PIRSES-GA-2013-612585 - MIDAS

Micro and Nanoscale Design of Thermally Actuating Systems

PEOPLE

MARIE CURIE ACTIONS

International Research Staff Exchange Scheme

Call: FP7-PEOPLE-2011-IRSES

Micro and Nanoscale Design of Thermally Actuating Systems

– MIDAS –

INTERIM REPORT

for the years

2014 - 2015

PIRSES-GA-2013-612585 - MIDAS

Micro and Nanoscale Design of Thermally Actuating Systems

Introduction

The ***main objectives of the MIDAS project***, identified within the framework of the FP7- IRSES Call are:

1. To set-up a network of collaborative applied research between partners involved in complementary activities with the aim to develop actuating materials and applications.
2. To explore novel paths for enhancing the functionality of thermally actuated materials belonging to the shape memory alloy group. The use of a knowledge diversity related to the formation and fields is expected to be the driving force in the effort to find new paths.
3. To identify innovative ideas worth to be considered by private companies for the development and optimization of novel applications.
4. To provide a framework for optimal transfer of knowledge between the partners and between generations of scientists via adequately tailored exchange programs for each type of exchange beneficiary.
5. To generate a proper environment for interaction with private entrepreneurs interested in exploiting the results of the research collaboration.
6. To provide knowledge to be shared in educational activities as well as for dissemination of information to other socio-economical actors and
7. To favor the collaboration and its expansion even beyond the funding provided by this call, via new joint grant applications, publications or conferences and seminars.

Participant Number	**Participant name**	**Participant short name**	**Country**
1 *Beneficiary* 1 (coordinator)	*Universitatea “Politehnica” din Timisoara*	*UPT*	*Romania*
2 *Beneficiary* 2	*FFCT -Universidade Nova de Lisboa*	*FFCT*	*Portugal*
3 *Beneficiary* 3	*Universitat de les Illes Baleares*	*UIB*	*Spain*
4 *Beneficiary* 4	*Cranfield University*	*CU*	*UK*
5 *Beneficiary* 5	*Laboratório Nacional de Energia e Geologia*	*LNEG*	*Portugal*
6 Partner 6	*Universidade Federal Fluminense*	*UFF*	*Brazil*
7 Partner 7	*University of Waterloo*	*WU*	*Canada*
8 Partner 8	*Indian Institute of Science*	*IISc*	*India*
9 Partner 9	*Russian Academy of Sciences*	*RAS*	*Russia*
10 Partner 10	*University of Science and Technology Beijing*	*USTB*	*China*

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WP 1 Structural optimization by Mechanical Alloying (MA)

Coordinating unit: LNEG, Dr. Filipe NEVES
Partners: FFCT, UFF, UPT, USTB

MIDAS report CENIMAT – Stay of Xingke Zhao (USTB, China)

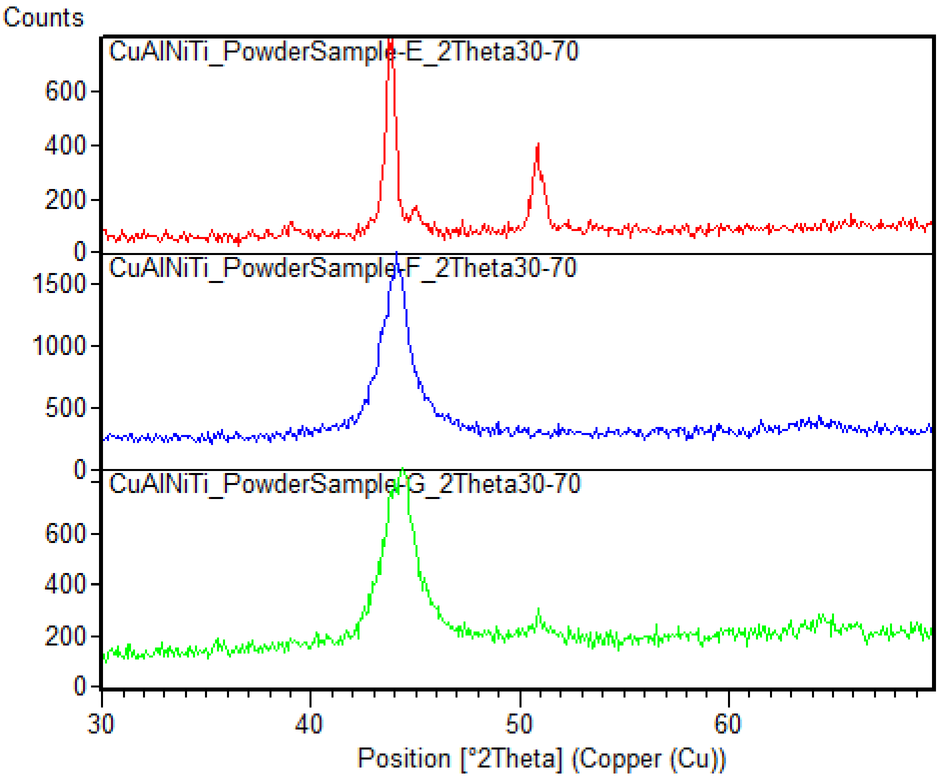
Period	Location of stay	People involved	Tasks
July 2015	LNEG + CENIMAT	Xingke Zhao (USTB) Filipe Neves (LNEG) F.M. Braz Fernandes (CENIMAT) João Pedro Oliveira (CENIMAT)	XRD, DSC and TMA

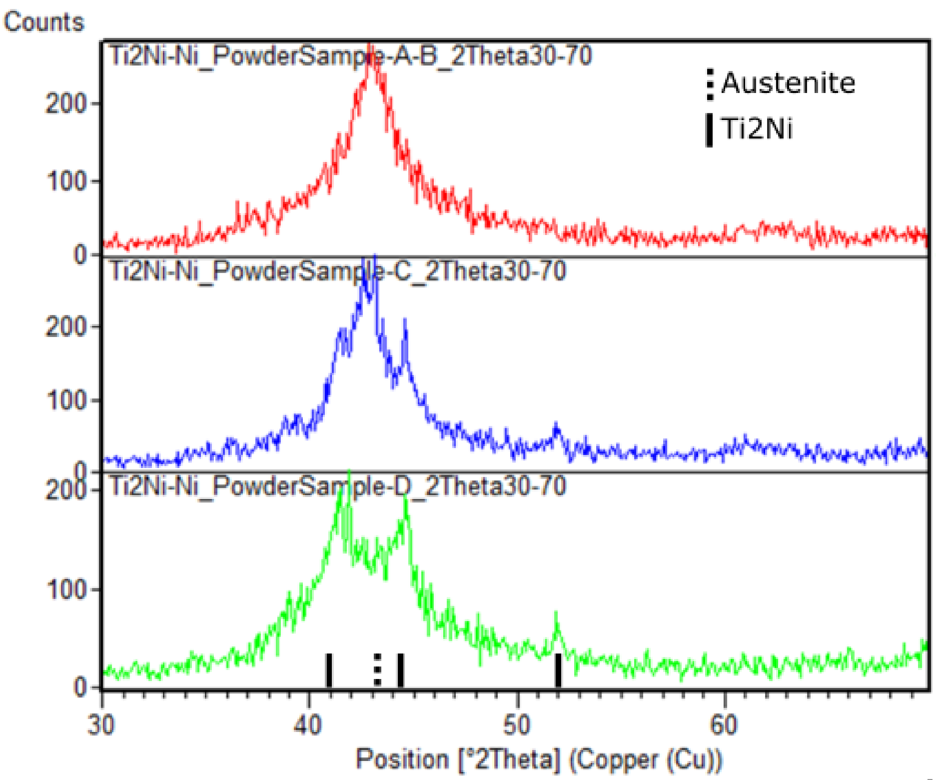
Task – Characterization of powder alloys
In the framework of MIDAS project and during his stay at CENIMAT, Xingke Zhao under the supervision of Francisco Braz Fernandes worked on the characterization of powder alloys.
Two different target compositions were envisaged: Cu-14Al-4Ni-0.5Ti (wt. %) starting with elemental powders of Cu, Al, Ni and Ti; Ti-55Ni (wt. %) starting with Ni and Ti_2Ni powders. For these target compositions, the processing parameters (milling time and speed) where varied. The tables below depict the processing parameters used for the two target compositions.

Target composition (wt%)	Milling speed (rpm)	Time (h)	Sample reference	Ball diameter (mm)
Ti-55Ni (starting with Ni and Ti_2Ni powders)	400	2	A/B	15
	400	2	C	
	300	2.5	T/U	
		2	D/J	
		1.5	O	
		1	M	
	180	2	K	

Target composition (wt%)	Milling speed (rpm)	Time (h)	Sample reference	Ball diameter (mm)
Cu-14Al-4Ni-0.5Ti (starting with elemental powders)	400	2	F	15
	400	1	H	
	300	4	E	
	300	2	G	
		1.5	P	
		1	R	
		0.5	Q; S	
	180	2	I	
	180	1/2	N	

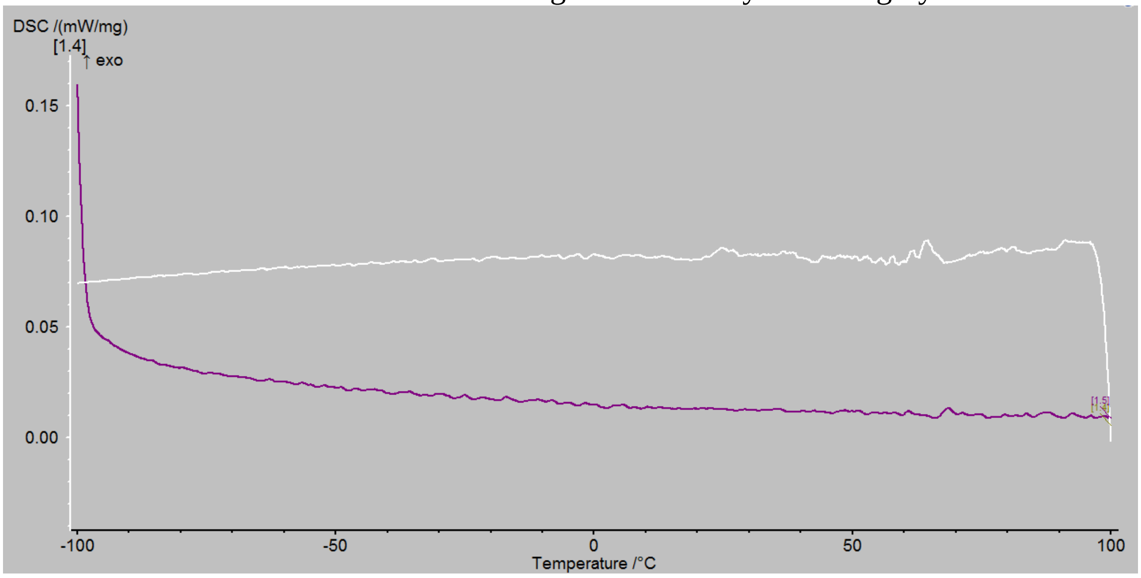
The effect of process parameters were assess by different characterization techniques used: X-ray diffraction, differential scanning calorimetry and dilatometry. The first was used to characterize the existing phases after powder processing of different materials, while the remaining two were used to analyse any possible structural transformation occurring in a given temperature range.
X-ray diffraction analysis was performed on different samples of the Cu-Al-Ni-Ti and Ni-Ti powder alloys (Figures below) and revealed significant microstructural modifications which are dependent on the process parameters. The study of the remaining samples is currently under study.



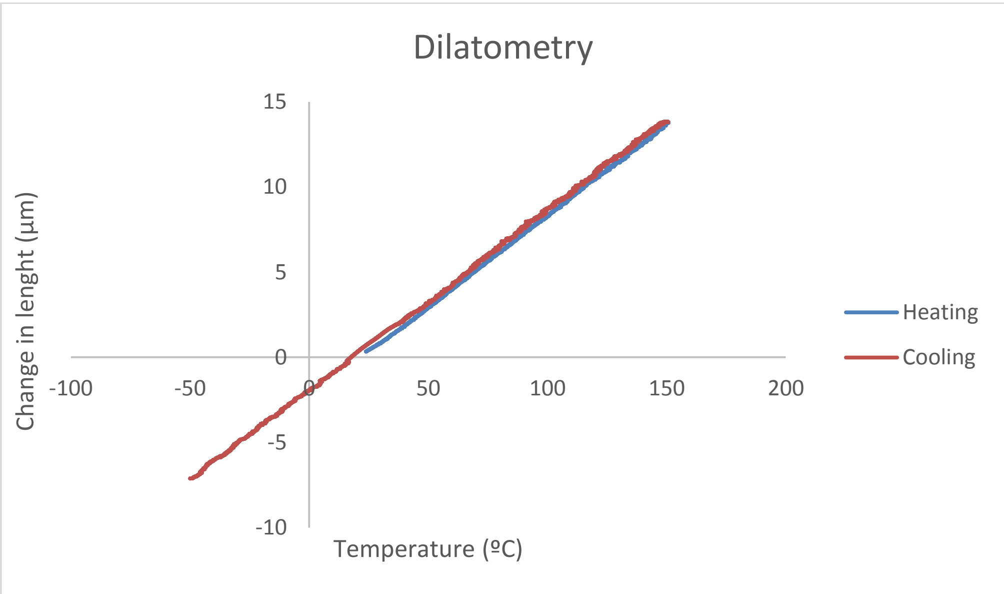


Phase analysis of the above patterns (from the Ni-Ti system) revealed that they are mainly constituted by austenite (black vertical lines in Figure below) and Ti_2Ni (green vertical lines in Figure below).

Characterization of a reference material D (from the Ti-55Ni target composition) by differential scanning calorimetry revealed that in the temperature range of -100 to 100 ºC no phase transformations occur.



The differential scanning calorimetry experimenets evidencing that no phase transformation occurred for the tested temperature range were confirmed by dilatometry (depicted below). This can be related to the fact that these powder alloys may require a specific heat treatment in order to allow for a reversible transformation to occur. This is currently under study.



The effect of the processing parameters on the microstructure of the produced powder alloys is currently under study, so that a correlation between the aforementioned characterization techniques can be performed. Additionally, differential scanning calorimetry and dilatometry experiments will be performed on other samples to test for possible phase transformations within a given temperature range.

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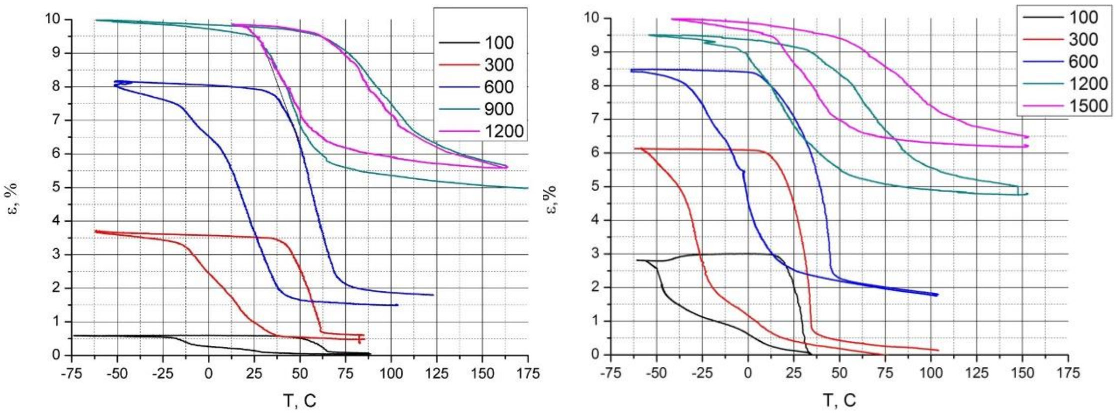
WP2 Structural control by plastic deformation (SPD)

Coordinating unit: FFCT, Professor Francisco Manuel BRAZ FERNANDES
Partners: IISc, UFF, RAS, USTB

MIDAS progress report – Pavel Mazaev (Kotel'nikov Institute of Radioengineering and Electronics of Russian Academy of Sciences**)**

Period	Location of stay	People involved	Tasks
14/09/2014 to 19/10/2014	CENIMAT	F.M. Braz Fernandes (CENIMAT) Viktor Koledov (RAS)	XRD and DSC

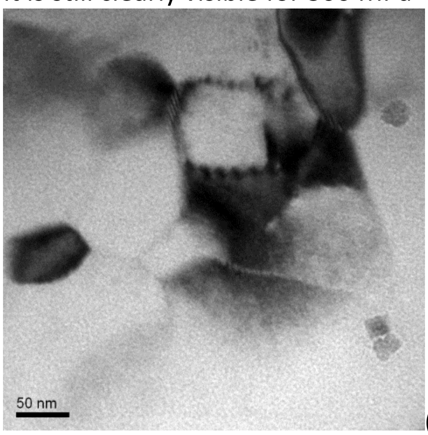
1 - Preliminary results obtained at RAS



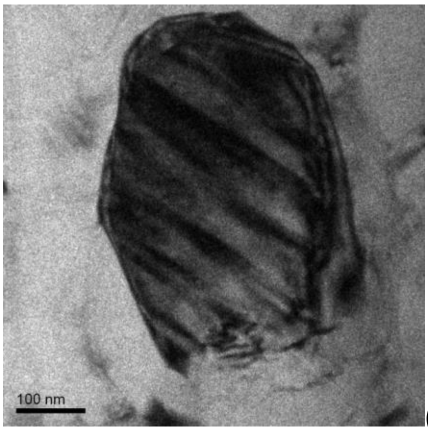
Strain versus temperature curves for different applied loads for

(a) coarse grained structure obtained by solubilization + quenching
(b) sub-micrometer grain size obtained by ECAP

In sample (a), two-steps phase transformation is detected only for 100 MPa load, while for sample (b) it is still clearly visible for 300 MPa



(a)

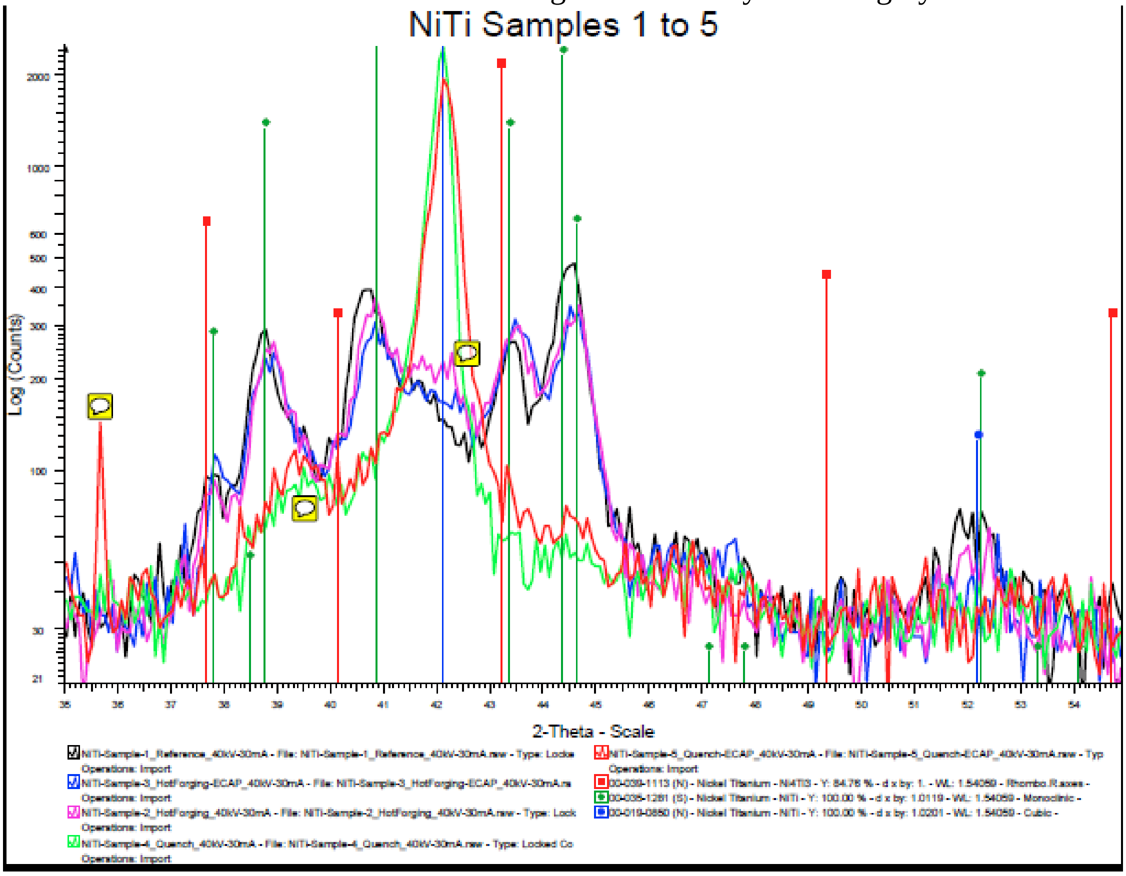


(b)

(a) Martensite twins can't be seen in the group of small (50-100nm) grains
(b) Martensite twins in grain 300x500nm

2 – Tests performed at CENIMAT

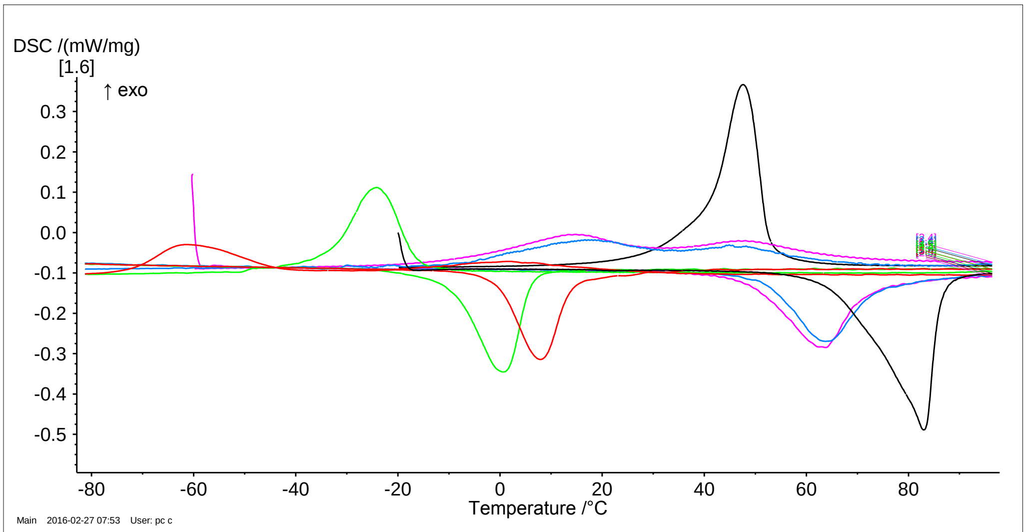
2.1 - XRD



Reference
Solubilization + Quenching
Solubilization + Quenching + ECAP
Hot-Forging
Hot-Forging + ECAP

XRD tests performed at room temperature: only the samples that have been previously subjected to solubilization + quenching are austenitic at room temperature. Or all the other conditions, the material is martensitic at room temperature.

2.1 - DSC



[#] Instrument	File	Date	Identity	Sample	Mass...	Seg...	Range	Atmosphere	C...
[1.4] DSC 204F1 Phoenix	Sample_1ref_2.ngb-sd7	2014-10-13	Sample_1ref_2	Sample_1ref_2	37.8	4/9	150°C/10.0(K/min)/-20°C	N2, 20.0ml/min / N2, 20.0ml/min	---
[1.6] DSC 204F1 Phoenix	Sample_1ref_2.ngb-sd7	2014-10-13	Sample_1ref_2	Sample_1ref_2	37.8	6/9	-20°C/10.0(K/min)/150°C	N2, 20.0ml/min / N2, 20.0ml/min	---
[2.4] DSC 204F1 Phoenix	Sample_2forging_2.ngb-sd7	2014-10-13	Sample_2forging_2	Sample_2forging_2	23.3	4/7	150°C/10.0(K/min)/-60°C	N2, 20.0ml/min / N2, 50.0ml/min	---
[2.5] DSC 204F1 Phoenix	Sample_2forging_2.ngb-sd7	2014-10-13	Sample_2forging_2	Sample_2forging_2	23.3	5/7	-60°C/10.0(K/min)/150°C	N2, 20.0ml/min / N2, 50.0ml/min	---
[3.4] DSC 204F1 Phoenix	Sample_3forging_ECAP.ngb-sd7	2014-10-13	Sample_3forging_ECAP	Sample_3forging_ECAP	24.9	4/8	100°C/10.0(K/min)/-100°C	N2, 20.0ml/min / N2, 50.0ml/min	---
[3.5] DSC 204F1 Phoenix	Sample_3forging_ECAP.ngb-sd7	2014-10-13	Sample_3forging_ECAP	Sample_3forging_ECAP	24.9	5/8	-100°C/10.0(K/min)/100°C	N2, 20.0ml/min / N2, 50.0ml/min	---
[4.4] DSC 204F1 Phoenix	Sample 4_quenched.ngb-sd7	2014-10-14	Sample 4_quenched	Sample 4_quenched	41.1	4/8	100°C/10.0(K/min)/-100°C	N2, 20.0ml/min / N2, 50.0ml/min	---
[4.5] DSC 204F1 Phoenix	Sample 4_quenched.ngb-sd7	2014-10-14	Sample 4_quenched	Sample 4_quenched	41.1	5/8	-100°C/10.0(K/min)/100°C	N2, 20.0ml/min / N2, 50.0ml/min	---
[5.4] DSC 204F1 Phoenix	Sample 5quenchedECAP.ngb-sd7	2014-10-14	Sample 5quenchedECAP	Sample 5quenchedECAP	41.2	4/8	150°C/10.0(K/min)/-100°C	N2, 20.0ml/min / N2, 50.0ml/min	---
[5.5] DSC 204F1 Phoenix	Sample 5quenchedECAP.ngb-sd7	2014-10-14	Sample 5quenchedECAP	Sample 5quenchedECAP	41.2	5/8	-100°C/10.0(K/min)/150°C	N2, 20.0ml/min / N2, 50.0ml/min	---

Created with NETZSCH Proteus software

Samples submitted to Hot-Forging and Hot-Forging + ECAP clearly show a two-steps phase transformation during cooling; during heating, the single peak is most probably a superposition of B19’ to R-phase and R-phase to B2. Ecap treatment after hot-forging does not show a significant difference on the transformation temperatures. The ECAP treatment has resulted in a decrease of Ms / Mf temperatures and an increase of As / Af temperatures compared to the simply solubilized+quenched sample.

3 – Scientific Dissemination

The following seminar has been presented to students and researchers from CENIMAT / FCT-UNL

Date: 15 de Outubro de 2014, 16h00
Local: Anfiteatro Leopoldo Guimarães
"Micro- and nanomechanical tools with shape memory effect for scientific researches, electronics and biomedical technology"
By Ph.D. student Pavel Mazaev
Kotel'nikov Institute of Radio-Engineering and Electronics of RAS (Russia)

Abstract: A significant part of the modern science aims to explore the micro- and nanoworld. But this study will never be complete if it is limited only by visual observation. For the full interaction with the micro- and nanoworld scientists and engineers produce various manipulators that can be used to manipulate the nanoobject under investigation study and even to change it.
However, many of the established manipulators have similar disadvantages such as a massiveness and an inability for the study of the biological samples. As the solution the scheme on the basis of the layered composite Ti50Ni25Cu25/Pt with shape memory effect has been proposed and tested. This scheme provides a giant reversible bending deformations using only one-way shape memory effect. Nanotweezers are activated by heating with a laser and the temperature range is only 40...70°C. Experiments on the manipulation of the micro- and nanosamples and biological objects were performed. Also a prototype nanotweezers based on a ferromagnetic Heusler alloy Ni53Mn24Ga23 with shape memory effect to manipulate objects by applying a magnetic field and, as a consequence, at a constant temperature was proposed [1-4].
To calculate the action force to the object of the nanotweezers' actuator a technique to determine the stiffness of the actuator based on similar technology for cantilevers of atomic force microscopes has been developed and tested.
Also a prototype of the alternative nanotweezers' heating system was proposed. It can eliminate the laser heating in favor of using an electric current driven heater. Such a system can be quit compatible with conventional micromanipulation systems, such as Kliendiek and Zyvex.

References 1. Irzhak A., Koledov V., Zakharov D. et. al. / Development of laminated nanocomposites on the bases of magnetic and non-magnetic shape memory alloys: Towards new tools for nanotechnology / Journal of Alloys and Compounds 586, S464–S468, 2014; 2. Irzhak A., Kalashnikov V., Koledov V. et. al. / Giant Reversible Deformations in a Shape Memory Composite Material / Technical Physics Letters, Vol. 36, No. 4, pp. 329–332, 2010; 3. Zakharov D., Lebedev G., Irzhak A. et. al. / Submicron-sized actuators based on enhanced shape memory composite material fabricated by FIB-CVD / Smart Mater. Struct. 21, 2012; 4. Kalimullina E., Kamantsev A., Koledov V. et. al. / Magnetic shape memory microactuator / Phys. Status Solidi C 11, No. 5–6, 1023– 1025, 2014.

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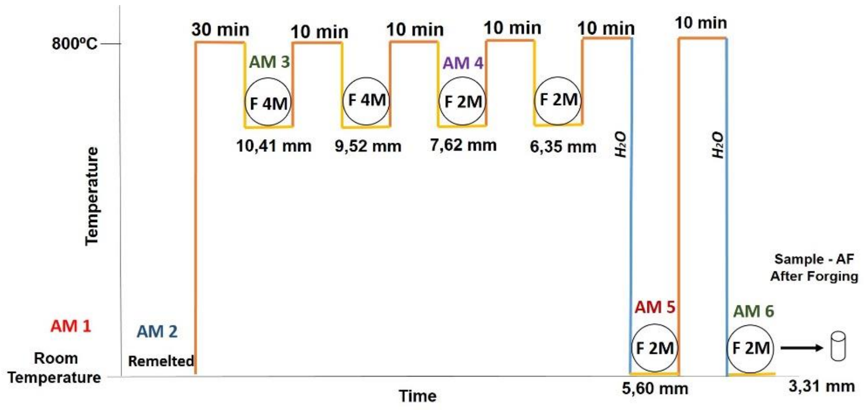
MIDAS report CENIMAT – Stay of Andersan dos Santos Paula (UFF, Brazil)

Period	Location of stay	People involved	Tasks
July 2015	CENIMAT	**Andersan dos Santos Paula (UFF)** F.M. Braz Fernandes (CENIMAT) Patrícia Freitas Rodrigues (CENIMAT) João Pedro Oliveira (CENIMAT)	XRD and DSC and EBSD

Task – Characterization of NiTi alloys subjected to different thermomechanical treatment (hot/cold forging) and heat treatments (solubilization and aging), according to the schematic below.

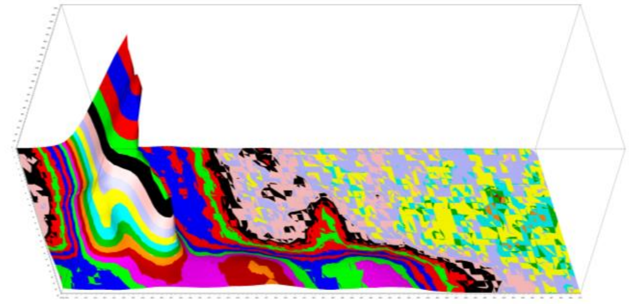


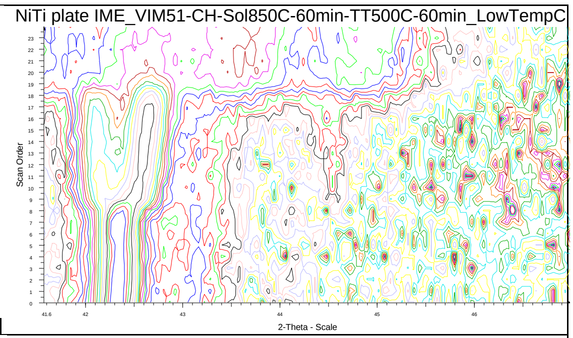
The development of NiTi alloys with shape memory effect and superelasticity is due to their special characteristics, which to be achieved should be subjected to strict manufacturing control during the melting and refining processes, thermal and mechanical treatment. This implies close monitoring and control of chemical composition and processing variables associated with the thermomechanical treatment. The first results of this work aimed to produce thin bar forged up to 3 mm diameter from alloys with distinct compositions elaborated in lab scale (VIM – Vaccum Induced Melting). According to the selected temperatures for reheating samples (before hot forging) and solution samples (before cold forging), problems related to crack formation during thermomechanical process were identified, but it was possible to obtain some samples to start two studies:

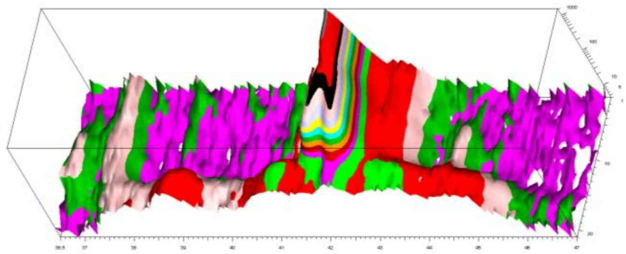
- the optimization of different conditions of the solubilization and aging heat treatments applied on the forged wire of Ni-rich NiTi alloy aiming an austenitic matrix at ambient temperature. The best condition for solubilization for this alloy was found to be 950ºC for 2 hours.

- the evidence of microstructural, microtextural, phase transformations and mechanical properties changes that could be related to recovery and recrystallization phenomena in NiTi alloys (an approximately equiatomic and nickel rich, proposed compositions).

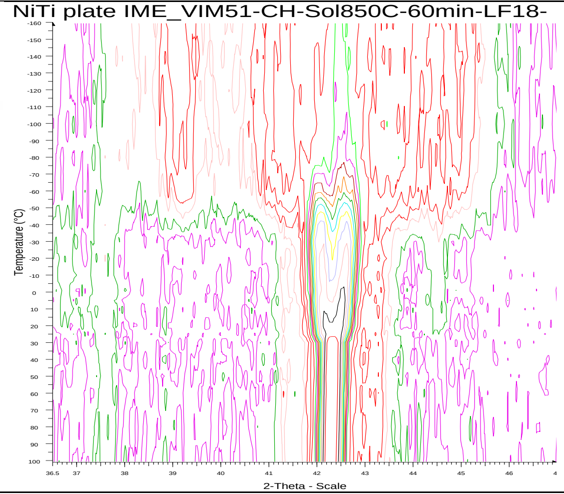
Task 1 – Structural investigation by non-ambient XRD





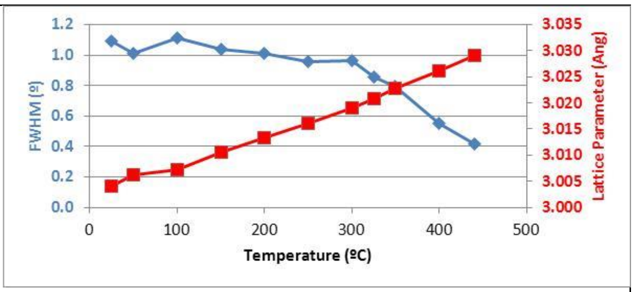


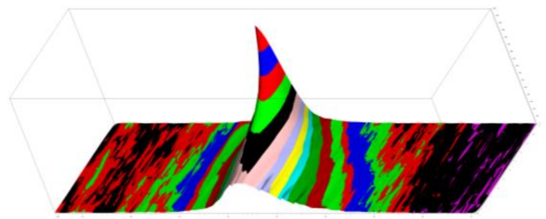
NiTi plate IME VIM51 Solubilization 850ºC, 60 min / HT 500ºC, 60 min. LF18, Low temperature characterization

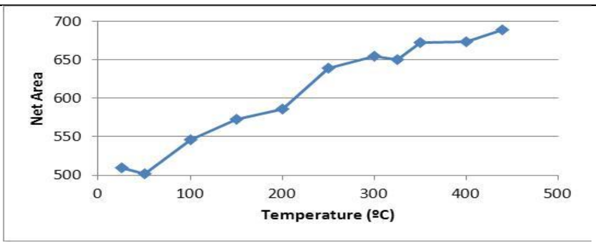


After aging at 500ºC, the two-steps phase transformation is clearly visible during cooling.

NiTi plate IME VIM51 Solubilization 850ºC, 60 min / HT 500ºC, 60 min. LF18,







From the XRD tests performed during heating up to 440ºC it is possible to identify (from the FWHM versus T) the sequence of recovery phenomena up to 300ºC and recrystallization above this temperature.

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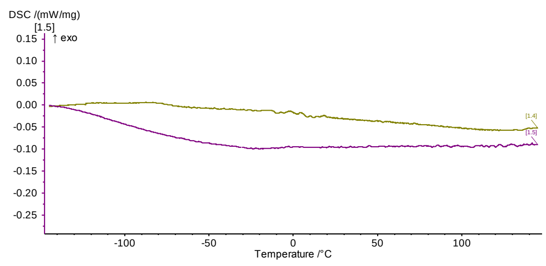
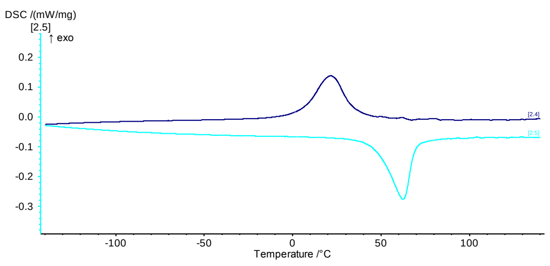
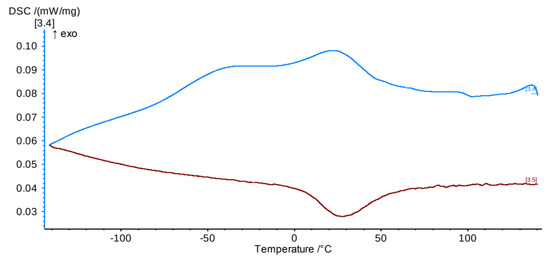
Task 2 – Thermal analysis by DSC



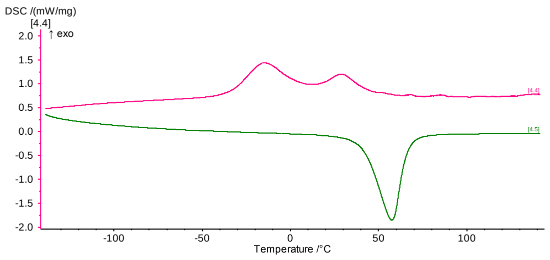
(a) VIM47_Ti_CR



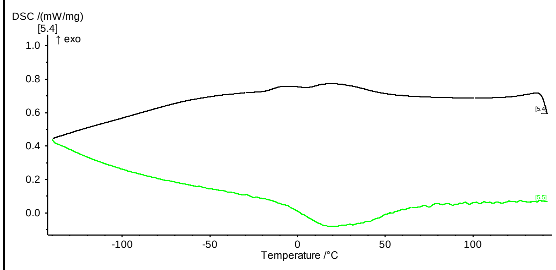
(b) VIM_47_AM3



(c) VIM_47_AM4

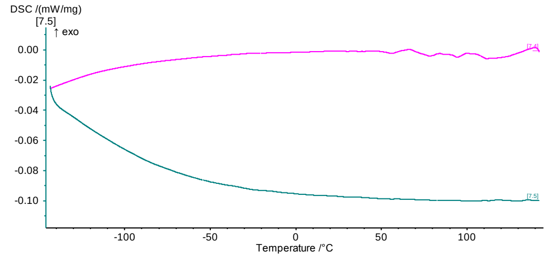


(d) VIM_47_AM5

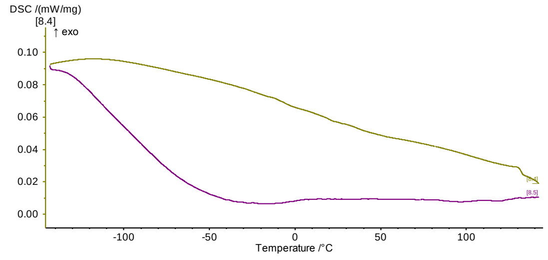


(e) VIM_47_AM6

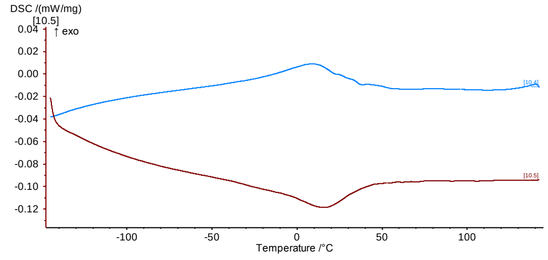
DSC curves of the material (a) as cast, and after the different steps of forging (b) AM3, (c) AM4, (d) AM5, (e) AM6.



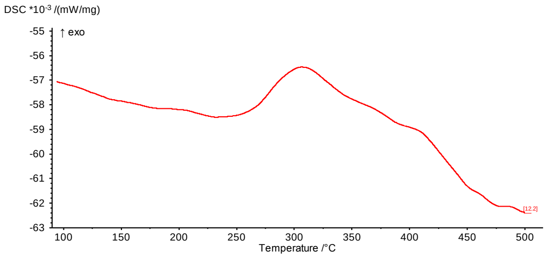
(a) VIM51_Eq_CR



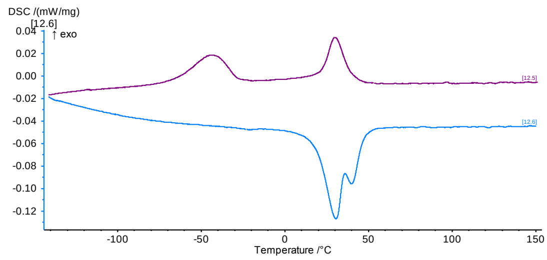
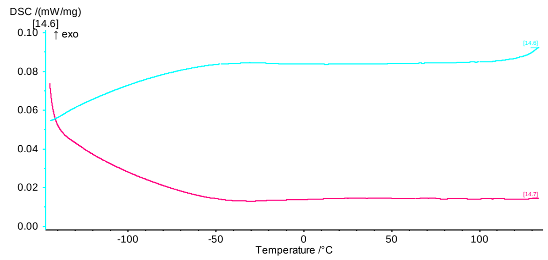
(b) VIM51_Eq_CR_refusao.ngb-sd7



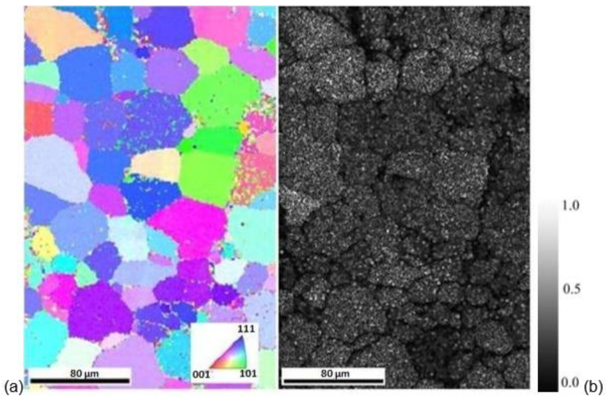
(c) VIM51-AM4



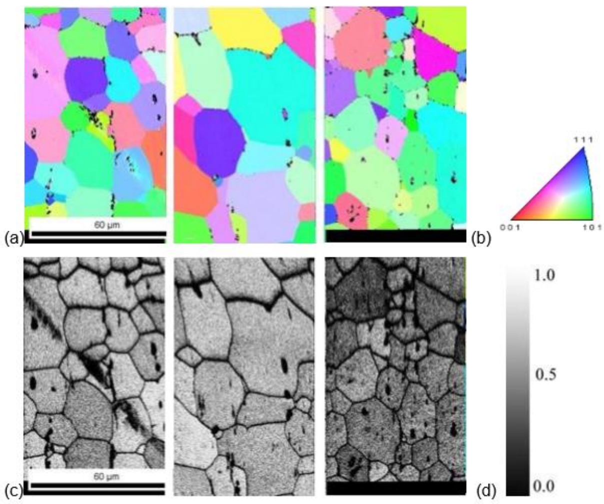
(d) VIM51-AM4C HT 500ºC

 (e) VIM51-AM4C after HT 500ºC	 (f) Vim 51_forge
DSC curves of the material (a) as cast, (b) after remelting, (c) after forging step AM4, and (d) during heating to 500ºC, (e) after heat treatment at 500ºC and (f) after forging.	

Task 3 – Structural investigation by EBSD



EBSD result for B2 indexed for final forged samples (a) orientation indexed map and (b) confidence index.



EBSD result for B2 indexed for final forged samples after solution heat treatment at 950ºC during 2 hours: (a) orientation indexed map and (b) confidence index.

The recovery and recrystallization phenomena were observed in parallel with precipitation. The following techniques were used (at room temperature): (i) X-ray diffraction to identify present phases, (ii) instrumented nanoindentation to evaluate the mechanical properties , and (iii) electron backscattering diffraction (EBSD), in a scanning electronic microscope (SEM) with lanthanum hexaboride filament (LaB_6), to observe the B2 phase microstructure and microtexture evolution.

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MIDAS progress report – Patricia Freitas Rodrigues (supervisors: F.M. Braz ernandes and Andersan dos Santos Paula)

Period	Location	People involved	Tasks
20/11/2015 to 26/12/2015	Universidade Federal Fluminense, Brazil	Andersan dos Santos Paula (UFF) Ladário da Silva (UFF) F.M. Braz Fernandes (CENIMAT)	Hot and cold forging, Nano-indentation testing, SEM, EDS, WDS

The following report presents 2015 most relevant results in the framework of MIDAS.
Results are part of WP2.

Task 1 – Thermomechanical Processing: Hot and Cold Forging

NiTi alloys are very attractive due to their functional properties. However, the major challenges in producing these materials with shape memory effect are the control of their composition, regarding the percentage ratio of Ni and Ti; and reduce of the impurities such as carbon and oxygen. The production of NiTi materials usually involve hot or cold thermomechanical processing. Understand the thermomechanical processing behavior during hot and cold rotary forging to produce NiTi wires rich in Ni is the most interest of this research.

The process performed, starting from casting and going to the hot and cold forging represents a major challenge, since the structural changes of the material during the processing needs more investigation. NiTi wires with approximately 3mm diameter were produced from NiTi alloy 51.52% Ni through hot and cold forging as shown in Figure 1. Like this, the mapping of the properties in order to associate processing variables (chemical composition, solidification and thermal processing and / or mechanical) to the in service behavior of the wires isthen possible.

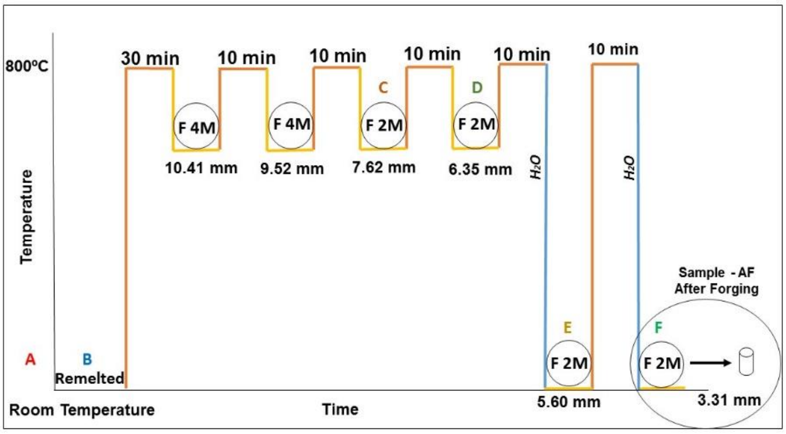

Figure 1 – Thermomechanical Processing Scheme

In Brazil the investigation aimed to perform the following analysis: (i) nanoindentation tests on samples of hot and cold forging steps, (ii) WDS measurements on as cast and remelted samples and (iii) scanning electronic microscopy observations. Also, previous results were discussed in order to assess the changes in the thermomechanical variables of hot and cold forging processing.

Task 2 - Characterization of Thermomechanical Processing

2.1 – Nanoindentation Test

Tests were performed on samples corresponding to the steps A, B, C, E and F of hot and cold work, according to the proposed thermomechanical processing. Nanoindentation tests were carried on a Shimadzu Vickers DUH-211S equipment, with Vickers indenter type using 20 seconds residence time in the maximum load. Each sample were subjected to 10 tests in different areas around the center point.

The results show the behavior of the loading and unloading curve with a relation between the force and depth of indentation, as in the example of Figure 2.

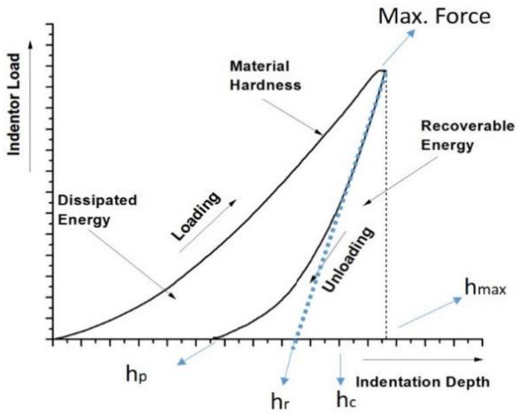

Figure 2 - Schematic diagram showing the different microstructural mechanisms leading to material hardness, energy dissipation and energy recovery during indentation of NiTi shape-memory alloy

As shown in Figure 2, it was possible to determine HV (mN / µm^2) the hardness indentation, F_{max} (mN) the maximum force applied, h_c (uM) the indentation depth bounded to the contact surface limited by the contact area between the indenter with the sample, h_{max} the maximum indentation depth (mM), h_r the intersection point of the tangent to the unloading curve.

In Figure 3, the behavior for the sample corresponding to the sample after the last step of forging (3 mm diameter) was observed (from ten different points). The results are being processed in order to map the mechanical behavior of the samples analyzed by nanoindentation test.

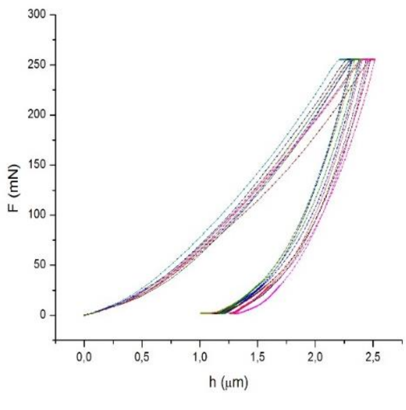

Figure 3 - Loading and unloading curves instrumented nanoindentation at 20ºC – NiTi Sample with 3mm (step AF, after forging).

2.2 – Wavelength Dispersive Spectroscopy (WDS)

The chemical composition of as cast and remelted samples were determined via microanalysis in the NiTi metal matrix using a dispersive wavelength spectrometer X-ray (WDS - Oxford Instruments controlled by INCA program) coupled to a SEM EIF EGF 450, with field emission filament (EGF). Values corresponding to the percentage of Ni and Ti obtained in the tests are shown in Table 1.

	Cast Sample		Remelted Sample	
	%at Ni	**%at Ti**	**%at Ni**	**%at Ti**
Sample	51,52	48,48	51,03	48,97

2.3 – Scanning Electron Microscope (SEM)
SEM observation are currently being carried on.

2.4 – Discussion - First Results
Discussions with Andersan dos Santos Paula made possible to identify some process variables that could be modified to improve the whole processing. Among these are the previous solubilization of ingot and additional heating between the forging steps. Besides that, it is required to verify the quality of surface finishing of the ingots in order to avoid folds with incrustation oxides during the steps of hot forging that could result in cracks initiation. However, it is necessary to continue the assessment in order to check the information obtained by more recent studies done.

WP3 Micro and nanoscale characterization (CHR)

Coordinating unit: UIB, Professor Eduard CESARI
Partners: FFCT, UPT, LNEG, UFF, IISc, RAS, USTB

PIRSES-GA-2013-612585 - MIDAS

Micro and Nanoscale Design of Thermally Actuating Systems

WP4 Welding and joining techniques for smart materials (WJ)

Coordinating unit: CU, Professor Stewart W. WILLIAMS
Partners: WU, UPT, FFCT

MIDAS researcher: João Pedro Oliveira (PhD student; supervisors: F.M. Braz Fernandes and Rosa Miranda, FCT/UNL)

Period	Location of stay	People involved	Tasks
27/05/2014 to 21/12/2014	Center for Advanced Materials Joining at the University of Waterloo, Canada	Norman Zhou (WU), Boyd Panton (WU), Zhi Zeng (WU) F.M. Braz Fernandes (CENIMAT) Rosa Miranda (UNIDEMI)	Laser Welding, TEM and Mechanical testing

1 - Laser welding of NiTi to Ti6Al4V and Stainless Steel 316L

NiTi possesses extremely interesting functional materials: superelasticity and shape memory effect. Being able to join this material with other engineering alloys is of great interest in order to obtain new applications in different fields. Among these engineering alloys Ti-based, such as Ti6Al4V, and stainless steel are of great importance as they are widely used in structural applications. Welding NiTi has some issues to the extreme affinity of Titanium to almost all elements in the periodic table. When trying to do dissimilar welding one has to be very careful in order to reduce the amount of brittle precipitates (or ideally prevent their occurrence) that can be formed upon cooling due to the mixing of the liquid mixture of both base materials.
Welding NiTi to stainless steel and Ti6Al4V is known to create brittle precipitates in the fusion zone, such as Ti_2Ni, Ni_3Ti, Al_3Ti or Fe_2Ti. A possible solution to overcome this problem is the introduction of a given material between both base materials. For this reason interlayer with thicknesses of 25 to 100 µm, where used. The interlayers chosen where of Cu, Fe, Co and Nb. All these materials are known to be part of the shape memory alloy system Ni-Ti-X, with X = Cu, Fe, Co and Nb. This means that potentially the introduction of such materials may decrease the amount of brittle intermetallics that are formed when NiTi an Ti6Al4V or stainless steel are welded together.

1.1 - Welding of NiTi to Ti6Al4V using interlayers

1.1.1 - Butt joint configuration

For the NiTi/Ti6Al4V welding butt and overlap joints were produced. In the butt joints configuration Cu and Nb interlayers were used. In this case, in order to promote joining of both materials the laser had to be offsetted to the Ti6Al4V side due to the high reflectivity of the interlayers. The positions of the laser is of crucial importance as if it is too close to the interlayer the majority of the energy is deflected and if it is placed far away from the interlayer the amount of energy reaching that region is not enough to promote its fusion.
When using the Cu interlayer although joining of both materials was obtained, it was observed using optical microscopy the existence of cracks in the fusion zone. One possible reason for this is that although the melted Cu helps in decreasing the amount of brittle precipitates, some of them are still formed upon cooling and the residual stresses during solidification are enough to create the cracks in the fusion zone. A possible solution to this problem is to use a interlayer with a higher thickness despite the fact that a recent study have shown that increase the amount of adding material when trying to join NiTi and Ti6Al4V is detrimental to the joint properties.
In the Nb interlayer case joining was again achieved despite the mechanisms for the bonding between the two base materials is quite different from the usual cases. The melting point of pure Nb is of about 2630 ^oC, while for NiTi and Ti6Al4V is of 1310 and 1660 ^oC, respectively. With such a high melting point for the Nb interlayer, the strategy is to place the laser in such a position that the

amount of energy travelling from the Ti6Al4V side (where the laser is focused) is enough to reach the NiTi and promote its melting. This way both base materials would be melted and they would bond with the solid Nb interlayer avoiding the mixing of both liquid materials and preventing the formation of the aforementioned brittle intermetallics. Joining was obtained with this set up and optical microscopy revealed a crack free welded joint.

A detailed microstructural analysis performed using TEM (transmission electron microscopy) was performed in order to analyze both interfaces: Ti6Al4V/Nb and NiTi/Nb.

In the Ti6Al4V/Nb interface it was observed that layer with about 30 nm was formed along, and between, the external grain boundaries of the Nb interface. This Ti-based layer has the same amount of Al and V of the base material. The difference is that some of the Ti is substituted by Nb which has migrated during the melting of the Ti base material. Energy-dispersive X-ray spectroscopy (EDS) performed on this layer revealed a composition of 59.88Ti-29.90Nb-6.43Al-3.87V (at. %). Diffusion of Nb to the Ti6Al4V melted region can be observed in a extension of about 250 nm.

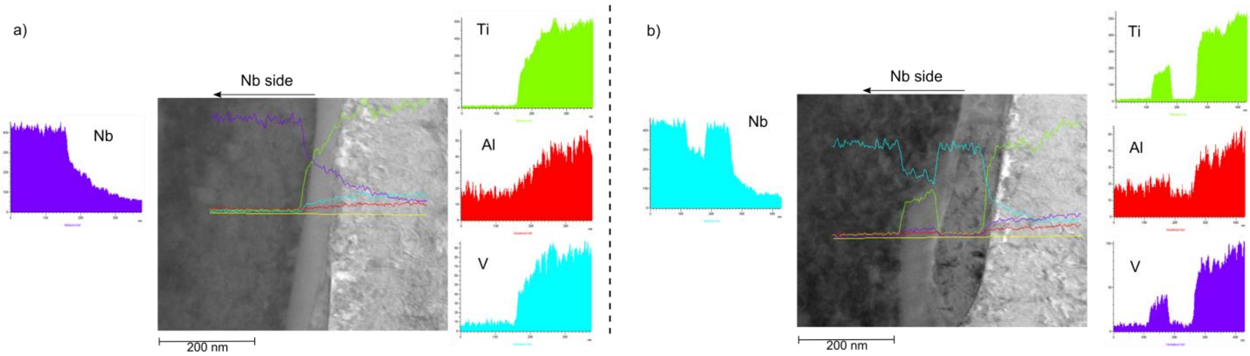

Figure 1 – TEM analysis and EDS measurements in the Ti6Al4V/Nb interface: a) Ti-based layer formed along the Nb interface; b) Ti-based layer formed between the external grains of the Nb interface.

For the NiTi/Nb interface a eutectic microstructure can be observed. In this case the intimate contact formed by the NiTi base material and the Nb interlayer creates a eutectic isotherm, which is 140 ^{o}C below the melting point of NiTi. This leads to a spontaneous melting of NiTi. Upon solidification two phases are expected austenitic NiTi and bcc-Nb. Selected area diffraction performed on the non-melted regions of the NiTi, but close the eutectic structure revealed the parent phase of NiTi – austenite. EDS analysis of selected spots on the eutectic structure revealed that the eutectic arms are Nb rich (above 30 at. %), while between those arms the amount of Nb is below 20 at. %.

Tensile tests were performed on three joints and the ultimate tensile strength was of about 300 MPa with an elongation at rupture of about 2.0 %. This is a significant improve when compared with the literature as the majority of the cases reported always suggest the presence of cracks in the fusion zone, which is known to be detrimental for the joints properties.

The main issue in such type of welding configuration is the position of the interlayer and the laser beam on the material. Now that it is proven that such a solution where a interlayer high very high melting point is used to avoid the mixing of the melted liquid of both base materials is effective to ensure a crack free weld precision system can be develop in order to optimize the welds properties and the reliability of the welding procedure.

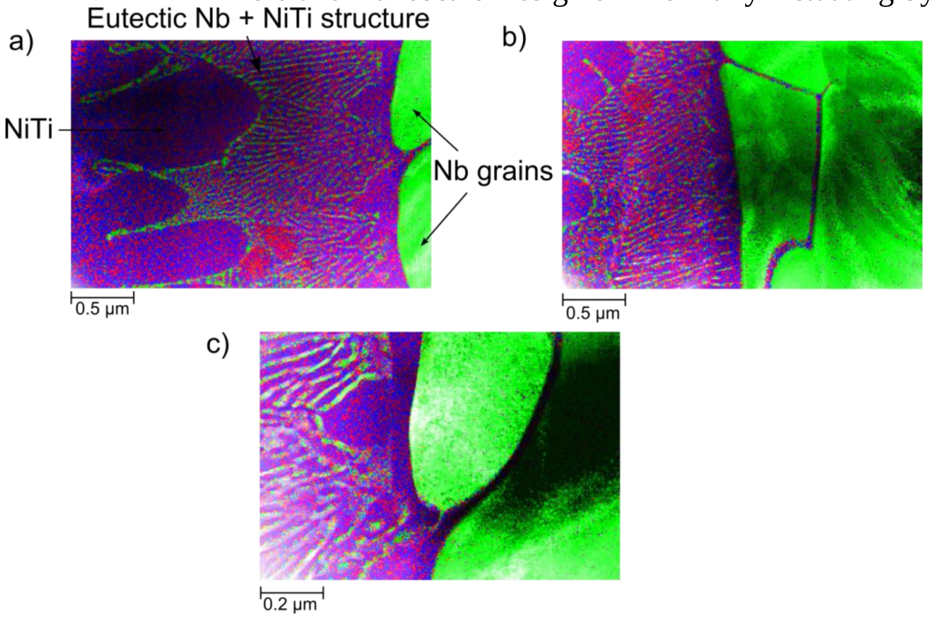

Figure 2 – EDS mapping of NiTi and Nb in the interface NiTi/Nb of the welded region.

1.1.2 - Overlap configuration

In the overlap configuration all four interlayers where used. The influence of the peak power on the penetration depth of the fusion zone was analyzed. All samples presented cracks in the fusion zone. The precipitates formed upon solidification and that are the precursors of the observed cracks are to be determined in the near future, by means of optical microscopy and x-ray diffraction.

1.2 - Welding of NiTi to Stainless Steel 316L using interlayers

In the NiTi/Stainless steel 316L case overlapped joints were produced but when observed with optical microscopy cracks were observed with every time of interlayer chosen. The butt joint configuration was also tried using again Cu and Nb interlayer but no joining was achieved. The origin precipitates formed in the fusion zone are to be determined as well.

2 - Laser welding of a Cu-Al-Mn shape memory alloy

Laser welding of Cu-Al-Mn shape memory wire, with possible use in seismic applications, was also performed. Crack-free welds were obtained.

Tensile tests revealed a very similar behavior between the welded specimens and the base material. The average ultimate tensile strength (UTS) and elongation at fracture for the base material were of 292 ± 46 MPa and 9.885 ± 0.425% while for the welded specimens they were 266 ± 17 MPa and 10.220 ± 1.564. This means that the welded specimens have, in average, 91.1% of the UTS value of the base material and 103.4% of the elongation at fracture. Fracture of the welded specimens always occurred in the base material far away from any influence of the welding. Scanning electron microscopy (SEM) revealed a fracture surface with a ductile character.

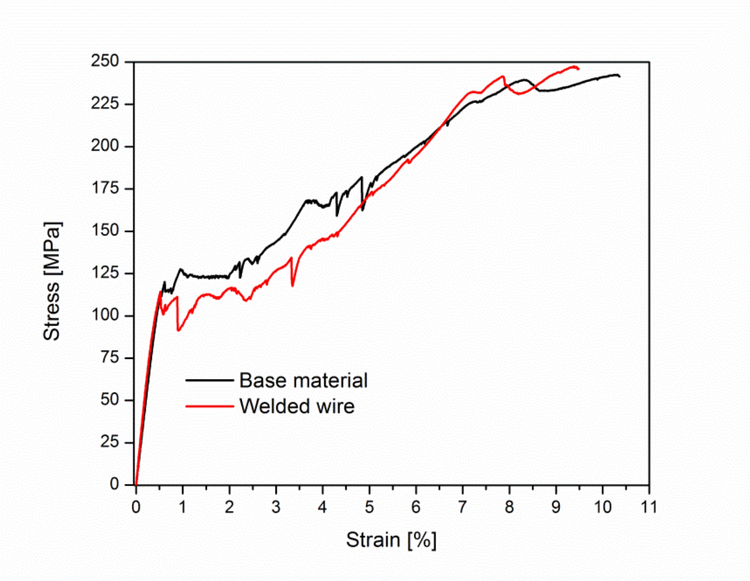

Figure 3 – Stress-strain curves for the base material and welded specimen.

The most significant differences observed between the welded specimen and the base material is the evolution of the accumulated strain and the absorbed energy with number of successful mechanical cycles (load up to 5% strain and unload up to 0 N, in a total of 10 cycles). A stabilized hysteretic response of the welded joint is attained with a very low number of cycles, which is important for structural applications, such as in seismic devices.

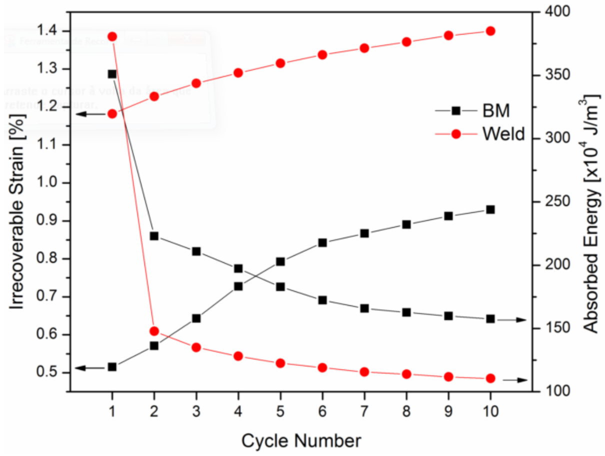

Figure 4 – Evolution of the accumulated irrecoverable strain and absorbed energy with the number of cycles for the base material and for the welded specimen.

EDS and hardness measurements performed to compare the differences between the base material and fusion zone revealed no significant differences in both measurements.

Good weldability of this alloy may, evidenced by the results presented, open new possibilities for the use of such alloy for applications where joining with another engineering materials may be required.

PIRSES-GA-2013-612585 - MIDAS

Micro and Nanoscale Design of Thermally Actuating Systems

MIDAS researcher: João Pedro Oliveira Oliveira (PhD student; supervisors: F.M. Braz Fernandes and Rosa Miranda, FCT/UNL)

Period	Location of stay	People involved	Tasks
12/11/2015 to 15/12/2015	Universidade Federal Fluminense	Andersan dos Santos Paula (UFF) Ladário da Silva (UFF) F.M. Braz Fernandes (CENIMAT) Rosa Miranda (UNIDEMI)	Microstructural characterization and ultra-micro hardness testing

During stay at the Universidade Federal Fluminense microstructural characterization of laser welding NiTi shape memory alloys was performed using an ultra-micro hardness tester. It is clear that a microstructural gradient exists in the welded joint as a consequence of the laser interaction with the material.

The most significant observation is that the fusion zone present a lower hardness (correspondent to blue colours in the Figure below) than in the heat affected zone and base material (correspondent to the yellow/green colours). This change in hardness is due to the formation of martensite in the thermal affected regions, being this effect more notorious in the fusion zone as more martensite is formed in this region.

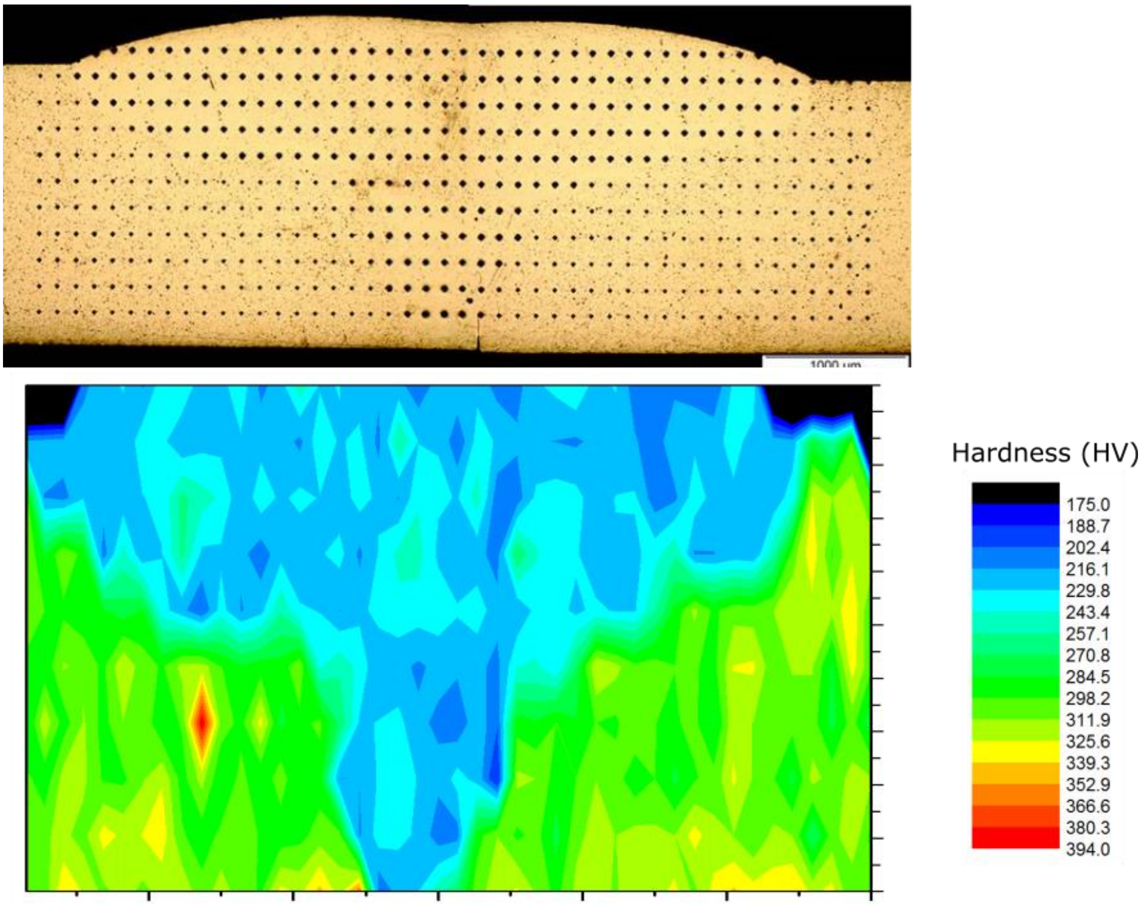

Figure 5 – Indentations made on a laser welded NiTi sample (top) and corresponding hardness map (bottom).

The effect of different laser welding parameters on the hardness in different locations of the welded joints is currently under study.

WP5 (AD) Applicative design

Coordinating unit: UPT, Prof. Corneliu M. CRACIUNESCU
Partners: RAS, LNEG, FCT, UFF

MIDAS researcher: Corneliu Craciunescu (UPT, Rmania). Stay funded by ERASMUS Grant.

Period	Location of stay	People involved	Tasks
21/04/2014 to 02/05/2014	CENIMAT	Corneliu Craciunescu (UPT) F.M. Braz Fernandes (CENIMAT)	Discussions about WP5 and WP2

During stay at the CENIMAT, discussions about the work performed by Corneliu Craciunescu on "Materials Innovation by Combinatorial Exploration" has been made and a seminar (29/04/2014) has been presented to the students and researchers.
Also discussions on work on severe plastic deformation (ECAP) and complimentary tests on running work has been made.

PIRSES-GA-2013-612585 - MIDAS

Micro and Nanoscale Design of Thermally Actuating Systems

Papers published

Work resulting from WP2

“Fracture modes during severe plastic deformation of NiTi shape memory alloys”. C.M. Craciunescu, R.J.C. Silva, F.M. Braz Fernandes. *Fizika Metalliv i Metallovedenie (Physics of Metals and Metallography)* 116:7 (2015) pp. 698-705 (DOI: 10.1134/S0031918X15070030). IF:0.672; IF5Y: -

Work resulting from WP5

“Shape memory effect of laser welded NiTi”. J.P. Oliveira, F.M. Braz Fernandes, N. Schell, R.M. Miranda. *Functional Materials Letters*, 18-6 (2015) 1550069. (DOI: 10.1142/S1793604715500691). IF:1.606; IF5Y: 1.47

“High Strain and Long Duration Cycling Behavior of Laser Welded NiTi Sheets”. J.P. Oliveira, R.M. Miranda, N. Schell, F.M. Braz Fernandes. International Journal of Fatigue 83 (2016) 195–200. IF: 2.275; IF5Y: 1.974

“Laser welded superelastic Cu–Al–Mn shape memory alloy wires”. J.P. Oliveira, B. Panton, Z. Zeng, T. Omori, Y. Zhou, R.M. Miranda, F.M. Braz Fernandes. *Materials and Design* 90 (2016) pp. 122–128. (DOI: 10.1016/j.matdes.2015.10.1250264-1275). IF: 3.501; IF5Y: 3.626

“Laser joining of NiTi to Ti6Al4V using a Niobium interlayer”. J.P. Oliveira, B. Panton, Z. Zeng, C.M. Andrei, Y. Zhou, R.M. Miranda, F.M. Braz Fernandes. *Acta Materialia* 105 (2016) pp. 9-15. (DOI: 10.1016/j.actamat.2015.12.021). IF: 4.465; IF5Y: 4.87

“Tungsten inert gas (TIG) welding of Ni-rich NiTi plates: functional behaviour”. J.P. Oliveira, D. Barbosa, F.M. Braz Fernandes, R.M. Miranda. *Smart Materials and Structures* 25 (2016) 03LT01 (7pgs). (10.1088/0964-1726/25/3/03LT01). IF :2.502; IF5Y: 2.74

“Martensite Stabilization During Superelastic Cycling of Laser Welded NiTi Plates”, J. P. Oliveira, F. M. Braz Fernandes, N. Schell, R. M. Miranda, Materials Letters (accepted for publication) DOI: 10.1016/j.matlet.2016.02.107. IF:2.489; IF5Y: 2.466

“On the Mechanisms for Martensite Formation in YAG Laser Welded Austenitic NiTi”, J. P. Oliveira, F. M. Braz Fernandes, R. M. Miranda, N. Scheel, (accepted for publication in Shape Memory and Superelasticity) DOI: 10.1007/s40830-016-0058-z

“Dissimilar laser welding of NiTi shape memory alloy and copper, Smart Materials and Structures”, Z. Zeng, B. Panton, J. P. Oliveira, A. Han, Y. Zhou, vol 24, 125036, 2015. DOI: 10.1088/0964-1726/24/12/125036. IF: 2.502

R. M. Miranda, E. Assunção, R. J. C. Silva, J. P. Oliveira, L. Quintino, Fiber laser welding of NiTi to Ti-6Al-4V, The International Journal of Advanced Manufacturing Technology, vol. 81, 1533-1538, 2015. DOI: 10.1007/s00170-015-7307-8. IF: 1.458

PIRSES-GA-2013-612585 - MIDAS

Micro and Nanoscale Design of Thermally Actuating Systems

Jornadas Materiais Estruturais - 2016
Anfiteatro CENIMAT
23/02/2016

14h20: Apresentação geral do grupo de investigação de Materiais Estruturais
F.M. Braz Fernandes

14h30: Structural, Thermal and Optical Characterization of Rare-Earth Doped Phosphate Glasses
R.C.C. Monteiro

15h00-15h30: Intervalo / visita aos posters

15h30: Characterization of the glaze and in-glaze pigments of the 19th century relief tiles from the Pena National Palace, Sintra, Portugal
M.L. Coutinho, J.P. Veiga, L.C. Alves, J. Mirão, L. Dias, A.M. Lima, V. S. Muralha, M. F. Macedo

16h00: NiTi shape memory alloys application for endodontics and orthodontics
F.M. Braz Fernandes, J.P. Oliveira, Joana Cruz, Rafaella Magalhães, Ana Rita Alves, S.V. Correia

16h30: Laser welding of NiTi shape memory alloys
J.P. Oliveira, R.M. Miranda, F.M. Braz Fernandes

17h00 Encerramento

Posters

On the surface silver enrichment on ancient higher silver alloys: an insight of the Portuguese silver coins from the age of the discoveries
R. Borges, R.J.C. Silva, M.F. Araújo, A. Candeias, L. Alves, V. Corrigedor

Tungsten-bearing molybdenite from Borralha
T.P. Silva, M.O. Figueiredo, J.P. Veiga, D. de Oliveira , M.J. Batista, F. Noronha

Steel slag as alternative raw-material for clinker production
M.M.R.A. Lima, J.P.B. Veiga, R.C.C. Monteiro

Natural hydraulic lime based grouts for old masonry consolidation
C. Patrício, M.M.R.A. Lima, P. Faria

Effect of ZnO/B2O3 ratio on the crystal growth in zinc borosilicate glasses
Ana Teresa G. Kullberg, Andreia Alexandra S. Lopes, João Pedro B.Veiga, Regina C. C. Monteiro

Formation and crystallization of zinc borosilicate glasses
A.T.G. Kullberg, A.A.S.Lopes, J.P.B. Veiga, M.M.R.A. Lima, R.C.C. Monteiro

Modelling of transverse segregation in centrifugally-cast functionally graded composites
A. Velhinho, G. Rodrigues, J.P. Mota

In-Situ Thermomechanical Analysis of NiTi Shape Memory Alloys, Using Synchrotron Radiation
J.P. Oliveira, P.F. Rodrigues, A.S. Paula, F.M. Braz Fernandes

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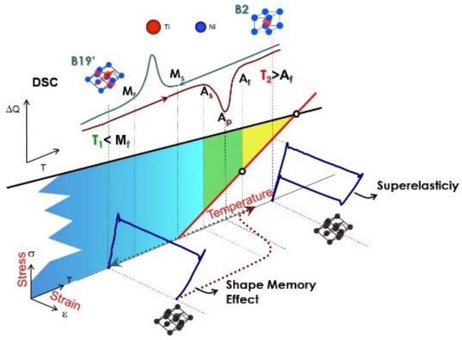
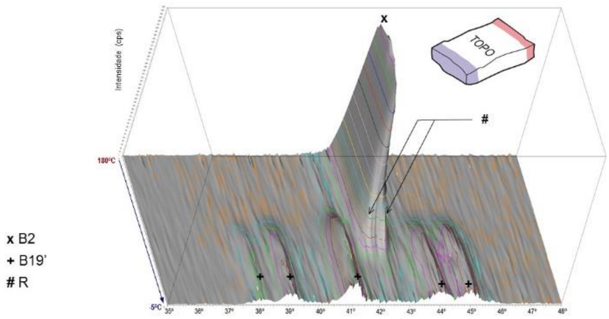
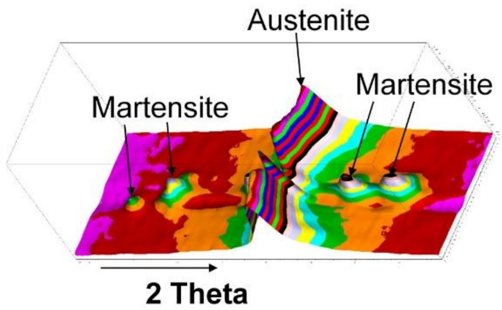
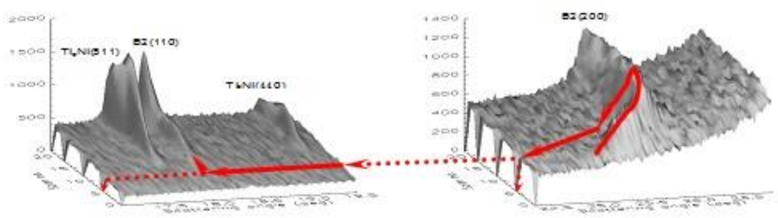
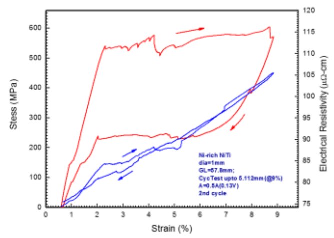


Workshop on Shape Memory Alloys Processing, Properties and Applications CENIMAT, 23/07/2015









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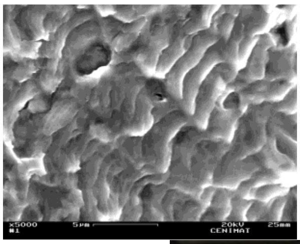
Micro and Nanoscale Design of Thermally Actuating Systems



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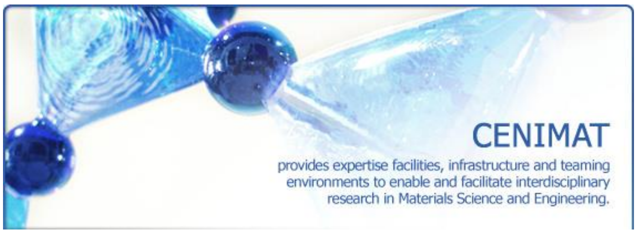

MIDAS

Micro and Nanoscale Design of Thermally Actuating Systems

SEVENTH FRAMEWORK PROGRAMME

PIRSES-GA-2013-612585 - MIDAS

Micro and Nanoscale Design of Thermally Actuating Systems

PROGRAMA

Autor(es)	Instituição	Apresentação	Hora
F.M. Braz Fernandes	CENIMAT	**Abertura. Apresentação do projecto MIDAS**	10h00 - 10h15
F.M. Braz Fernandes	CENIMAT	SMAs at CENIMAT	10h15 - 10h45
Andersan S. Paula	IME / MIDAS	Produção de arames e chapas de NiTi	10h45 - 11h15
Coffee Break / Posters			11h15 - 11h45
Xingke Zhao	USTB / MIDAS	Some Studies in Joining of NiTi alloys	11h45 - 12h15
Raffaella Magalhães	CENIMAT	Aplicação de arames de NiTi em ortodontia	12h15 - 12h45
Almoço Livre			12h45 - 14h00
João Pedro Oliveira Rosa Miranda F.M. Braz Fernandes	CENIMAT UNIDEMI	NiTi laser welding	14h00 - 14h30
André Cavaleiro Ana Sofia Teresa Vieira F.M. Braz Fernandes	CEMUC CENIMAT	Ni/Ti reactive multilayers for joining NiTi shape memory alloys to Ti aloys	14h30 - 15h00
Coffee Break / Posters			15h00 - 15h30
Filipe Neves	LNEG	Processing of Ni-Ti alloys by Powder Metallurgy	15h30 - 16h00
F.M. Braz Fernandes	CENIMAT	Conclusões. Encerramento.	16h00 - 16h15

PIRSES-GA-2013-612585 - MIDAS

Micro and Nanoscale Design of Thermally Actuating Systems

Posters			
Ana Alves João Pedro Oliveira F.M. Braz Fernandes	CENIMAT	Analysis of the effect of heat treatment on endodontic files	**P1**
Fernando Ferreira Telmo Gomes dos Santos João Pedro Oliveira F.M. Braz Fernandes	CENIMAT UNIDEMI	Production and characterization of functionally graded materials from NiTi shape memory alloys	**P2**
Edgar Camacho João Pedro Oliveira F.M. Braz Fernandes	CENIMAT	Aplicação de ligas com memória de forma a processos de união	**P3**
Joana Cruz Rafaella Magalhães F. M. Braz Fernandes	CENIMAT	Comparative Study of NiTi Orthodontic Wires	**P4**
Barbey Harold João Pedro Oliveira Rafaella Magalhães F. M. Braz Fernandes	CENIMAT	The use of NiTi and NiTiCu in orthodontic wires	**P5**
André Cavaleiro Ana Sofia Ramos F. M. Braz Fernandes C. Baehtz Teresa Vieira	CEMUC	NiTi formation from Ni/Ti multilayers: Thermal cycle vs. reaction temperature	**P6**
Rui M.S. Martins N. Barradas E. Alves D. Henke H. Reuther N. Schell M.J. Carmezim T.M. Silva J.C.S. Fernandes	IST CENIMAT HZDR HZG	Ni-Ti surface with depressed nickel concentration prepared by plasma immersion ion implantation	**P7**
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Micro and Nanoscale Design of Thermally Actuating Systems

Hora		
10h00 10h15	Abertura Distribuição documentação / Apresentação MIDAS	
10h15 10h45	Oral1	
10h45 11h15	Oral2	
11h15 11h45	Coffee Break / Posters	
11h45 12h15	Oral3	
12h15 12h45	Oral4	
12h45 14h00	Almoço livre	
14h00 14h30	Oral5	
14h30 15h00	Oral6	
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PIRSES-GA-2013-612585 - MIDAS

Micro and Nanoscale Design of Thermally Actuating Systems

SMAs at CENIMAT

FM Braz Fernandes
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Studies of SMA at CENIMAT have been focussed on processing, characterization and applications, mostly for NiTi alloys.
Thin films of NiTi have been produced by sputtering and their growth has been followed by in-situ XRD. The stacking sequence of the thin films deposited on different substrates has been analysed.
Thermomechanical processing of Ti-rich and Ni-rich NiTi alloys has been analysed using different characterization techniques: DSC, XRD, dilatometry and electrical resistivity. A complimentary study of severe plastic deformation was performed on NiTi and CuAlNi alloys.
Joining by welding, namely laser welding has been investigated in order to identify the changes on functional properties (superelasticity and shape memory effect) associated to structural changes induced by laser.
The electrical resistivity has been used to study the effect of thermal stresses on thin films. Also, on bulk materials, the influence of deformation and structural transformations (thermal and stress assisted) has been investigated. The stress/strain monitoring by electrical resistivity measurement has been analysed for different engineering applications.
Applications of NiTi alloys in dentistry (endodontics and orthodontics) have been studied. The structural characterization of endodontic files with and without heat treatment have been performed by XRD and DSC, including situations simulating the in service bending, in order to understand the fatigue behaviour in rotation / flexion. Orthodontic wires were studied in order to identify the most adequate testing conditions for simulation of the in service loading.

Projeto de pesquisa: produção de arames e chapas de NiTi

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O presente projeto de pesquisa, vinculado às ligas com memória de forma de NiTi, destina-se a definir parâmetros de processamento mais adequados na obtenção de produtos de distintas geometrias (arames e chapas), resultantes processamentos via forjamento rotativo e laminação (a quente e a frio) e tratamentos térmicos entre passes. Com base em ligas elaboradas em escala laboratorial, faz-se numa primeira etapa a avaliação da evolução das propriedades termofísicas e estruturais ao longo das etapas de processamento, com uso de técnicas de análises térmicas como Calorimetria Diferencial de Varredura (DSC) e análise Dilatométrica / Termomecânica (TMA), além da avaliação das propriedades mecânicas por nanoindentação instrumentada e caracterização das propriedades microestruturais e texturais, por meio de Difração de Raios X (DRX) e Difração de Elétrons Retroespalhados (EBSD) no Microscópio Eletrônico de Varredura (SEM), a temperatura ambiente. Em uma etapa mais avançada do projeto, com base em condições texturais/termofísicas mais interessantes, quanto ao efeito de memória de forma e superelasticidade, visa-se proceder a uma avaliação da estabilidade nas transformações por ciclagem térmica (DSC) e observação detalhadas da estrutura por Microscopia Eletrônica de transmissão (TEM).

Some Studies in Joining of NiTi alloys

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NiTi shape memory alloys(SMA) have been widely applied in many fields due to their excellent properties in shape memory effect, super-elasticity, damping, biocompatibility and mechanical properties. However, those properties of SMAs based on thermo-elastic martensitic transformation are very sensitive to their chemical compositions as well as microstructures, which determines NiTi SMAs a poor weldability.
Several methods, covering three types of welding techniques, have been conducted in University of Science and Technology Beijing (USTB) in joining NiTi SMAs for nearly ten years. Ag-28Cu alloy and Zr-based alloy have been used as brazing filler metals, and SnAgCu alloy has been used as soldering filler metals. Laser welding methods including with different filler materials have been studied, transient liquid phase diffusion bonding methods are now our ongoing research.

NiTi laser welding

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This communication aims to discuss the mechanisms for the occurrence of martensite in the heat affected zone and in the fusion zone, at room temperature, in laser welded NiTi shape memory alloys. For this purpose, synchrotron radiation was used together with a simple thermal mathematical model. Two distinct mechanisms are proposed for the presence of martensite in different zones of a weld, which affects the mechanical and functional behaviour of a welded component.
Despite the presence of martensite in significant amounts at room temperature in the fusion zone, superelastic behaviour and the shape memory effect have been identified in laser welds. A multistep shape memory effect was observed in laser welded NiTi sheets. This effect was noticed in the heat affected zone and on the fusion zone of the welds. Despite a similar effect was already reported in laser processed NiTi wires it was never reported for laser welded NiTi shape memory alloys. This discovery may allow new applications for the use of laser welded NiTi joints where this effect can be required, for example, in actuators or sensors.

Structure and morphology of the $Zn_xMg_{1-x}O$ nanowires studied using shape memory composite nano-tweezers

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The nanowires (NWs), nano rods, nano whiskers are an important class of materials with the great potential for applied and fundamental basic research. The cross section of NWs is typically cylindrical, hexagonal, square, or triangular and is uniform with a high aspect ratio. Recently the new technology of 3D-nanomanipulation is proposed based on composite bimetallic structures with shape memory effect (SME). The present paper reports application of the new nanotweezers system for experimental investigation of the individual nanowires of $Zn_xMg_{1-x}O$ which is the example of submicron sized objects whose individual properties are difficult to study by standard methods. We describe the technology of preparation of $Zn_xMg_{1-x}O$ NWs, the process of the selection of individual NWs by composite nanotweezers with SME in vacuum chamber of FIB device and experimental study of their structure and morphology by TEM.

Ni/Ti reactive multilayers for joining NiTi shape memory alloys to Ti aloys

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Reactive nanoscale multilayers can be used to assist the diffusion bonding process of NiTi shape memory alloys, to themselves and to other alloys. This study is focused on the reaction-assisted diffusion bonding (RABD) process of NiTi to Ti-6Al-4V using magnetron sputtered Ni/Ti nanomultilayers as filler materials. For this purpose, experiments were carried out at the High Energy Materials Science beamline (P-07) at German Electron Synchrotron (DESY). The oven with load capabilities at P07 is ideal to assess the structural evolution during the bonding process. Prior to RABD, Ni/Ti multilayer thin films, 2.5 µm thick and with 12 and 25 nm modulation periods, were directly deposited onto the materials being joined. The NiTi and Ti-6Al-4V coated parts were placed with the films facing each other in the oven, heated by induction to the maximum temperature and quenched to room-temperature after a holding period of 30 min. During the thermal cycle a 10 MPa pressure was applied. Post bonding characterization was carried out by field emission scanning electron microscopy.
The use of Ni/Ti multilayer thin films allowed the NiTi/Ti-6Al-4V joining temperature to be decreased; sound joining without pores or cracks was achieved at 600 ºC. Reaction of the Ni/Ti fillers and interdiffusion between base and filler materials occurred promoting joining between the coated parts. The formation of undesired intermetallic phases, such as $NiTi_2$, can be minimised by reducing the bonding temperature.

Processing of Ni-Ti alloys by Powder Metallurgy

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Micro and Nanoscale Design of Thermally Actuating Systems

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Powder Metallurgy (PM)is a process that can be defined as the fabrication of metal pieces involving mixing and compaction of metal powders (elemental or alloy powders), followed by a densification heat treatment. PM makes it possible to produce a virtually nonporous piece having properties almost equivalent to the fully dense parent material. Diffusional processes during the heat treatment are central to the development of these properties. The high precision forming capability of PM offers the ability to produce a variety of component shapes (near net shape components) with complex features and good dimensional precision minimizing subsequent machining operations. Throughout the last two decades, PM processing routes have gained considerable interest for NiTi fabrication: can avoid problems associated with casting; enables an exact control of the chemical composition; offers the ability to produce a variety of component shapes minimizing subsequent machining operations. However, special attention has to be given to the amount of impurities (especially oxygen and carbon) that are almost unavoidable during PM and casting processing of Ni-Ti alloys. Several conventional PM methods including self-propagating high-temperature synthesis (SHS), reactive sintering, hot isostatic pressure (HIP), hot extrusion and field-activated pressure assisted synthesis have been used for the fabrication of NiTi alloys. In comparison with conventional PM routes, the introduction of a mechanical alloying step offers new possibility in obtaining micro and nanostructured powders with metastable structure that affect the consolidation process. This presentation will cover the research work that has been carried out in LNEG (/INETI) related with the processing of Ni-Ti alloys by powder metallurgy.

Aplicação de arames de NiTi em ortodontia

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A Ortodontia é a área da Medicina Dentária que visa a correcção das más posições dentárias e deformidades dento-faciais através da utilização de fios acoplados a peças coladas aos dentes. Inicialmente, os fios ortodônticos eram feitos em ouro, em seguida em aço inoxidável, e a partir de 1970, observa-se crescente utilização das ligas de níquel titânio, devido a suas propriedades de memória de forma e superelasticidade. A apresentação visa mostrar o uso clínico de fios de níquel titânio, especialmente em relação às espessuras do fio utilizadas, geometria e variedade na fabricação dos fios.

Analysis of the effect of heat treatment on endodontic files

Ana Rita Alves, João Pedro Oliveira, FM Braz Fernandes
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Nickel-titanium (NiTi) endodontic files are used for over two decades, replacing stainless steel ones, as they shows greater capacity to bending and torsion associated with a greater recovery of deformation. The superelastic properties of NiTi are very important and become interesting taking into account the objective of this component. Until this day, NiTi endodontic files have been subject of studies in order to improve the performance of these medical devices. The main problem of using these alloys as endodontic instruments, relates to the fact that they present a high risk of fracture. The fracture may occurs due to repeated cycles of rotation with bending and twisting forces (due to the curvature of the tooth canal. The first case occurs on average, about 44% of the time and the second case 56%.
It is important to note that the existing NiTi endodontic files, have several distinct characteristics, such as composition, design and manufacture. In the manufacturing process of the files, these are subjected to thermomechanical treatments, which determine the phase transformation temperatures and characteristics of the component. All these characteristics affect the mechanical properties and hence the behavior of the component. The objective of this study is to obtain a better performance of these components (at mechanical level) by heat treatments in order to modify the transformation temperatures.
In this work, the influence of the heat treatments in three different files (MTwo, K3 and K3XF) has been studied, determining the transformation temperatures of the different phases by thermal analysis using Differential Scanning Calorimetry. The main objective is obtaining the end of austenitic transformation temperatures (during the martensite → austenite transformation) below the oral temperature (about 37ºC). A recent study analyzed the files as-received, with heat treatment of 350ºC/1hr and 400ºC/1hr, yielding results that show some differences comparing to the literature. Furthermore, these results also show that for these treatments the end of austenitic transformation temperatures is higher than 37ºC, which is not adequate for clinical use. These are the main reasons for the continuation of this study and the choice of the temperatures of the treatments in the range of 250 and 300ºC.
In addition to the thermal characterization, a second part of the work aims at the mechanical characterization of these files, to prove the influence of these treatments on their performance and their lifetime. This characterization will be performed with devices that simulate the file work situation, one with the file in torque and the other in rotation/bending.

Production and characterization of functionally graded materials from NiTi shape memory alloys

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The present work aims for the production of controlled functionally graded NiTi through structural changes, taking advantage of its high sensitivity to thermal treatments. For a controlled functional gradient, thermal treatments are made on small segments in Ni-rich NiTi, through the controlled injection of current.

The limitations that are intended to overtake with this work are the low temperature range of thermally induced martensitic transformation and the Lüders-type deformation behavior that NiTi alloys exhibit during stress induced transformation. Thus, when a threshold value of stress or temperature is reached, these alloys perform a full transformation, rendering difficult a progressive control of displacement. Despite some authors try to overtake this problem, they use limited systems with rather difficult functional gradient control: some use furnaces with a temperature gradient; others use geometrically graded NiTi; and others use some expensive and limited laser surface anneal methods.

The suggested method, based in results of non-conventional heat treatments in NiTi using electrical current, intend to be capable of perform heat treatments on selected regions of the material, allowing to control the transformation temperatures along those different regions as desired. Moreover, it was pretended to create a method that could be easily upscaled to the industrial level reducing the production time and cost of these materials.

The experimental apparatus for the heat treatments consists in 12V battery in series with an electrical resistance to decrease the current and a MOSFET that works as an ON/OFF switch. Besides, there are elements in the circuit for control and monitoring the current, voltage and temperature, being all parameters controlled and modulated in a LabVIEW environment. This way, an automatic system has been created, capable to modulate the gate voltage of the MOSFET based on the temperature measured by the thermocouples, allowing to control the current through NiTi strips and hence their temperature.

Prior to heat treatments with electrical current, were performed solution treatments, cold work and crystallization in order to determine which of these could create a greater gradient. The transformation temperatures were obtained from differential scanning calorimetry (DSC).

Comparative Study of NiTi Orthodontic Wires

Barbey Harold, João Pedro Oliveira, Rafaella Magalhães, FM Braz Fernandes

In this study, superelastic NiTi and NiTiCu orthodontic wires (0.46 x 0.64 mm^2) were analyzed. The determination of phase transformation temperatures along with the identification of the predominant phase at room and intraoral temperatures were accomplished by DSC analysis. Structural characterization was performed through XRD in situ analysis from -150 to +100ºC in ordef to identify the transformation sequences. Superelastic behavior was analyzed through tensile tests.

Ni-Ti surface with depressed nickel concentration prepared by plasma immersion ion implantation

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Ni-Ti is commonly used in biomedical applications. The shape memory effect and superelasticity of Ni-Ti assure the recovery of the original shape even after large deformations and the maintenance of a constant applied force in correspondence to significant displacements. However, the wide spectrum of applications in implantology imposes special requirements on the biocompatibility of Ni-Ti.

The alloy ($\approx$ 50.4 at.% Ni) selected for this study is austenitic (superelastic) at body temperature. In the frame of the AIM-74 and SPIRIT-77 projects, plasma immersion ion implantation (PIII) has been employed to modify and improve the superficial region of the alloy. The formation of titanium oxynitride (TiN_xO_y) was achieved by ion implantation of nitrogen. A Ti-rich oxide layer was obtained during the experiments carried out with oxygen. Thus, the parameters to obtain a Ni-depleted surface, which serves as a barrier to out-diffusion of Ni ions from the bulk material, have been successfully established. The high value of film resistance (measured by electrochemical impedance spectroscopy) suggests a very good corrosion resistance, which can be associated with the low Ni concentration at the surface of film. Furthermore, nanostructured Ni-Ti surfaces have been produced.

Synchrotron radiation-based X-ray diffraction data acquired in transmission mode show that the PIII technique only changes the structure of the Ni-Ti alloy top layer preserving superelastic behaviour at body temperature (PIII experiments carried out without intentional heating of the substrate holder). Techniques like thermal oxidation and nitriding also lead to an improved corrosion resistance and Ni-depleted Ni-Ti surface but require high processing temperatures leading to modification of the phase transformation characteristics and loss of specific mechanical properties.

Comparative Study of NiTi Orthodontic Wires

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In this study, superelastic NiTi and NiTiCu orthodontic wires (0.46 x 0.64 mm^2) were analyzed. The determination of phase transformation temperatures along with the identification of the predominant phase at room and intraoral temperatures were accomplished by DSC analysis. Superelastic behavior was analyzed through tensile tests. 3-point bending tests were performed on a model design which included brackets to compare wires' behavior. Wire slippage inside the brackets and friction caused by wire-bracket-ligature combinations on bending and pulling tests, respectively, are also discussed.

Strain monitoring with NiTi SMA: principles and applications

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Ni-Ti alloys are employed in several complementing fields such as biomedical, space, civil, robotics, and sensor-actuator devices. The most important Ni-Ti characteristic is the double sensor/actuator property, useful in a number of applications. Excellent biocompatibility and resistance to corrosion makes the Ni-Ti alloy one of the most interesting among shape memory alloys (SMAs). The martensitic transformation in NiTi follows either a single stage A-M or a two stage A-R-M (A = austenite, B2 structure; R = R-phase, rhombohedral structure; M = martensite, B19' structure), depending on the thermal and/or mechanical treatment given. For SMA applications, it is very important to characterize the different phases of NiTi on thermal cycling under constant stress or with load cycling. Electrical Resistivity (ER) measurement has proven to be a good probe for the identification of various phases in SMA. The ER variation shows the following characteristics: [24, 25] - ER of all phases (austenite, R-phase and martensite) increases linearly with increasing temperature but the slopes are quite different. - R-phase shows generally higher ER than austenite phase and its value further increases with decreasing temperature. This has been associated with the continuous increase of rhombohedral distortion angle of the R-phase with decreasing temperature. A linear relationship is observed between ER and strain. The characteristic slope is slightly dependent on the applied stress and on the number of thermal cycles. This result is extremely important in terms of implementation of SMA materials in actuators, sensors, and other devices that depend upon accurate understanding of the stress-temperature transformation space.

Applications of strain monitoring are possible using the signal of electrical resistivity: movement control in robotics, structural-health monitoring of buildings, load control of structures subject to the action of wind and/or waves.

Aplicação de ligas com memória de forma a processos de união

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O efeito de memória de forma pode ser interessantemente utilizado para realizar processos de união de componentes diversos. Com efeito, a primeira aplicação industrial das ligas Ni-Ti foi a de uma manga de união de tubagens do circuito hidráulico do avião de combate F-14 da Marinha de Guerra americana. Depois disso, tem sido frequentemente referenciada na literatura a possibilidade de utilização do efeito de memória de forma para a realização de uniões por rebites. Embora conceptualmente interessante, o certo é que não existem indicações de uso industrial alargado deste tipo de união. Uma patente recente (2013) no domínio da aeronáutica abre perspectivas interessantes para este tipo de processos de união, combinando a acção do efeito de memória de forma, o encruamento tanto do material de união como das superfícies do material a unir e, por último, a histerese térmica de transformação.

Neste trabalho são apresentados resultados, que incluem caracterização mecânica e termo-mecânica, que permitem testar a eficácia de funcionamento deste processo de união.

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Micro and Nanoscale Design of Thermally Actuating Systems

Aging treatment of forged wires of NiTi (Ni-rich) alloy for superelastic applications.

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NiTi alloys with memory shape effect, superelasticity properties and further specific characteristic can only be developed under a process with a rigorous control on the production process during the steps of fusion, refine, thermal and mechanical treatments (1). Among the factors that can affect the material's structure and its memory shape behavior or superelasticity at a given work condition, few can be highlighted namely: thermal and thermomechanical treatments; Ni and Ti content; incorporation of alloying elements; presence of impurities (Carbon and Oxygen) and phase transformations. Therefore, it is mandatory to control the chemical composition and thermomechanical treatment's conditions (2,3).

The present study aims to understand the influence of aging treatment to obtain an austenitic structure at room temperature, into a wire of a NiTi alloy rich in Ni, produced by rotary forging. Also to evaluate the phase transformation temperature behavior and mechanical behavior to facilitate the superelastic behavior at room temperature.

The material studied in the present work is a Ni-rich NiTi alloy produced by the vacuum induction melting process (VIM) in a vacuum furnace. An ingot called VIM74 with approximately 49.2%at of Ti and 50.8%at of Ni was the purpose of this study. The hole material was subdivided into smaller samples, of approximately 90 g each, by through-cut electro-discharge to be recasted in the arc melting furnace. After the recast process, the samples passed through a rotary forging thermomechanical process, which started with hot forging followed by cold forging in the final sequences with interspersed stages of heat treatment.

Thermophysical and mechanical properties of the alloy studied were assessed by differential scanning calorimetry (DSC), conventional hardness and ultramicrohardness, under different thermal solubilization processing conditions of 950°C for 120 minutes and three different conditions of aging (350ºC, 400ºC and 450ºC for 30 minutes).