsible for the hysteresis widening [4].

The width of the transformational hysteresis for undistorted $Ni_{47}Ti_{44}Nb_9$ specimens annealed at 850°C is about 55°C ($M_s = -90$ °C, $A_s = -35$ °C). This hysteresis width can be increased to 150°C with a 16 % tensile deformation at - 60°C. In this case, M_s will stay at about -90 °C, while A_s is raised to 60°C. It is obvious that the transformational

Table 1
CRITICAL POINTS OF SAMPLE S1, PREVIOUSLY ANNEALED AT 800 °C/12 h

Test No.	Temperature interval	M_f (°C)	M_s (°C)	A_s (°C)	A_f (°C)	ΔH_{cool} (J/g)	ΔH_{heat} (J/g)	Hysteresis (°C)
12	+50 → -100	-87	-32	-	-	16.5	-	
13	0 → -150	-78	-33	-	-	18.5	-	
14	-100 → +50	-	-	-31	+14	-	17.4	47
15	+30 → -100	-90	-40	-	-	12.5	-	
16	-100 → +50	-	-	-34	+11	-	16.1	53
17	+30 → -100	-92	-45	-	-	10.8	-	
18	-100 → +50	-	-	-38	+7	-	15.9	53
19	+30 → -100	-94	-46	-	-	12.4	-	
20	-100 → +50	-	-	-41	+3	-	15.6	51
21	+30 → -100	-97	-47	-	-	14.3	-	
22	-100 → +40	-	-	-50	+4	-	14.2	49
23	+30 → -150	-110	-53	-	-	17.2	-	

Table 2
CRITICAL POINTS OF SAMPLE S2, PREVIOUSLY ANNEALED AT 900 °C/12 h

Test No.	Temperature interval	M _f (°C)	M _s (°C)	A _s (°C)	A _f (°C)	ΔH _{cool} (J/g)	ΔH _{heat} (J/g)	Hysteresis (°C)
24	+30 → -125	-55	-49	-	-	9.9	-	
25	-100 → +75	-	-	-32	+27	-	11.0	50
26	0 → -150	-110	-38	-	-	10,6	-	
27	-100 → +50	-	-	-36	+10	-	9.5	61
28	0 → -150	-115	-48	-	-	10.8	-	
29	-100 → +50	-	-	-40	+5	-	9.2	64
30	0 → -150	-120	-54	-	-	10.6	-	
31	-100 → +50	-	-	-40	0	-	8.3	67
32	0 → -150	-130	-55	-	-	9.6	-	
33	-100 → +50	-	-	-40	0	-	7.6	72

hysteresis after deforming at -60 °C is remarkably increased but the phenomenon takes place also on thermal cycling [4], however the transformations temperatures being different.

As for Ni₅₀Ti₄₈Nb₂ alloy, one may notice that all critical points drop when increasing the number of cycles for both samples, S1 and S2.

For the sample S1, the bursting kinetic of the first cooling cycle was attributed to the fact that the compound particles found in the structure hinder the martensitic transformation progress. Once reached a certain temperature, sufficiently low so that the driving force to provide the stress needed for particles deformation (at least equal to their yield strength value), the transformation will occur.

One can also notice a continued decline of the M_s value when increasing the number of cycles, because the transformation is controlled by dislocations caused by thermal cycling. With increasing number of cycles, the density of dislocations formed in the matrix also increases. Some of them disappear along the previous reverse transformation but the rest tend to an equilibrium configuration and will hinder the martensitic transformation onset. They will jog the coherent twin planes and result in a friction force, consequently the energy (the driving force) required for martensite transformation to take place is higher, therefore the martensite M_s point on cooling decreases, as well as the M_f point.

Miyazaki et al. [5] found that M_f and M_s temperatures lowers with increasing number of thermal cycles. The drop is fast in the beginning but gradually values stabilize with increasing number of cycles. The investigation done by transmission electron microscopy showed dislocations created along the first cycle that further impede other dislocation to move; their arrangement tend to stabilize when increasing the number of thermal cycles [5].

The decrease in the M_s value is greater for an alloy of this composition than for a equiatomic NiTi alloy which showed, after multiple cycles, a decrease in the value of M_s of approximately 2 degrees [6,7]. For the studied alloy, there was a drop of 21 degrees after 7 cycles of the M_s value.

The obtained curves express in fact the dependence C_p = C(T); the feature of these curves show a relaxation tendency, a lagging of the kinetic of transformation, a growth of the incubation period for the A→M transformation; the relaxation noticed for the reverse transformation, M→A, is also expressed by a significant decreasing in the value of the transformation enthalpy, that was attributed to reactions between dislocations phenomenon until an equilibrium configuration was reached. The same declining tendency is found for A_s and A_f.

For the first two cycles, the values A_s for the two differently annealed samples are very similar. The range A_s-A_f, however, is greater for the sample S2, for the first two cycles and, after the achievement of the equilibrium configuration of dislocations it returns to a lower value, ensuring the reliability in service of such a part.

Therefore, thermal cycling of a Ni₅₀Ti₄₈Nb₂ alloy appear to be a possible method of lowering the temperature M_s. The aim is to increase the hysteresis width, interspacing M_s from A_s, as much as possible. The Ni₅₀Ti₄₈Nb₂ alloy stabilization occurs after the application of 20 alternated cooling and heating cycles.

The Ni downward influence on the transformation temperatures is well-known, a surplus of 1% Ni leading to a lowering of A_s with 10 degrees and M_s with 6 degrees [8]; another important drop of M_s was reported by Frenzel et al (2010): 10 °C/0.1 at% Ni if the nickel content exceeds 50.5 at% [9]. The M_s point decrease of 21 degrees has been assigned to the synergistic influence of Ni and Nb, thus to their concentration increase in the matrix, as against the less stronger effect of Ni content in the NiTi equiatomic alloy.

One may compare the results obtained by the DSC thermal cycling applied to the samples annealed in two different conditions: 800°C/12h and 900°C/12h. When comparing cycles of the same order for both samples, one can find differences between M_s values between each of the cycles considered.

In the Ni₅₀Ti₄₈Nb₂ alloy the precipitation of the near - β phase of a NbTi alloy containing 80 at % Nb reported to be found in Ni₄₇Ti₄₄Nb₉ alloy [4] does not occur, this being in accordance with the equilibrium diagrams of NbTi and NbNi systems. Precipitates which occur are from the NiTi system - Ti₂Ni - and also compounds based on solid solutions of Ni, Ti and Nb such as Ni_{53.5}Ti₄₂Nb_{4.5} or Ni₄₆Ti_{32.5}Nb_{21.5} [10]. Their composition makes them less involved than the soft near - β phase in the mechanism of martensitic and reverse transformation [4], their niobium content being much less than 80% and consequently their hardness being higher.

For the sample S2, the first cooling cycle shows the same explosive kinetic feature, due to the local micro deformations of the compounds, revealing the necessity of applying a higher driving force for the sample annealed at 900 °C/12 h, due to the increase in size of the compounds present in the matrix; one can also consider that the lower number of (larger) compounds involves less dense areas of deformed material at the interface matrix-compound, prone to generate nucleation centers, thus a smaller number of dislocations having very close Burgers vectors. The driving force of the transformation will need to be higher,

so the M_s point corresponding to the sample annealed at 900 °C/12h will be lower.

Once these deformations completed, the compounds will no longer be a barrier to the transformation, the required driving force for second order cycles being smaller; we can see in each of these cases a return of M_s point to higher values. The effect could be attributed to registration errors for the sample annealed at 800°C/12 h, but it is obvious for the second sample annealed at 900 °C/12 h. For subsequent cycles, the decrease of the M_s point is resumed, a phenomenon already explained by the increase in the matrix dislocations density formed during the successive transformations A→M and their configuration stabilization [5].

The same relaxation of the transformation phenomenon should be noted in both cases, the curves being increasingly flattened; this phenomenon was assigned, on the one hand, to the decreasing role played by compounds in the transformation, and on the other hand, to a preferential nucleation caused by martensitic transformation induced dislocations.

Examining the transformation temperatures shown in tables 1 and 2, one can see a more rapid decrease of the M_s point for the sample annealed at 800 °C/12 h, even if the value of M_s obtained in the first cycle is higher; for S2, the sample annealed at 900 °C/12 h, the value of M_s given by in the first cycle is lower but the subsequent decline is slightly slower. However, the smaller M_s values obtained through cycling for the sample S2 annealed at 900 °C/12 h are more important than the M_s decline rate.

For the sample treated at 900 °C/12h, the smaller ΔH_{cool} and also ΔH_{heat} may be explained by the fact that the coherence degree between the compounds and the matrix drops (even to extinction); by coalescence of the compound particles the matrix-compound interfacial energy decreases, thus decreasing internal energy. It is to be remembered that in condensed phases $\Delta H \approx \Delta U$.

When examining results from heating cycles - austenite to martensite transformation - one can see that the transformation enthalpy decreases slowly but continuously for both samples, as the number of cycles increases. This phenomenon was attributed to a reaction between the dislocations until reaching an equilibrium configuration. By cycling, the degree of coherence of the compound particles with the matrix continuously decreases, due to the twinning and untwining at the matrix - compound interface. A similar effect occurs when a discharge of energy by local plastic flow takes place.

Considering the hysteresis, if one defines it as $(M_s + M_f)/2 - (A_s + A_f)/2$, its values were calculated for each set composed of one cooling + one heating cycles, for both S1 and S2 samples and reported in tables 1 and 2.

While there is no linear evolution of the hysteresis values for sample S1, it is easily noticed that the hysteresis values are higher for sample S2, when increasing the number of thermal cycles.

One can therefore conclude that, in order to reach lower transformation temperatures and an increase of the hysteresis, aiming to improve the reliability of a $Ni_{50}Ti_{48}Nb_2$ alloy, it is advantageous to perform an annealing at 900 °C/12 h prior to thermal cycling.

In order to synthesize, one can see that transformation temperatures during the direct and the reverse transformations of $Ni_{50}Ti_{48}Nb_2$ decreases with increasing number of thermal cycles.

The shift of the transformation temperatures may be ascribed to the crystal structure, namely to the defects among which one can quote dislocations, stacking faults

and some disarray in the structure of ordered NiTi. It is presumed that there is an upper limit of the quantity of the transformation generated defects present in the NiTi alloys, that is reached when the amount of the induced defects is the same as that of the defects annihilated during the transformation, after applying a large number of transformation cycles; this phenomenon was found in several NiTi alloys when many alternating thermal cycles were performed by differential scanning calorimetry [7,11,12]. Before reaching a stable configuration, the number of microstructural defects generated by the transformation may be higher (or lower) than the number of defects eliminated by the same transformation, leading to changes in the critical points values. The temperature shift reduces with increase of the number of transformation cycles, up to reaching the structural defects equilibrium configuration.

It has to be mentioned that the material processing history, among which plastic deformations and annealing heat treatments are found, is responsible for the resulting transformation temperatures.

Conclusions

The transformation behaviour subsequent to thermal cycling of the $Ni_{50}Ti_{48}Nb_2$ alloy suggest that creation, disappearance and rearrangement of defects take place along transformation cycles.

The shift of the transformation temperatures in shape memory alloys, due to the multiple alternated transformations, is a characteristic phenomenon and is important for the stability of each phase [11]. Hence it has been shown that after producing and plastic deformation, the material needs an additional stabilization treatment by thermal cycling for ensuring minimum differences in the repetitive functional behavior.

The transformation behavior of the $Ni_{50}Ti_{48}Nb_2$ alloy was investigated by differential scanning calorimetry in order to reveal the effect of thermal cycles on the material significant features. The thermal cycles tend to shift to lower values the transformation temperatures of both phases, martensite - M_s and M_f - and austenite - A_s and A_f .

Differences were reported between the critical points values of the alloy previously annealed at 800 °C/12 h and 900 °C/12 h, further submitted to thermal cycling by differential scanning calorimetry. Thus one can see that the shape memory alloy annealing temperature and holding time have significant influence on the material thermo-mechanical behavior.

An annealing at 900 °C/12 h prior to thermal cycling of a $Ni_{50}Ti_{48}Nb_2$ alloy sample gives lower critical points and higher hysteresis values as compared to those of the sample annealed at 800 °C/12h, also submitted to thermal cycling. These two features enhance the reliability of parts made of this alloy.

The choice of some annealing parameters to be previously applied on a part designed for a requested application will rely on the resulting transformation temperatures, on the hysteresis width but also on some other features, such as the corrosion behavior of the shape memory alloy.

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