THERMAL STABILITY OF MARTENSITIC TRANSFORMATION RANGE OF A NITINOL SHAPE MEMORY ALLOY AFTER ELASTIC COMPRESSION

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Abstract: Nitinol material exhibit new and useful properties as shape memory effect and super elasticity opening many fields of applications. Two materials, both NiTi, one with shape memory effect as full material cylinder and second super-elastic as tube were compressed with a 4% degree. The initial and compressed samples were analyze by dilatation behavior point of view heating in room temperature – 200 ºC range Samples were mechanically put together and compressed in similar conditions as the other material parts. After the compression test the "composite" material was heated until 200 ºC on dilatometer. All samples were heated for more cycles until a stabilization of the temperatures transformation domain was observed. The effect of super-elastic material on exhibiting of shape memory effect under temperature variation during the martensitic domain was also observed.
Key words: shape memory effect, superelasticity, compression.

1. INTRODUCTION

Over the last two decades shape memory alloys (SMA) have attracted great interest in various applications ranging from aerospace (Achitei et al., 2009) and naval (Cimpoeşu et al., 2010) to surgical instruments, medical implants and fixtures (Martynova et al., 1991, Bujoreanu et al., 2011). The use of SMAs has promoted extensive research on developing SMA constitutive models. Among SMAs, NiTi alloy has been used most extensively due to its large flow stress and shape memory effect (SME) strain. Most recently, porous NiTi have attracted increasing attention for possible application in medical implant devices and as high energy absorption structural material.

At the microscopic level, the distinct mechanical properties of shape memory alloys are produced by a reversible thermo-elastic martensitic transformation (1Lieberman et al., 1955). Of the dozen or more (Hodgson et al. 1990) inter-metallic alloys that undergo a thermo-elastic martensitic transformation, equiatomic NiTi alloys have the greatest promise for wide-scale applications due to their exceptional physical and mechanical properties (Hodgson et al. 1990).

Owing to intense research efforts around the world, the mechanisms of deformation are well-characterized in polycrystalline NiTi shape memory alloys subjected to monotonic tensile loading conditions.

However, the characteristics of deformation in polycrystalline NiTi subjected to compression (Lohan et al. 2011) and cyclic loading conditions (Melton and Mercier, 1979) deviate significantly from the well-documented monotonic tensile response. In polycrystalline NiTi materials deformed under monotonic compression, the critical transformation stress level is higher, the transformation stress–strain slope is steeper, and the recoverable strain levels are smaller compared with tensile results (Lohan et al. 2011).

Furthermore, during mechanical cycling, the stress–strain response of polycrystalline NiTi demonstrates a lowering of the critical transformation stress level, an increase in the transformation stress–strain slope, and a decrease in the transformation hysteresis compared with the first loading cycle (Melton and Mercier, 1979). More recent experimental efforts have confirmed the tension-compression asymmetry (Orgeas and Favier, 1995, Jacobus at al., 1996, Achitei et al., 2010, Liu et al., 1998) and cyclic effects (Xie et al., 1998, Orgeas and Favier, 1998, Gall and Sehitoglu, 1999, Cimpoesu et al., 2010) in polycrystalline NiTi for a wide range of NiTi alloys and testing conditions.

Shape memory alloys are typically functional materials. Their unique properties like thermal and mechanical memory and superelastic properties lend themselves to a variety of applications. The shape memory effect involves the reversible thermoelastic crystallographic phase transformation or martensitic

transformation from a high temperature parent phase to a low temperature product phase (Otsuka and Shimizu, 1986).

In general, there are two types of martensitic transformations, a single stage A→M and a two-stage A→R→M where A is the high temperature austenitic phase, R is the intermediate rhombohedral phase and M is the low temperature martensitic phase.

The two-stage martensitic transformation in NiTi has been studied using DSC and electrical resistivity measurements (Uchil et al., 1998). The existence of two-stage martensitic transformation in NiTi has been reported by many investigators through electrical resistivity (ER) and DSC measurements (Lo et al., 1993).

The uni-axial dilatation with temperature is very sensitive to phase transformation in a material and can be used to study the transformation behaviors of a shape memory alloy. Quenching dilatometry has been used for the study of precipitation kinetics of Cu-Al-Ni shape memory alloys by Recarte et al. (Recarte et al., 1997). Authors have shown that dilatometric measurements are equally reliable in characterizing various phases of nitinol by comparing these with ER measurements (Uchil et al., 1999).

The purpose of the present work is to investigate the nature of martensitic transformation in the NiTi alloys using the dilatometric measurements. Temperature hysteresis is compared and the effect of early thermal cycles on transformation temperatures is discussed. The material with SME was external free constrain covered by a superelastic NiTi tube and both subjected of elastic compression. The composite structure after compression was investigated through dilatometry also on three cycles.

2. EXPERIMENTAL DETAILS

A nitinol shape memory alloy under bar form with 3.5 mm diameter and a super-elastic nitinol tube form with 3.55 mm inside diameter were analyze by linear thermal behavior before and after a compression test.

The materials were acquisitioned from Saes Getters USA Company. Mechanically cut under water cooling flux two NiTi materials, with a 7 mm length, were subject of compression tests made on Instron equipment keeping the material compression on elastic domain.

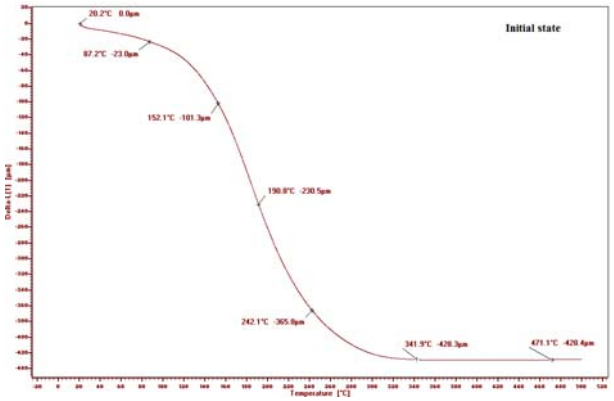
After each compression test a dilatometer analyze was realized from room temperature to 200 °C paying respect for the martensitic transformation domain of nitinol material with shape memory effect in case of multiple heating cycles and to 500 °C in single test case.

The linear-thermal analyses were carried out on a Linseis 75H dilatometer using a 10 K/min heating rate and a water cooling system to control the furnace equipment temperature. The experiments were realized in air. A heat treatment furnace, Vulcan 200 type, was used to apply a treatment to NiTi alloy by 1000 °C heat and free cooling.

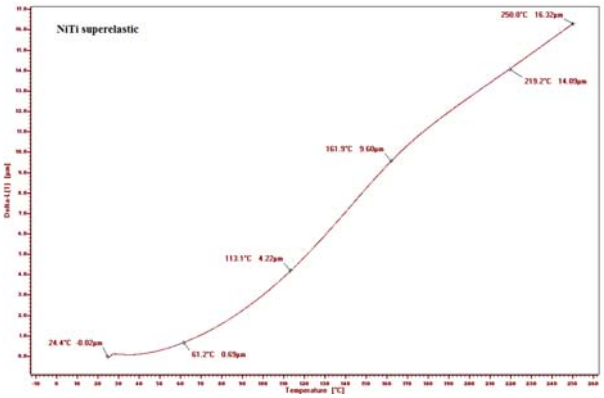
3. EXPERIMENTAL RESULTS

Two NiTi materials first a plain cylinder shape memory alloy and second a super-elastic tube were analyze by them dilatation characteristics with temperature modification separate at begin and as a complex structure after that. Using the Linseis dilatometer equipment the materials behavior at heating was registered and presented in figure 1 and 2 for different state situations of the shape memory alloys. In figure 1 a) and b) the shape memory alloys behavior with temperature variation, S.M.A.s with shape memory effect respective superelasticity, are presented.

First material exhibits a classical s.m.a. behavior with a effective contraction of the material during the martensite transformation domain. The superelastic material exhibit a classic dilatation with 4.22 µm at 110 °C and 9.6 µm at 161.9 °C. The shape memory effect parameters like MS and MF temperatures, the martensite transformation range, half of transformation range by temperature or dilatation point of view, actual dilatation range and recovery dimension at the half of the temperature range and at the other half are presented in table 1.



a)



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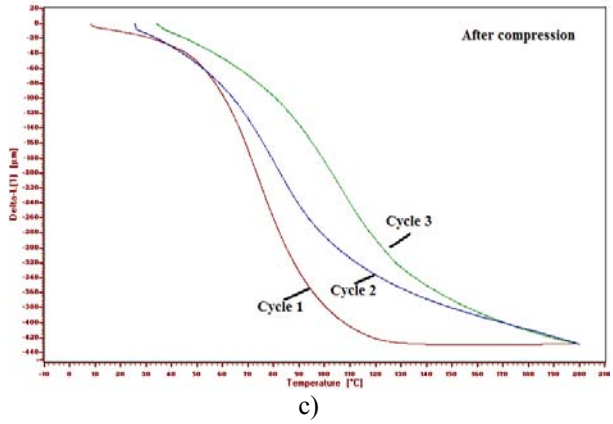

c)

Fig.1. Dilatometric results a) shape memory alloy, b) super-elastic alloy and c) three cycles of composite structure

Shape memory alloy with SME exhibit at the first test, in initial state, a very large transformation domain of 168 °C and a contraction of 371 μm with same contraction value for both transformation range segments. The material initial state, delivered by the producer, permits the control and modification of the SMA properties. Both transformation points start and finish of martensitic range, are high at 283 respective 115 °C.

Materials, the s.m.a. with SME and superelastic one, putted together with the plain one in the middle and the superelastic tube on exterior were subjected of compression in the same time until a 4% degree in elastic range of metallic materials and the results are further to be comment in this article the thermo-dimensional behavior is observed and analyzed. In figure 1 c) the compose structure (smas with SME and superelasticity) dilatation variation with temperature is presented on three heating cycles. The transformation domain decrease to 54 °C increasing the shape memory structure control capacity. The martensitic transformation points decrease with more than half having values of 110 and 56 °C temperatures much reliable for practical applications. All heating cycles have appropriate values with a very good thermal and dimensional stability.

Table 1. Dilatometric parameters and results for all shape memory NiTi sample tests and for composed structure NiTi SMA + NiTi super-elastic after a compression operation

Nr. crt.	NiTi shape memory alloy	Sample diameter [mm]	ΔA [°C]	A_s [°C]	A_f [°C]	A_{50-1} [°C]	A_{50-2} [°C]	ΔA_{50} [°C]	ΔL_A [μm]	ΔL_{50-1} [μm]	ΔL_{50-2} [μm]
1	Initial state	19.2	168	115	283	199	225	26	371	185.5	185.5
2	After compression Cycle 1	18.85	54	55.5	108.5	82.5	80	2.5	50	21	29
3	After compression Cycle 2	18.89	54	56	110	83	82	1	54	30	24
4	After compression Cycle 3	18.85	57	50	107	78.5	78.8	0	58	29	29
5	After 200 °C heat treated Cycle 1	18.62	20	88	108	98	95.75	2.25	6.25	2	4.25
6	After 200 °C heat treated Cycle 2	18.62	18	92	110	101	102	1	8.2	4.2	4
7	After 200 °C heat treated Cycle 3	18.62	20	90	110	100	100.5	0.5	6.8	3.5	3.3
8	After 1000 °C heat treated Cycle 1	18.5	28	95	123	109	109	0	2.1	1	1.1
9	After 1000 °C heat treated Cycle 2	18.5	19	88	107	97.5	98	0.5	2.2	0.9	1.3
10	After 1000 °C heat treated Cycle 3	18.5	17	87	104	95.5	96	0.5	2.3	1.1	1.2
11	After compression and heated at 200 °C	18.49	48.5	52	100.5	76.25	78	1.75	43	18	25

Final steps in production of superelastic nitinol wires, tubes or plain cylinders are often cold drawing to a desired diameter followed by straight annealing.
Straight annealing consists of heating a pre-loaded (20-100 MPa) cold drawn material at an appropriate temperature (450-700°C). It ensures an optimum straight shape and desired functional properties of a shape memory material based on nitinol. A very important step in a following fabrication of shape memory elements from the straight annealed superelastic state is the shape setting. It involves a short (several minutes) heat treatment of the material which is wound in a desired pattern on a mandrel. The shape setting treatment is generally carried out at moderate temperatures (around 500°C) and its purpose is to induce relaxation of a material for achievement of a desired stable shape. Moderate temperatures and short times are used to prevent the permanent deformation of shape memory alloys and to maintain their superelastic behavior.
In general, nitinol shape memory alloys exhibit three phases, the high-temperature B2 austenite phase (structure of CsCl), low-temperature B19´ martensite phase (monoclinic structure) and intermediate temperature R-phase (rhombohedral structure).
Transformations of these phases are of a great importance, because they determine the superelastic and shape memory characteristics of nitinol, as well as its mechanical and functional properties and performance. These transformations can proceed by various ways, B2↔B19´, B2↔R, R↔B19´, depending on thermal and mechanical history of alloys. The direct transformation of austenite B2 to martensite B19´upon cooling generally occurs when an alloy is in a solution annealed state, i.e. annealed at a high temperature and water quenched. Upon subsequent ageing, the solid solution decomposes to form Ti3Ni4 precipitates.
For force actuator elements and precise auctioning elements the material was analyzed by middle temperature and linear compression point of view. This analyze help the engineer to control the dimensional recovery of the element at proper temperatures and for especially application cases.
Cases like the material after compression and third heating cycle, position 4 in table 1, and after 1000 ^{o}C temperature heat treated first cycle present a 0 variation between linear and temperature middle M→A transformation. In initial state sample case this huge variation of temperature transformation middle point is based on the material tensioned state after the cold drowing obtaining process.
All the other cases present small differences that can be put on the measurement system variation, sample movement during experiment or reduce modifications of martensitic transformation behavior.
On the compose structure a heat treatment until 250°C was apply with free materials cooling. The dilatation results, position nr. 11 from table 1, present a reduce of martensitic range in temperature to 48.5°C and with few Celsius degree of martensitic transformation points.
In initial case the compression of the material under martensitic transformation effects present a high dimensional value of 371 μm, all of them recovered in two equal phases. A seven time smaller compression the material exhibit in already compressed form in all heating cycles. The compression value even increase from 50 to 58 μm paying respect for temperature contribution.
The material compression value under temperature modification decrease at small values, around 6 or 2 μm, in case of heat treatment samples with no mechanical compression apply in initial state. It also can be observe a narrowing of the transformation temperature domains for heat treated samples transforming this material in an extremely sensitive shape memory alloy.
In the compressed sample case a heat treatment application until 200 ºC decrease the transformation domain range and also the compression degree confirming the precipitates appearance and evolution. Both heat treatment and compression operations modify the material shape memory effect behavior.
In compressed SMAs case big compression variations are observed until the stabilization heating cycle influencing the material activation in highly sensitive application.
The shape memory alloy behavior at heating was tested through dilatometry after two heat treatments at 200 and 1000 °C. Three heating cycles were applied to follow the thermal stabilization of the material and especially of the martensitic domain. In the first heat treatment case, until 200°C, of the shape memory alloy with memory effect the transformation range is around 20°C, a very appropriate value for actuators type applications, and reliable values of A_S and A_F in the 110 °C maxim value of austenitic phase start.
The material exhibit in this state a very high thermal and dimensional stability with possible recuperation dilatation of 6-8 μm.
All stages of precipitation strongly influence both phase transformations and mechanical characteristics of a material, mainly yield strength and tensile strength.
In figure 2 a) the shape memory alloy linear behavior at temperature variation, after a heat treatment until 200ºC was applied through precise controlled temperature equipment, is presented using three heating cycles. In the same figure at point b) the results after dilatation tests in case of NiTi with SME alloy heat treated to 1000°C are exposed.
The material exhibit in the first case a double transformation range on heating based on first order martensitic variants transformation and second type variants after a period.

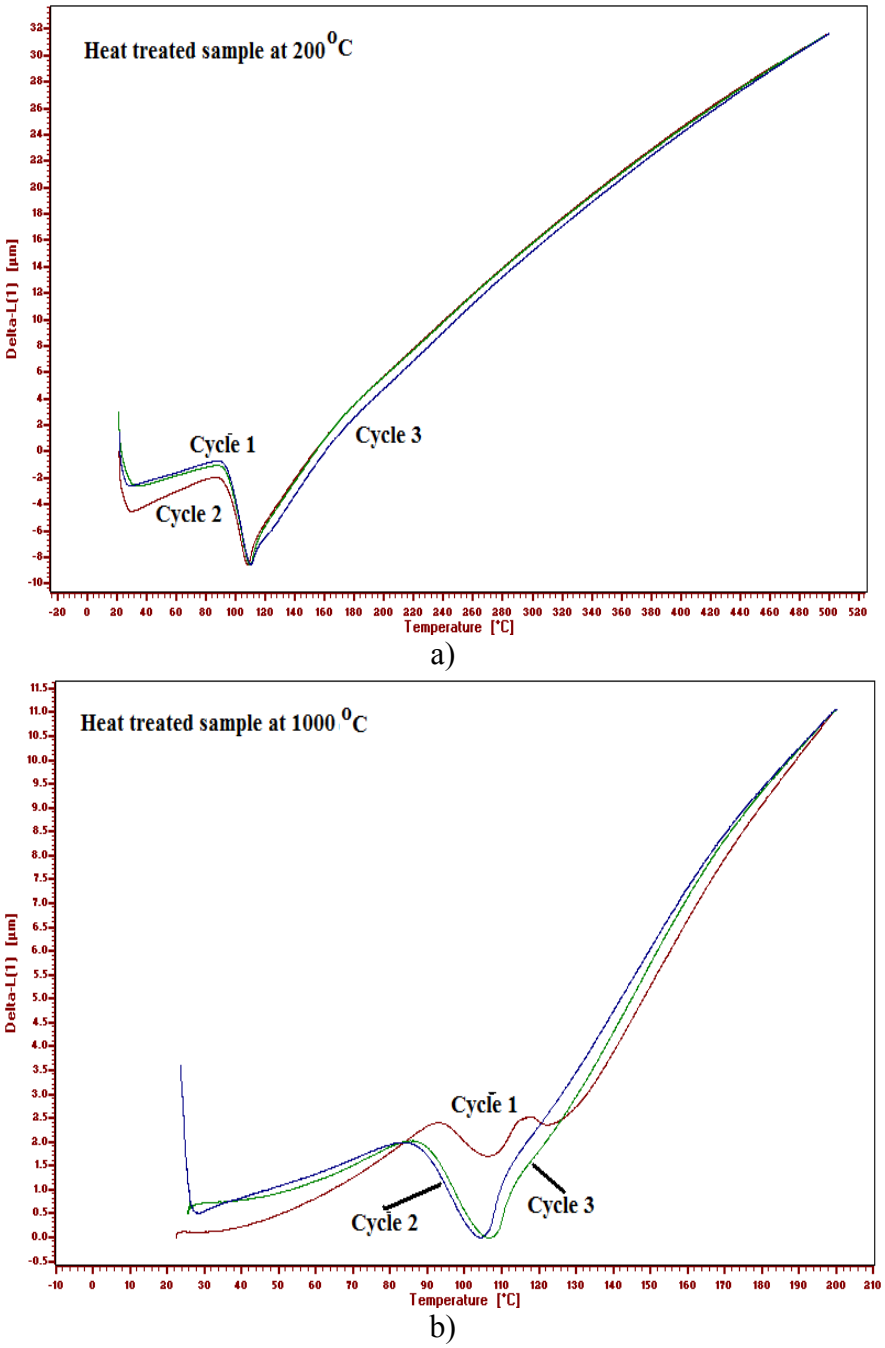

Fig.2. Dilatometric results on NiTi shape memory alloy after a heat treatment of a) 200 °C and b) 1000 °C

Applying a high heating temperature in the first cycle in the material occur different crystallization and precipitates forming phenomena. This behaviour was not observed on second and third heating cycles when the material has the transformation domain in one stage with a better recovering linear value.

The martensitic transformation range is reducing between 17-19 °C with a good stability after the first heating cycle.

4. CONCLUSIONS

Two commercial shape memory alloys, first as plain cylinder with shape memory effect and second as superelastic tube, of NiTi materials were subject of dilatometry separately and together to establish them thermo-linear behavior at temperature change. The shape memory material exhibit a large martensitic transformation range in initial state based on final production deformation operation applied. The transformation As and Af temperature points are also at high values.

Compressing the material and helping the shape memory alloy with external superelastic tube the material exhibit smaller transformation points and temperature range increasing the controlled applications number. Same behavior, by thermo-linear point of view, was obtained through heat treatments of the material with SME but the material exhibit different evolutions for different heat treatment temperatures applied.

The observed development of mechanical properties and transformation behavior is related to precipitation processes occurring in the shape memory material during heat treatments. At least until stabilisation increasing the temperature the NiTi matrix composition is in equilibrium with Ni3Ti precipitates and has less nickel content. Therefore, at high temperatures, i.e. over 800 ºC, the matrix is composed of NiTi with low nickel content. As a result a higher As temperature is obtained as compared to the material heat treated at 200 ºC.

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5. REFERENCES

1.Achitei, D., Galusca, D. G., Vizureanu, P., Carabet, R., Cimpoesu, N., (2009). *Aspects regarding thermo-mechanical fatigue of shape memory alloys*, Metal. Int., 14(3), 45-48.

2.Achitei, D. C., Vizureanu, P., Stanciu S.; Stefanica R. G.; Cimpoesu N., (2010). *Studies concerning thermal conductivity for some copper base memory shape alloys*, Proceedings of ModTech 2010: NewFace of TMCR, pp. 15-18, ModTech Publishing House, Slanic-Moldova, Romania.

3.Bujoreanu, L. G., Lohan, N. M., Pricop, B., Cimpoeşu, N., (2011), *Thermal Memory Degradation in a Cu-Zn-Al Shape Memory Alloy During Thermal Cycling with Free Air Cooling*, J of Mater. Eng. and Perform., 20(3), 468-475.

4.Cimpoesu, N., Axinte, M., Cimpoesu, Hanu, R., Nejneru, C., Achitei, D. C., Stanciu, S., (2010), *Behavior simulation of a copper based shape memory alloy under an external solicitation*, J. of Optoelectronics and Advance Mater., 12(8), 1772-1776.

5.Cimpoeşu, N., Stanciu, S., Meyer M., Ioniță, I., Cimpoeşu, Hanu, R., (2010). *Effect of stress on damping capacity of a shape memory alloy CuZnAl,* J. of Optoelectronics and Advance. Mater., 12(2), 386-391.

6.Gall, K., Sehitoglu, H., (1999). *The role of texture in tension–compression asymmetry in polycrystalline NiTi*, Inter. J. Plasticity 15(1), 69- 92.

7.Hodgson, D.E., Wu, M.H., Biermann, R.J., (1990). *Shape Memory Alloys*, Metals Handbook 2, 897.

8.Jacobus, K., Sehitoglu, H., Balzer, M., (1996). *Effect of stress state on the stress-induced martensitic transformation in polycrystalline Ni-Ti alloy*, Metall. Mater. Trans. A, 27(10), 3066-3073.

9.Grimberg, R., Udpa, L., Savin, A., Steigmann, R., Vizureanu, P., Brumă, A., Udpa, S.S., (2008). *Remote field eddy current control using rotating magnetic field transducer: Application to pressure tubes examination*, Research in Nondestructive Evaluation, 19(4), pp. 202-218.

10.Lieberman, D.S., Wechsler, M.S., Read, T.A., (1955). *Cubic to orthorhombic diffusion less phase change – experimental and theoretical studies of AuCd*, J. Appl. Phys., 26, 473-484.

11.Liu, Y., Xie, Z., VanHumbeeck, J., Delaey, L., (1998). *Asymmetry of stress–strain curves under tension and compression for NiTi shape memory alloys,* Acta Mater., 46(12), 4325- 4338.

12.Lo, Y. C., Wu, S. K., Horng, H. E., (1993). *A study of B2↔B19↔B19′ two-stage martensitic transformation in a Ti50Ni40Cu10 alloy,* Acta. Metall. Mater., 41(3) 747-750.

13.Lohan, N. M., Pricop, B.; Bujoreanu, L.-G., Cimpoesu., (2011). *Heating rate effects on reverse martensitic transformation in a Cu-Zn-Al shape memory alloy*, Int. J. of Mat. Research, 102(11), 1345-1351.

14.Martynova, I., Skorohod, V., Solonin, S., (1991). *Shape memory and superelasticity behavior of porous Ti-Ni material*, J Phys IV, C4, 421- 426.

15.Melton, K.N., Mercier, O., (1979). *Fatigue of NiTi thermoelastic martensites*, Acta Metall., 27(1), 137-144.

16.Orgeas, L., Favier, D., (1998). *Stress-induced martensitic transformation of a NiTi alloy in isothermal shear, tension and compression,* Acta Mater. 46(15), 5579- 5591.

17.Orgeas, L., Favier, D., (1995). *Non-symmetric tension-compression behaviour of Ni Ti alloy,* J. Phys. IV Colloq. 5, 605-610.

18.Otsuka, K., Shimizu, K., (1986). *Pseudo-Elasticity and Shape Momory Effects*, International Metals Reviews, 31(3), 93-114.

19.Recarte, V., Perez-Saez, R. B., No M. L., San Juan, J., (1997). .*Dilatometric Study of the Precipitation Kinetics in Cu-Al-Ni Shape Memory Alloys,* J. Phys. IV France 7 C5329 – 334.

20.Uchil, J., Mohanchandra, K. P,. Mahesh, K. K, Ganesh Kumara, K., (1999). *Dilatometric and electrical resistivity measurements in various phases of nitinol,* Proc. SPIE Vol. 3675, 321.

21.Uchil, J., Mohanchandra, K.P., Ganesh Kumara, K., Mahesh, K. K., (1998). *Study of critical dependence of stable phases in Nitinol on heat treatment using electrical resistivity probe,* Mat. Sci. Eng. A 251 58

22.Xie, Z., Liu, Y., Van Humbeeck, J., (1998). *Microstructure of NiTi shape memory alloy due to tension–compression cyclic deformation*, Acta Mater. 46(6), 1989-2000.

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