International Journal of New Technology and Research (IJNTR)
ISSN:2454-4116, Volume-3, Issue-3, March 2017 Pages 47-51

The Effect of Thermal Ageing on The Transformation Temperatures of Superelastic Nitinol Tubing

A. Kokkinos, V. Kostopoulos, D. Aslanidis

Abstract **-Ni- Ti shape memory alloys (nitinol) have become widely known for both their shape memory effect and their pseudoplasticity (superelasticity). Their properties are depending upon the thermomechanical processing during the manufacturing phase of the material. Thermal ageing is the long term exposure of the shape memory alloys at a relatively high temperature (in some cases long term exposure (more than 240 h) at temperature close to austenitic transformation could be considered as a post-processing treatment phase used for the final tuning of the transformation characteristics).**

In the present paper, the effect of thermal ageing on the transformation characteristics is analyzed and discussed.

Index Terms- **shape memory alloys, superelasticity, transformation temperatures**

I. INTRODUCTION

For a nitinol alloy with defined chemical composition, both the thermal (or transformation characteristics) and the mechanical properties are strongly influenced by processing conditions:

- The amount of cold work (or area reduction during wire/tube drawing)
- The temperature of heat treatment
- The time of heat treatment, and
- The applied load during the heat treatment.

Having all these parameters known, the nitinol uses can better understand and further manage the thermal and mechanical properties of their components and devices. Within this understanding, the post thermal processing is an alternative approach to apply a final tuning of nitinol properties. Thermal ageing is understood the heat treatment of the device in moderate temperatures (less than 350C) for prolonged time (up to 240 hours).

Under this concept, superelastic nitinol tubing and shape memory wire have been selected for ageing process. The selected tubing is used for precision laser cutting in manufacturing of superelastic medical devices. The selected wire is used in actuator application using the shape memory effect. Samples of both materials have been thermally aged and subsequently analyzed with Differential Scanning Calorimetry (DSC) [1] in order to reveal the stability of the associated transformation temperatures.

Next to DSC measurements several other measuring techniques are applicable because there is a whole list of characteristics which change in shape memory alloys: sound, color, hardness, expansion, yield strength, Young's modulus, damping, internal friction, acoustic emission, electrical resistance, magnetic properties, electromotive force, thermoelectric power, heat capacity, thermal conductivity, lattice spacing and electron density waves [2]. The start and finish of the martensitic transformation and the reverse transformation can clearly be noted. The benefit of this technique however is that no load is applied on the sample and the measurement can be done immediately on a piece of wire without extensive sample preparation.

II. EXPERIMENTAL

The material characteristics are shown in Tables 1 for the superelastic tubing which was provided by AMT (Herk-de-Stad, Belgium). Nitinol tubing is a standard superelastic material used in medical devices manufacturing.

Table 1 Superelastic tubing composition and transformation temperatures.

Superelastic Nitinol Tubing	
Dimensions	
Outside Diameter (mm)	1.015
Wall Thickness (mm)	0.150
Alloy Composition	
Nickel (wt%)	55.94
Titanium (%)	44.05
Transformation Temperatures (based on DSC)	
M_f (^oC)	-100
M_s (^oC)	-78
A_s (^oC)	-28
A_f (^oC)	+28

Specimens were subjected to a DSC Mettler Toledo STAR® System. The Mettler Toledo STAR® System has a DSC30 module in operation with the Mettler Toledo TC15 TA Controller (thermal analysis) allows DSC measurements form -170°C to 600°C. The measurement is based on the Boersma or heat flux principle. Samples are placed in the oven manually, together with an empty reference cup. The experiment parameters are composed in a PC and sent to the TC15 where the segments of the temperature program are controlled. During a measurement the data are transferred to the PC for an on-line curve in the module control window.

A. Kokkinos, Applied Mechanics Laboratory –Department of Mechanical Engineering and Aeronautics, University of Patras, Greece
V. Kostopoulos, Applied Mechanics Laboratory –Department of Mechanical Engineering and Aeronautics, University of Patras, Greece
D. Aslanidis,@mt medical technologies – Daelemveld 1113, 3540 Herk-de-Stad, Belgium

The specimens weighted on a micro-balance device (Mettler AT250). The weight varied between 33.01mg and 34.66mg.

The samples were separated into two groups. The first group is exposed to 65°C while the second group exposed to 150°C. The exposure time was defined for 2h, 24h, 120h, and 240h. After every exposure, a specimen was prepared for DSC measurement. The specimen was cut with saw cutting system at 400 rpm in presence of sufficient cooling to minimize the accumulation of residual stresses in the specimen. The DSC temperature range (scan) was as following:

1. Room temperature to 150°C (NOT RECORDED).
2. Stabilization at +150°C for 1min
3. Scan from +150°C to -120°C (RECORDED).
4. Stabilization at -120°C for 1min
5. Scan from -120°C to 150°C (RECORDED).
6. Stabilization at +150°C for 1min

The first heating is used as a stress-release heating and the associated recording is not representative, and therefore, it is not recorded.

III. CHARACTERIZATION OF SHAPE MEMORY ALLOYS

DSC is an analytical technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. DSC is a thermal method that measures the change in heat flow which is associated with the martensitic and austenitic phase transformations through a controlled cooling - heating cycle as shown in Figure 1. The test sample is a small piece of tubing, free of any external stress during testing. Once the DSC measurement is performed and recorded, the transformations are indicated with their start, peak and finish temperatures, which are most often determined using the tangent method. During cooling, possible phase transformations are the transformation from austenite (A) to R-phase (R) and the transformation from either austenite (A) or from R-phase (R) to martensite (M). During heating the reverse transformation from martensite to R-phase (R') and from either martensite (M) or R'-phase to austenite (A) can occur.

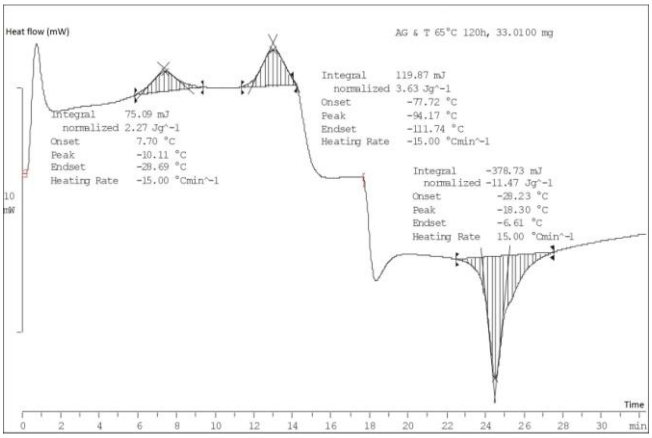

Fig.1 DSC Experiment with an R-phase region during the martensitic transformation (heat flow versus time plot).

Nitinol is characterized by the transformation temperatures from the very start. The compositional accuracy required when melting the alloys, is mostly more precise than the errors in chemical analysis. Therefore, in most cases for quality control purposes not the chemical analysis but the transformation temperature itself is measured. Therefore, it is very interesting to analyze the tubing samples in terms of transformation temperatures. This will allow the direct comparison between various processing steps and the final material condition.

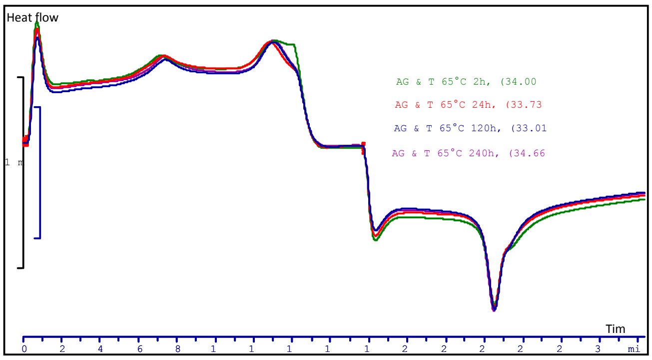

Fig. 2 DSC experiments to NiTi tubes after thermal ageing to 65°C for 2h, 24h, 120h and 240h. All transformation characteristics and temperatures remain stable during ageing (heat flow versus time plot).

Figures 2 and 3 show the DSC measurements of the transformation behaviour of NiTi tubes with different thermal exposure time to 65°C and 150°C (heat flow versus time), respectively. The results are normalized, because the weight of specimens is not exactly the same. All recorded transformation temperatures and associated transformation energies are shown in Table 2.

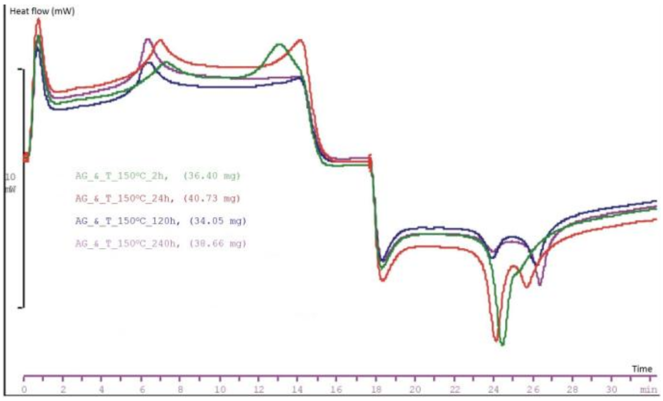

Fig. 3 DSC experiments to NiTi tubes after thermal ageing to 150°C for 2h, 24h, 120h and 240h (heat flow versus time plot). The R'→ A peak is shifted at higher than the original temperatures.

Based on Table 2, the ageing effect at 65°C on the reverse transformation characteristics is negligible. Only after long exposures (above 120h), the Mf (forward transformation) is slightly shifted toward lower temperatures.

On the other hand and during ageing at 150°C, significant transformation shifts were recorded (see Table 2 and Figures 3 and 4).

- The A→ R forward transformation is shifted towards higher temperatures

- Transformation separation of the reverse transformations M→R' and R'→ A based on the tangential method,
- The R'→ A reverse transformation temperatures are decreased, and
- The R'→ A peak has moved towards higher temperatures (>28°C).

The negligible effect of ageing at 65°C shows that no significant diffusion or structural reorganization take place due to low temperatures and the associated low driving forces. The practical evidence is that nitinol tubing can be processed at temperatures up to 65°C without changes on the transformation characteristics.

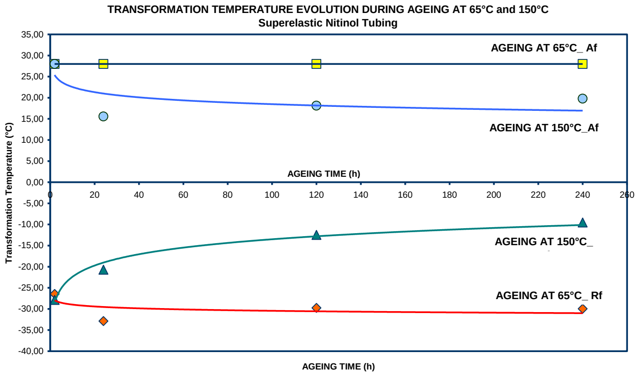

Fig 4 Evolution of the reverse transformation temperature A_f and the forward transformation temperature R_f as function of the ageing time at ageing temperatures of 65°C and 150°C.

On the other hand, the ageing at 150°C can be used to modify and tune the final transformation characteristics of the tubing. Based on literature, ageing phenomena are closely linked to multi-stage transformations.

The multi-stage transformation has been reported in the literature for NiTi alloys subjected to ageing treatment [3]. Several hypotheses have been proposed for this unusual transformation behaviour. Favier et al. [2] attributed this phenomenon to ageing-induced precipitates. They suggested that elastic internal stress fields created by coherent precipitates locally assist the formation of martensites adjacent to the precipitates, whereas regions away from precipitate particles are not directly affected. Bataillard et al. [4] later provided transmission electron microscopic evidences demonstrating the effect of local stress fields around Ni4Ti4 precipitates on the multi-stage martensitic transformation behavior of a Ti-51.14at%Ni alloy aged at 520^{o}C, in support of the precipitate hypothesis for Ni-rich alloy.

This hypothesis, however, has not been confirmed by microstructural analysis for near equiatomic NiTi alloys (<50.2at% Ni) [5]. Tsuchiya et al. [6] reported a study of the effect of severe high pressure torsion on the mechanical and transformation behavior of NiTi. In this work, they observed that the B2→R transformation temperature increased with the decreasing ageing temperature after the severe deformation, suggesting a grain size effect.

For aged nitinol tubing, the low temperature treatment complicates the analysis of the current data based on existing literature. Structural relaxation, local precipitation reorganization under long exposures and high nickel mobility may contribute to the transformation temperatures as are shown in Figure 4.

IV. Conclusion

Nitinol tubing is used in manufacturing various medical devices where the material can be exposed to various ageing processes. This paper analyzed the influence of ageing processing on the properties of nitinol superelastic tubing. DSC measurements were performed on tubing after exposure at 65°C and 150°C for various periods. DSC measurements on specimens from long exposed to 150°C tubing exhibited a two-stage transformation behavior A↔R↔M and a clear phase transformation between M→R' and R'→A.

This unusual ageing-induced behavior in Ni-rich alloys might be associated to the precipitates and the local stress fields associated with them.

REFERENCES

[1] J.S. Zhu, R. Gotthardt, Phys. Lett. A **132**, 279 (1988).

[2] D. Favier, Yinong Liu, P.G. McCormick, Scripta Metall. Mater. **28**, 669 (1993).

[3] L. Bataillard, R. Gotthardt, J. de Phys. IV 5, C8-647

[4] L. Bataillard, J.-E. Bidaux, R. Gotthardt, Philosophical Magazine A **78**, 327 (1998).

[5] Yinong Liu, X. Chen, P.G. McCormick, J. Materials Sci. **32**, 5979 (1997)

[6] Peterlechner M, Waitz T, Gammer C, Antretter T, Martensitic phase transformations of nanocrystalline NiTi shape memory alloys processed by repeated cold rolling. Int J Mater Res 102:634–642, (2011).

Table 2: Transformation temperatures of tube specimen after ageing processing at 65°C and 150°C for 2 – 24 -120 and 240 h in air. All transformations were defined with the tangential method.

AGEING CONDITIONS			**REVERSE TRANSFORMATION**							
Temperature		**Time**	**$R`_s$**	**$R`_p$**	**$R`_f$**	**$R`$**	**A_s**	**A_p**	**A_f**	**A**
°C		*h*	*°C*	*°C*	*°C*	*J/g*	*°C*	*°C*	*°C*	*J/g*
1	65	2	-28,40	-18,29	-6,52	Combined M → R' and R'→ A transformations			28,00	-11,65
2	65	24	-28,02	-18,32	-7,33				28,00	-11,54
3	65	120	-28,57	-18,30	-6,24				28,00	-13,53
4	65	240	-28,74	-18,86	-6,67				28,00	-13,54
5	150	2	-29,47	-19,49	-8,03				28,00	-11,63
6	150	24	-34,29	-24,72	-13,82	-6,16	-14,72	-0,39	15,57	-4,11
7	150	120	-38,63	-26,75	-12,25	-3,82	-7,47	7,48	18,12	-4,92
8	150	240	-40,31	-25,96	-5,24	-2,11	0,00	9,63	19,80	-4,81

AGEING CONDITIONS			**FORWARD TRANSFORMATION**							
Temperature		**Time**	**R_s**	**R_p**	**R_f**	**R**	**M_s**	**M_p**	**M_f**	**M**
°C		*h*	*°C*	*°C*	*°C*	*J/g*	*°C*	*°C*	*°C*	*J/g*
1	65	2	14,57	-5,07	-26,46	2,87	-78,01	-94,39	-98,30	2,36
2	65	24	14,57	-8,83	-32,87	4,06	-75,01	-91,17	-106,88	2,94
3	65	120	10,75	-10,11	-29,76	3,03	-77,29	-94,17	-109,52	3,92
4	65	240	9,97	-9,55	-29,95	3,20	-78,29	-94,12	-109,52	3,04
5	150	2	14,34	-8,39	-27,86	2,85	-77,57	93,97	-109,54	2,36
6	150	24	11,36	-3,52	-20,69	3,69	-94,00	Low temperature R → M transformation		
7	150	120	16,88	5,09	-12,48	4,25				
8	150	240	15,87	5,47	-9,53	4,66				

A.Kokkinos, Dr. Mechanical Engineer
Academic position: Adjunct Professor
Technological Educational Institute
of Ionian Islands, Kefalonia, Greece
Department of Sound Technology

2001 Employment at the Laboratory of Applied Mechanics, Department of Mechanical Engineering and Aeronautics, University of Patras, and cooperation with the orthopeadic prof. Doctors, Mr. H. Panagiotopoulos and Mr. A. Fortis, with result a publication with the title:
"Viscoelastic Properties of Cartilage Subchondral Bone Complex in Osteoarthritis"
2002 Registration at the Post-Graduate Course of Studies of the Department of Mechanical Engineering and Aeronautics, University of Patras, for the acquisition of PhD. Duration of the course : six semesters. Subject of the experimental thesis : "Design of an intramedullary limb lengthening device using Shape Memory Alloys".
2002-today Member of the Technical Chamber of Greece
2003 Design of a device which estimates damping to specimens contains piezoelectric particles.
2003 Participation to the Leonardo Da Vinci Program, collaboration to the experimental procedures and to the production line of @MT – medical technologies company, producing Shape Memory Alloys.
2007 Presentation of the doctorate and acquisition of PhD as a Mechanical Engineer, at the University of Patras, Greece.
2008- today Collaboration with the Applied Mechanics Laboratory, at the Mechanical and Aeronautics Department, University of Patras, Greece
2010-today Collaboration with the Technological Educational Institute of Ionian Islands, Kefalonia, Greec as Adjunct Professor

- Research work, new materials for musical instruments, composite materials, carbon, acoustical behavior for isotropic and anisotropic materials.

V.Kostopoulos Dr. Mechanical Engineer
Academic position: Professor Director of the Laboratory of Applied Mechanics and Vibrations, Department of Mechanical Engineering & Aeronautics, University of Patras, Greece.

1980: Degree in Mechanical Engineering (Dip. Eng.), National Technical University of Athens, Greece
1987: PhD in Applied Mechanics (Wave Propagation & Scattering of Thermo-Elastic Waves, Non - destructive testing of Composite Materials)

- 2003 - today Member of the Advisory Council for Aerospace Research in Europe (ACARE)
- 2003 - 2006 National Delegate of FP6 Aerospace Program Committee
- 2007 National Delegate of FP7 Transport (including Aeronautics) Program Committee
- Member of the National States Representative Group of JTI 'CLEAN SKY'.
- Elected Member of the Council of the European Society for Composite Materials (ESCM)
- Member of the Editorial Board of the Journal 'Composite Science and Technology'
- Member of the Editorial Board of the Journal 'Mechanics of Advanced Materials and Structures'
- Member of the Editorial Board of the Journal 'Research & Reviews in Polymers'
- Associate Editor of the 'International Journal of Aerospace Engineering'
- Reviewer in 32 International Scientific Journals
- Evaluator of research proposals for EU, UK, Belgian, Sweden, Greek and Cyprus research foundations

101 publications in referee Journals
157 presentations in International Conferences
4 books (2 International and 2 in Greek)
6 chapters in international books
32 Invited Lectures in International Conferences
Co-organizer of 38 International Conferences
Main Supervisor of 14 completed PhD theses
Patents: 2 European and 5 National ones.
Google Scholar: Kostopoulos Vassilis

D.Aslanidis, Dr. Metallurgical Engineer

Director Engineering RTD Materials Processing Medical Health Technologies Smart Devices and Co.
Professional Materials and Metallurgical Engineer Specialized in Surface Technologies and Applied Electrochemistry
Expert in Medical Device Materials and Technologies
Areas of Expertise:

- Applied Electrochemistry-Deposition Technologies
- Medical Device Materials And Technologies
- Metallurgy
- Prototyping
- Research And Development
- Shape Memory Alloys-nitinol-actuators-components
- Surface Science And Technologies

2011 Aircraft systems with shape memory alloy (SMA) actuators, and associated methods US 7878459 B2