

# Heat Treatment Influence upon Precipitates Chemical Composition and Transformation Temperatures of a NiTi Shape Memory Alloy

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*The paper presents the results of tests made in order to reveal structural changes consisting in appearance and disappearance of several precipitates and subsequent transformation temperatures changes of a shape memory Ni<sub>50.6</sub>Ti<sub>49.4</sub> alloy by differential scanning calorimetry (DSC); scanning electron microscopy (SEM) together with energy dispersive spectroscopy (EDS) are also performed. Changes in these temperatures are reported, as a consequence of submitting the material to some ageing heat treatments.*

*Key words: Shape memory alloy (SMA), NiTi precipitates, differential scanning calorimetry (DSC)*

Shape memory alloys (SMA) received a lot of interest and intensive research during the last few decades, due to their many applications in different domains of activity: aviation, producing special medical instruments, robotics, actuators, antennas, etc. [1].

The scientific literature concerning the shape memory alloys (SMA) are vast; nevertheless the field remains an active area of research, and the understanding of the mechanisms involved at all scales, from the crystalline lattice to the macroscopic scale, as well as the connection of these structural aspects with their properties are still subject of controversy, even after more than 20 years of research.

NiTi based shape memory alloys (SMA), such as near-equiatomic NiTi (with a composition of 53 to 57% Ni by weight) known as Nitinol, were first discovered in the early 1960's. NiTi SMAs present advantages like a high corrosion resistance, a good fatigue resistance and an exceptional biocompatibility, thereby making them one of the most preferred material for the most part of shape memory effect applications being considered today [2].

Its applications are based on its properties, as for instance the fact that it has a strong undeformable state at high temperature (austenite) and a deformable state (martensite) at a lower temperature. The shape memory NiTi alloys possess the ability to undergo shape change at low temperature and retain this deformation until they are heated, at which point they return to their original shape [3].

NiTi shape memory alloys are known to exhibit different transformation sequences depending on many factors including alloy composition, thermomechanical treatment history and testing conditions [4]. NiTi SMAs present three different phases: the B2 phase known as austenite (A), the monoclinic phase known as martensite (M), and sometimes, under certain conditions, the rhombohedral phase known as premartensitic R phase [5].

Thus, the most important features involved in the characterization of a SMA material are the phase transformations temperatures. These alloys are presenting

a hysteretic behaviour, and there are several transformation temperatures to speak about: the austenite start temperature ( $A_s$ ), the austenite finish temperature ( $A_f$ ) during heating, the martensite start temperature ( $M_s$ ) and the martensite finish temperature ( $M_f$ ) during cooling. Additionally, an intermediate phase (R phase) often appears during cooling, having its own start temperature ( $R_s$ ) and finish temperature ( $R_f$ ), before the transformation proceeds to martensite at lower temperatures [6]. All the three martensitic - type transformations exhibited by binary near - equiatomic NiTi alloys are hysteretic, as expected for first-order phase transformations [5].

Shape memory effect (SME) consists in turning back a sample strained below  $A_s$  to its initial form by heating it at a temperature higher than  $A_f$ , thanks to the reverse transformation. Strain may be obtained by a tensile stress, a compression or a bending. As long as these do not increase too much, more than a critical value, the reverse transformation on which the shape memory effect is based upon takes place (up to 8% shape recovery is possible).

Superelasticity occurs when Nitinol is mechanically deformed at a temperature above its  $A_f$  temperature. This deformation causes a stress induced phase transformation from austenite to martensite. The stress induced martensite is unstable at temperatures above  $A_f$ , so that when the stress is removed, the material will immediately spring back to the austenite phase and its pre-stressed position. This high degree of elasticity, called superelasticity, is the most attractive property of Nitinol (NiTi alloy) and the most widely used for.

Advantages and disadvantages of NiTi shape memory alloys compositions and their usual applications are to be analyzed. The price of producing such an alloy is still high and involves some difficulties due to its special properties, but precisely those ones that make NiTi one of the alloys of the future (flexibility, biocompatibility, excellent corrosion resistance, etc.). Adding the shape memory effect (SME) through special treatments to NiTi alloys may turn them in exceptional materials of the future, offering more and diverse perspectives and wide applications. Some of these

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particular properties of the NiTi SMA are: ability to be electrically heated for shape recovery, stable transformation temperature [7].

Due to this unusual macroscopic behaviour NiTi SMAs applications are numerous: from medical stents to micro-actuators, from devices protecting buildings from vibrations to orthodontic wires or from GSM antennas to bridges elements.

Generally speaking, there is no predictable influence of a heat treatment on such a NiTi alloy, no matter the chemical composition. The equilibrium diagram gives information on this behaviour, according to the chemical composition of a given alloy, and even so structural changes are to be identified by research studies and are often unexpected.

Considering this, the present paper purpose is to find what structural changes (consisting in appearance and disappearance of some precipitates of various chemical composition) are generated by some ageing heat treatments in a Ni<sub>50.6</sub>Ti<sub>49.4</sub> shape memory alloy, and consequently what are the changes in its transformation temperatures, the main feature that assigns such a device applicability.

### Experimental part

The SMA chosen for DSC and other tests was Ni<sub>50.6</sub>Ti<sub>49.4</sub>. Among richer in nickel NiTi alloys, this is roughly a low one (low nickel NiTi alloys have up to 50.4 % at. Ni and high nickel NiTi alloys have about 51.2% at. Ni).

The material properties depend on structural changes. These are influenced by:

- chemical composition (alloying elements, precipitates, impurities);
- production methods;
- heat treatment and other machine work.

The heat treatment has a greater influence on NiTi alloys properties when increasing Ni concentration at above 50.5 % at. This phenomenon has been proved experimentally [8]. When NiTi alloys with more than 50.5 % at. Ni are submitted to ageing, three types of precipitates may appear in their structure, as follows:



Among them, only TiNi<sub>3</sub> is a stable phase, the other being metastable. Concerning the volume fraction, Ti<sub>3</sub>Ni<sub>4</sub> is reported to be the most important precipitate to be found because it improves mechanical properties due to a very fine precipitation [9].

NiTi shape memory alloys are hard to obtain because of special conditions needed for an appropriate processing, imposed by these materials properties. Melting and casting these alloys are of extreme importance for their chemical composition and consequently on their properties, needed for a chosen device: for instance, the variation of Ni concentration may significantly affect the phase transformation temperature *austenite* ↔ *martensite* [10].

Samples tested and presented in this paper were obtained as follows:

### Melting and vacuum casting in induction furnace

Small titanium plates and nickel bars were used to melt the NiTi alloy. Their purities were (according to the manufacturer's technical specifications):

- Ni 99.7 % (Mn 1100 ppm, Fe 400 ppm, C 400 ppm, Si 300 ppm, Cu 150 ppm, Mg 100 ppm)
- Ti 99.5 % (Fe 1500 ppm, O 1500 ppm, C 200 ppm, N 120 ppm).

The most indicated production method is melting in high frequency induction furnaces (10-30 kHz), these assuring a better homogenization of the whole cast [11].

The alloy was melted at *Metal Products Research Institute of Shanghai*. A 5 kilograms batch was melted in a high frequency induction furnace with CaO crucible. The starting melting temperature was of 1700°C in order to ensure a fast titanium melting and then lowered down to 1450°C. The melt was cast in special water cooled copper moulds, conferring a high quality ingot surface and avoiding impurities contamination.

Such alloys melting must be done in high vacuum or inert gas furnaces, considering titanium very high affinity for oxygen.

Alumina or magnesia crucibles are not recommended, because oxygen found in the crucible compositions reacts with the melt, contaminating it. Neither graphite crucibles are indicated because of a potentially high graphite contamination of the melt.

### Forging

After scale and impurities elimination, bar – shaped ingots of 5 cm diameter were obtained and afterwards hot forged at 850°C down to 10 mm diameter thin bars.

### Cold wire drawing

A recrystallization heat treatment at 750°C was performed after forging, followed by several hot extrusions at 800°C, with 15% reductions between passings in such a way that wires of different diameters were obtained, including those of 0.48 mm diameter.

The last wire drawing passage was a cold one. The alloy chemical composition was determined by X-ray fluorescence spectroscopy: Ni<sub>50.6</sub>Ti<sub>49.4</sub>.

### Heat treatments

For our particular tests, the steps of the procedure used in order to obtain NiTi wire samples showing shape memory behaviour were those mentioned above, plus, as follows:

- first heat treatment: quenching without polymorphic changes, at 750°C/ 25 min/ water;
- second heat treatment: artificial ageing according to table 1. Ageing was done at two different temperatures, two different holding times at the chosen ageing temperatures and two cooling rates. All combinations between these parameters are to be found in table 1.

The tests performed on NiTi samples were, as follows:

Scanning electron microscopy (SEM) investigations, performed on a microscope Philips ESEM XL 30 TMP, equipped with an EDX spectrometra.

Differential scanning calorimetry (DSC) tests were performed on a Netzsch DSC 200 F3 Maia instrument which

**Table 1**  
PARAMETERS CHOSEN FOR THE ARTIFICIAL AGEING

Sample no.	Sample diameter [mm]	Temperature [°C]	Holding time [min]	Cooling rate [°C/ s]
1.	0.48	450	45	5
2.	0.48	510	45	5
3.	0.48	450	45	25
4.	0.48	510	45	25
5.	0.48	450	75	5
6.	0.48	510	75	5
7.	0.48	450	75	25
8.	0.48	510	75	25

offers the advantage that by using liquid nitrogen, the temperature range extends from -170 to 600°C.

## Results and discussions

Prior to all results presentation, some considerations are to be made on  $Ni_4Ti_3$  precipitates, especially on their morphology and evolution on heat treatments performed at different temperatures and holding times, in some other alloys having close compositions to  $Ni_{50.6}Ti_{49.4}$ . Many authors studied  $Ni_4Ti_3$  precipitates shape and size [12-14]. It seems that the heat treatment temperature and also the holding time are of great influence on the growth of these lens – shape precipitates. The heat treatment temperature will influence on the size and also the shape of the precipitate, changing the  $e/d$  ratio where  $e$  is the lens thickness and  $d$  its diameter. When the temperature raises, the  $e/d$  ratio drops, the precipitate becoming thinner and longer [13]. For comparable heat treatment temperatures and holding times, Bataillard [13] found that precipitates grow by ageing treatments up to 550°C (holding time – 1 h) and then dissolve, Khalil Allafi [14] found that precipitates grow by heating up to 500°C (holding time – 1 h) and then dissolve, Frick [15] found that precipitates grow by heating up to 550°C (holding time – 1.5 h) and then dissolve.

The  $Ni_4Ti_3$  precipitates or interfacial dislocations can act as nucleation centers for the formation of the R phase [13, 14].

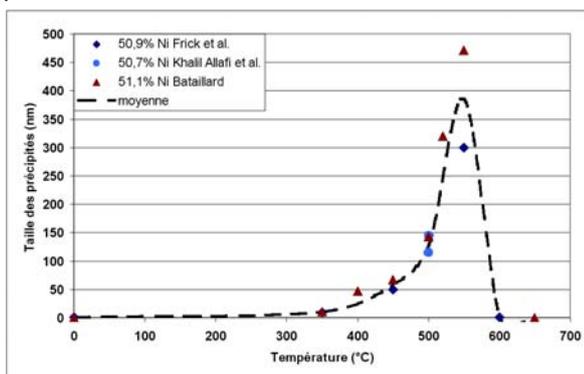


Fig.1. Evolution of precipitates diameter as a function of the heat treatment temperature (holding time: Bataillard and Khalil Allafi: 1h, Frick: 1.5h [13, 14, 15])

This behaviour is usually explained by the fact that the lattice mismatch between precipitate and matrix induces a stress field in the surrounding matrix, favouring particular variants of the phases. The formation of  $Ni_4Ti_3$  precipitates not only introduces a strain field in the surrounding matrix, it also affects the composition of the retained matrix since the precipitates are enriched in Ni on the original material's account having a near-equiatomic composition. The local change of the matrix chemical composition, due to the higher Ni content in the precipitates, was also mentioned in some papers as having an influence on the local transformation temperatures, as is the case for concentration changes at the bulk level [13,16].

### Scanning Electron Microscopy (SEM) investigations

A global micrograph of the matrix, no matter the sample, is shown in figure 2.

Among many different precipitates found in the alloy, two of the most representative are shown:

The identified precipitates are:  $NiTi_2$ ,  $Ni_3Ti_4$ .

### Differential Scanning Calorimetry (DSC) Investigation Results

As previously presented, thin wires treated under the conditions reported in table 1 were investigated by

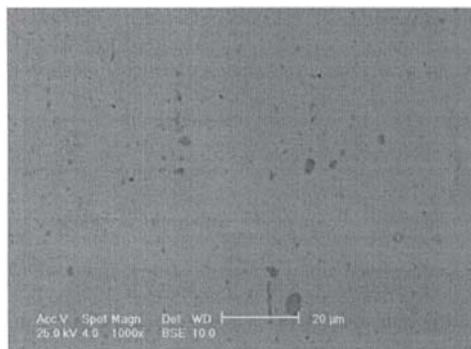


Fig. 2a. Secondary electrons micrograph of the whole sample, x 1000

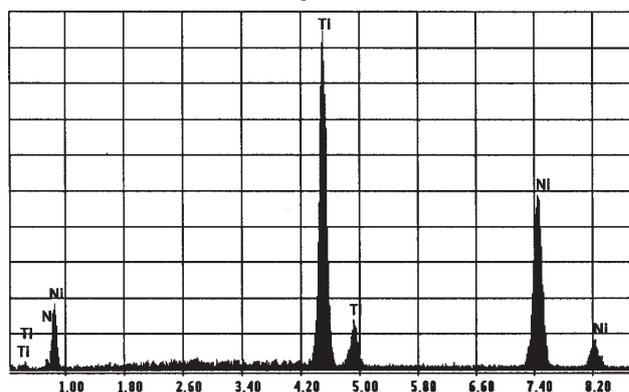


Fig. 2b. EDS analysis of the NiTi matrix

Element	Wt %	At %
TiK	44.71	49.77
NiK	55.29	50.23
Total	100	100

Fig. 2c. Quantitative analysis for EDS, Fig. 1b

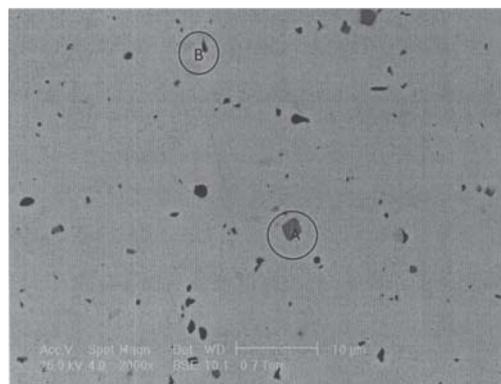


Fig. 3a. Choice of two precipitate particles supposed to have different chemical composition, identified as A and B

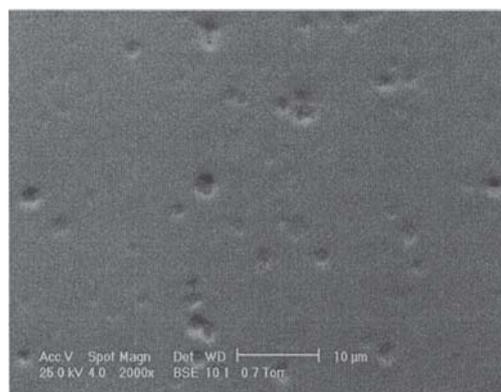


Fig. 3b. Topography of the surface presented in figure 2a

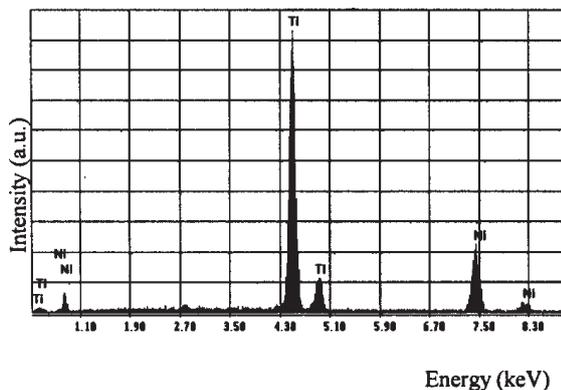


Fig. 4a. EDS analysis- X-rays energy dispersion spectrum for precipitate A

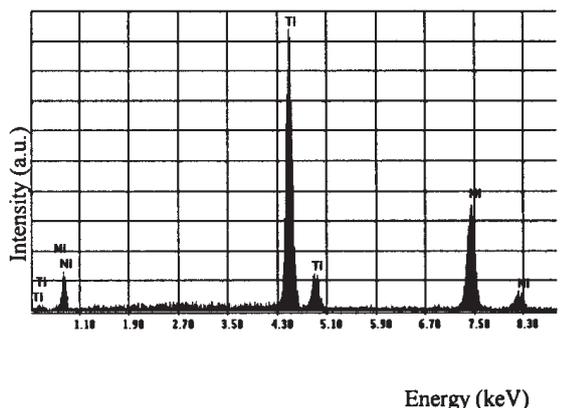


Fig. 5a. EDS analysis- X-rays energy dispersion spectrum for precipitate B

### Precipitate – detail A

Element	Wt %	At %		
TIK	64.23	68.76	Ti/(Ni+Ti)	11/16
NIK	35.77	31.24	Ni/(Ni+Ti)	5/16
Total	100	100		

Probable stoichiometry of the precipitate:  
NiTi<sub>2</sub>

Fig. 4b. Quantitative analysis for EDS, figure 4a

### Precipitate – detail B

Element	Wt %	At %		
TIK	51.5	56.55	Ti/(Ni+Ti)	13/23
NIK	48.5	43.45	Ni/(Ni+Ti)	10/23
Total	100	100		

Probable stoichiometry of the precipitate:  
Ni<sub>3</sub>Ti<sub>4</sub>

Fig. 5b. Quantitative analysis for EDS, figure 5a

differential scanning calorimetry. The main purpose of DSC tests was to determine the transformation temperatures of our shape memory alloy (Ni<sub>50.6</sub>Ti<sub>49.4</sub>), to examine if the transformation as a whole is a two-stage or a three-stage one and to establish if ageing conditions do have or not an influence on the alloy transformation temperatures.

Thin wires of diameter  $\Phi = 0.48$  mm previously aged at different temperatures (T), holding time (t) and cooling rate (v) were submitted to DSC.

The transformation temperatures (as called critical points, presented in the introduction) were determined and added in table 2. A column showing the precipitates found in the samples was also added.

Some of the resulting DSC curves are shown in figure 6 and 7. All curves are presented in figure 8.

The alloy Ti<sub>49.4</sub>Ni<sub>50.6</sub> shows on cooling a two – stage transformation, as follows:



Samp le,no.	Tempe rature, T [°C]	Cooling rate, v [°C/s]	Holding time, t [min]	M <sub>f</sub> [°C]	M <sub>s</sub> [°C]	R <sub>f</sub> [°C]	R <sub>s</sub> [°C]	A <sub>s</sub> [°C]	A <sub>f</sub> [°C]	Precipitates
1.	450	5	45	-43.3	-28.7	15	29.2	25.8	36.3	Ni <sub>3</sub> Ti <sub>4</sub> , NiTi <sub>3</sub>
2.	510	5	45	-38	-30.5	-5.9	13.6	9.7	21.1	Ni <sub>2</sub> Ti <sub>3</sub>
3.	450	25	45	13.9	31.4	-	-	17.5	26.8	Ni <sub>2</sub> Ti <sub>7</sub> , Ni <sub>3</sub> Ti <sub>4</sub>
4.	510	25	45	-36.4	-30.4	-7.7	16.4	7.1	20.7	NiTi <sub>3</sub> , Ni <sub>6</sub> Ti <sub>7</sub>
5.	450	5	75	-44.9	-31.4	17.4	33	25.5	34.8	NiTi <sub>2</sub> , Ni <sub>3</sub> Ti <sub>4</sub>
6.	510	5	75	-36.6	-23.7	-4.1	15.6	13.2	21.8	Ni <sub>2</sub> Ti <sub>3</sub> , Ni <sub>3</sub> Ti <sub>4</sub>
7.	450	25	75	10.7	32.5	-	-	18.5	29.7	
8.	510	25	75	-35.3	-24.8	-3.9	15.8	11.2	22.6	

The R phase seems to be favoured by performing ageing heat treatments on some NiTi alloys. This phase is unwanted because of inducing a greater instability of properties; also, it does not offer the large memory effects of the martensite phase, such that it is, more often than not, an annoyance. When austenite transforms to the R phase, its energy is reduced and its propensity to transform to martensite is lessened, leading to a larger austenite-martensite hysteresis. This may reduce, for instance, an actuator efficiency.

The appearance of the R phase, described in many scientific works [8,10] is determined by the following elements:

1. All NiTi alloys having a low content of Ni (aprox. 50.4% Ni) shows a three – stage transformation (an intermediate R phase on cooling) and all NiTi alloys having a high Ni content (aprox. 51.2% Ni) show, after ageing, a two – stage transformation (without R phase), the number of peaks being independent on the holding time, in an intermediate interval of ageing temperatures (400 - 500°C) [17].

2. The number of transformation peaks in NiTi alloys having an intermediate content in Ni (51% Ni) depends on the holding time of the ageing. These alloys show a three – stage transformation after a short ageing holding time and a two – stage transformation after longer ageing holding times [17].

**Table 2**  
AGEING PARAMETERS FOR WIRES OF  $\Phi = 0.48$  mm AND TRANSFORMATION TEMPERATURES DETERMINED BY DSC

The Ni<sub>50.6</sub>Ti<sub>49.4</sub> alloy is thus an overstoichiometric in nickel alloy, but with a low content of nickel. No matter the ageing holding time at ageings performed in the (400 - 500°C) interval, the material will show a three - stage transformation as follows:

A → R → M on cooling and M → A on heating.

This transformation sequence is confirmed when examining the transformation temperatures: the transformation on cooling of the austenite to martensite is done by passing through an intermediate phase R, while martensite transformation on heating results directly in austenite, without passing through an intermediate phase.

Nickel influence on NiTi alloys critical points is well known; a simple approach tells us that 1% of a nickel surplus will determine a drop of 10 degrees of A<sub>s</sub> and of 6 degrees of M<sub>s</sub> [18]. According to other studies, the variation is not linear [19, 20].

In the following we shall attribute the variations of the transformation temperatures mainly to a change in the nickel content of the matrix; another possible explanation would be that of the influence of the augmentation or diminution of the number of the different precipitate particles on the beginning of the transformation by delaying it (shifting M<sub>s</sub>, M<sub>f</sub> points towards lower values and A<sub>s</sub>, A<sub>f</sub> towards higher values) or by forwarding it (shifting M<sub>s</sub>, M<sub>f</sub> points towards higher values and A<sub>s</sub>, A<sub>f</sub> towards lower values).

Concerning our alloy, overstoichiometric with a low nickel content, a multiple stage transformation is attributed to a matrix structural non-homogeneity, as well compositional as from the internal stresses point of view, appeared as a consequence of the coherent Ni<sub>4</sub>Ti<sub>3</sub> precipitates formation [8].

An intermediate A → R transformation is accompanied by a drop of the martensitic critical points and a

transformation hysteresis expansion. These phenomena are attributed to several factors :

- Changes in the number of transformation stages and
- Resistance force exerted by the matrix at structural changes.

The variation of the resistance force opposed by the matrix is linked to the evolution of the Ti<sub>3</sub>Ni<sub>4</sub> precipitates morphology [8].

Analysing the transformation temperatures shown in table 1 together with the data given by the energy-dispersive X-ray spectra (EDS) for the matrix and different precipitates we can conclude:

1. The raise of the ageing temperature leads to a drop of R (M) and A<sub>s</sub> as a result of a nickel excess (samples #2 vs #1, #4 vs #3, #6 vs #5, #8 vs #7). This will derive from Ti<sub>3</sub>Ni<sub>4</sub> precipitate particles dissolution, at higher temperatures; as a result of this dissolution, the matrix will be richer in nickel than in titanium (4 > 3). The dynamics of formation, growth and dissolution of these precipitates is incompletely understood; however, Miyazaki [8] noticed a higher density of Ti<sub>3</sub>Ni<sub>4</sub> precipitates after ageing the alloy at 400°C. Up to 480°C, these precipitates grow and their density lowers. When transgressing this ageing temperature, precipitates diminish up to 600°C by dissolution [8]. Ni<sub>3</sub>Ti<sub>4</sub> precipitates are submitted to the same mechanism, EDX analyses showing that they grow up to 500°C and then diminish by dissolution up to 600°C [21].

2. Submitting a sample to a stress field can lead to a shift of transformation temperatures in both directions, depending on the relative difference between the stress and the strain. Generally, for martensitic displacive transformations with multiple variants (twins) being able to move, applying an uniaxial stress field will lead to a raise of transformation temperatures. It has been settled that stress has a greater influence on T<sub>B2→M</sub> than on T<sub>B2→R'</sub> due to the fact that B<sub>2</sub> → M transformation shows a greater deformation than B<sub>2</sub> → R transformation.

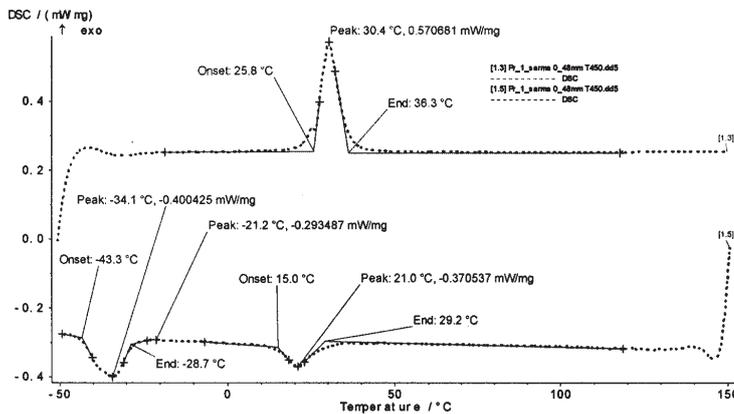


Fig.6. DSC curves on cooling (down) and on heating (up) for sample #1 (450°C/45min/5°C/s)

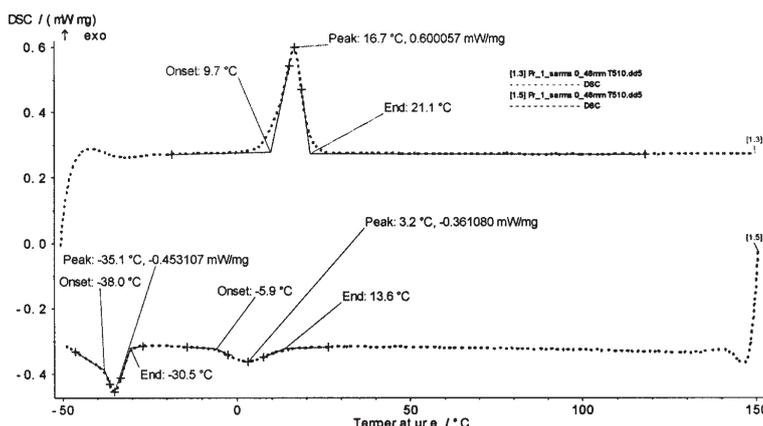


Fig.7. DSC curves on cooling (down) and on heating (up) for sample #2 (510°C/45min/5°C/s)

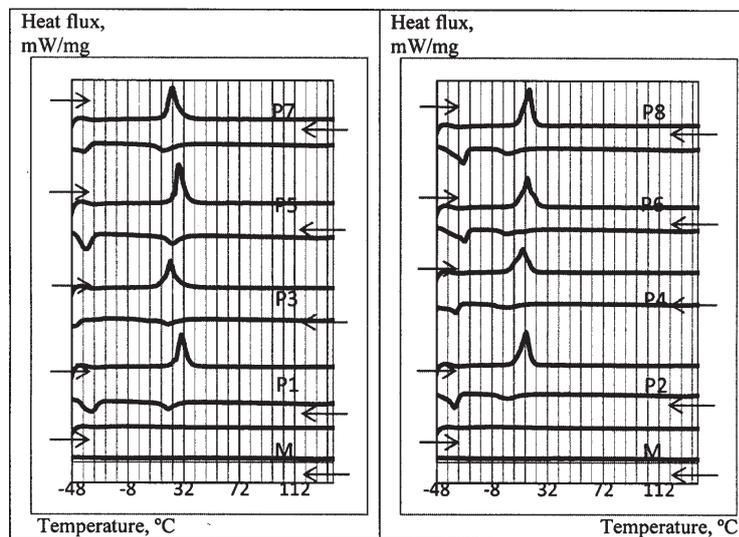


Fig. 8a. DSC curves for samples 1, 3, 5, 7

Fig. 8b. DSC curves for samples 2, 4, 6, 8

3. Formation and raise of precipitates when ageing at temperatures up to 480°C lead to the formation of stress fields concentrated around them. Thus, transformation temperatures on cooling (R and M) will raise; the effect of stress may cause transformation temperatures to shift in either direction depending on the relative direction of the stress and transformation strain. Generally, for displacive transformations that have multiple choices of variants, a simple local stress field causes increases of transformation temperatures. The raise must also be assigned to the matrix depletion in nickel by formation of nickel-rich  $Ti_3Ni_4$  precipitates. Their dissolution can lead to a diminution of the stress field or even to its disappearance and also to a nickel excess in the matrix, all these leading  $R_s$  and  $M_s$  to drop [8].

4. It can be estimated that sample cutting in order to perform DSC tests generates stresses in the samples; these can lead M and R transformation temperatures to shift towards higher values.

5. The appearance of the R phase is suppressed for samples #3 and #7, thus for samples aged at 450°C/45 min. These were submitted to cooling after heat treatment at a greater rate, of 25°C/s. For an alloy having such a composition, R phase should appear no matter the ageing conditions, in an intermediate temperature interval (400 - 500°C). The cooling rate seems to have a determinant influence; it is responsible for a raise of the internal stress level. Thus, the transformation  $B_2 \rightarrow R$  will be discriminate in favour to  $B_2 \rightarrow M$  transformation [22].

6. We can also notice that the appearance of the R phase leads to the transformation to extend on a greater temperature interval (for instance between 33°C and -45°C for sample #5). When R phase misses, the transformation temperature interval is smaller.

7. Ageing temperature variations thus reveal as a mean of readjust transformation temperatures to needed values, of course, in a reasonable temperature interval. However, we can see that  $R_s$  varies within a range of 15 degrees. This is due, most certainly, to sample cutting that induces local deformations, leading to a raise of  $R_s$  values.

It has to be mentioned that application temperatures will be at least superior to  $A_s$  with 10 degrees. Producers selling SMA NiTi alloys indicate a range deviation of the transformation temperatures of +/- 5 degrees. Therefore, we consider that a 5 degrees supplement may ensure the material reliability and the reproducibility of the material behaviour along several exploitation cycles.

8. The R phase transformation temperatures raise with the increasing ageing holding time (#1 vs #5, #2 vs #6), at a constant ageing temperature. The raise of the temperature  $T_{B_2 \rightarrow R}$  is mainly attributed to a matrix depletion in nickel, near the  $Ti_3Ni_4$  precipitate particles, and also to the internal stresses effect due to precipitates formation [22]. Not only  $Ti_3Ni_4$  precipitates are involved, but also the titanium-richer ones, of different compositions, identified by SEM. Between all precipitates possible to be found, only  $TiNi_3$  and  $Ti_2Ni$  are stable. These are more predictable concerning their nucleation, growth and dissolution and even so, they may have unexpected effects on transformation temperatures. Metastable precipitates, by their nature, are even less predictable concerning their nucleation, growth and dissolution and also on their effect on the critical points.

9. The effect of rising ageing temperatures is less obvious on  $A_s$  and  $A_f$  temperatures of samples #1 and #5; for samples #2 and #6 we can observe a 3.5°C raise for  $A_s$ .

10. There was no coherent influence of the ageing holding time on the  $A_f$  values.

11. It would be inaccurate to attribute transformation temperature changes only to the quantitative variation of an only one precipitate,  $Ti_3Ni_4$ . The examination of secondary electron images and EDS diffraction spectra reveal the existence of some titanium-rich precipitate particles, stable or metastable, whose appearance may be explained by the NiTi equilibrium diagram or considering some chemical composition non-homogeneities in several microvolumes. These phases, by their formation or dissolution, hence by accumulation or release of a greater number of titanium atoms in their adjacent zones, can lead to changes of the transformation temperatures. It is to be noticed the coexistence (revealed by EDS analyses) of the  $Ti_3Ni_4$  nickel-rich precipitate and of the titanium-richer  $Ni_3Ti_4$ . The result of the competition between precipitation, coalescence and dissolution phenomena of all these precipitates will dictate the values of the transformation temperatures. Being on the permanent influence of formation and dissolution of these precipitates, the matrix is subject to a permanent change of its chemical composition. Undoubtedly it causes changes of the transformation points in an uncontrollable manner.

12. Most of the precipitates identified by SEM - EDS are titanium-richer. Their coalescence, as a result of an ageing temperature rising, will lead to a titanium depletion and consequently to a nickel enrichment of the matrix adjacent

zones, resulting in a drop of the transformation temperatures. The matrix will be thus richer in nickel and  $M_s$  (or  $R_s$ ) and  $A_s$  will drop. These observations were made on comparing temperatures of the following samples: #1 vs #2, #5 vs #6, #3 vs #4 and #7 vs #8.

13. The identification of some richer – titanium precipitates does not make them very numerous.  $Ti_3Ni_4$  will have the greater influence; its distribution will be both intergranular and intragranular, particles having very small dimensions (about 1000 nm), to small to be seen in SEM at usual magnifications [23].

## Conclusions

The shape memory alloy chosen for the present study was  $Ni_{50.6}Ti_{49.4}$ . Among richer in nickel NiTi alloys, this is roughly a low one. Small quantities of impurities such as carbon, oxygen, nitrogen may impair the properties of such an alloy, shifting in an uncontrollable manner its transformation points (300 ppm of oxygen lowers the  $M_s$  point with 50 degrees [18]) and thus making it incompatible with a specific application. This is why it is essential to obtain such an alloy in high frequency induction furnaces with calcium oxide crucibles or continuously water-cooled copper crucibles [18].

All low nickel NiTi alloys (50.4% Ni) exhibit three-stage transformation and all the high nickel NiTi alloys (51.2% Ni) exhibit two – stage transformation after ageing, the number of peaks being independent of ageing time at intermediate temperature range (400 - 500°C) [8].

The number of transformation peaks of intermediate nickel NiTi alloys (51% Ni) shows ageing time dependence. It exhibits three-stage transformation after short time ageing and only two – stage transformation after longer ageing time [8].

Thus we can easily enframe our alloy ( $Ni_{50.6}Ti_{49.4}$ ) as being a low nickel NiTi alloy. As expected, DSC curves show three-stage transformations. This means that martensite - to - austenite transformation ( $B19' \rightarrow B2$ ) shows normal aspect, with a single peak, while austenite – to – martensite transformation shows a premartensitic transformation ( $B2 \rightarrow R \rightarrow B19'$ ), peaks of the R phase and of the martensite being clearly separated. The R phase, usually unwanted in these alloys, disappears only under a specific combination of ageing temperature and cooling rate (450°C/25°C/s).

Formation of  $Ti_3Ni_4$  precipitates and also titanium – richer precipitates such as  $NiTi_2$ ,  $Ni_3Ti_4$  on ageing, their non-linear and unpredictable manner of coalescence and dissolution which leads to enrichment or depletion in nickel and titanium of these precipitates and their adjacent zones, dislocations induced by global processing are, for the Ni-rich NiTi alloys, the main causes of transformation temperatures ( $M_s$ ,  $M_f$ ,  $A_s$ ,  $A_f$ ) changes.

Thus it is possible, by combining different parameters such as ageing temperature, holding time, cooling rate after

ageing, to obtain the required thermomechanical characteristics for a previously designed application.

All physical investigations performed revealed structural aspects of the tested samples, as well as the major influence of the heat treatments upon their properties. These are relevant for their future applications. This shows also that interdisciplinary studies have to be still developed in order to characterize more accurately this modern SMA.

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