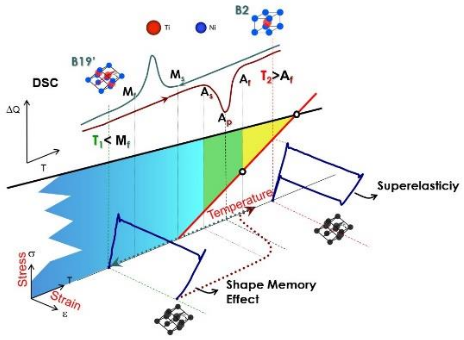
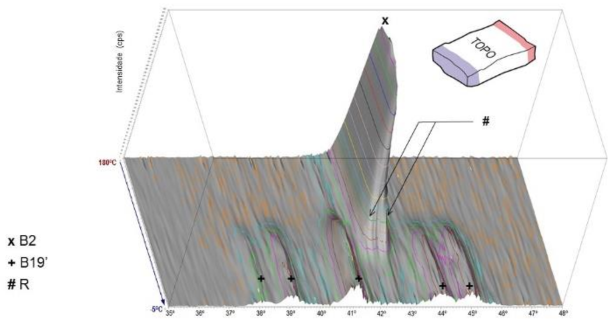
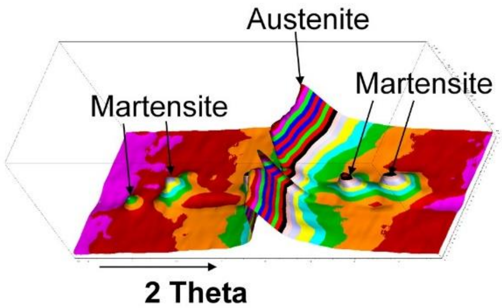
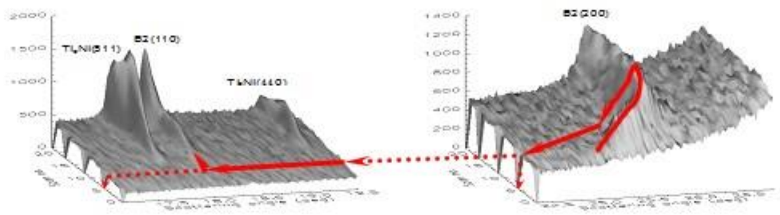
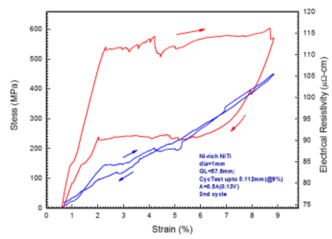


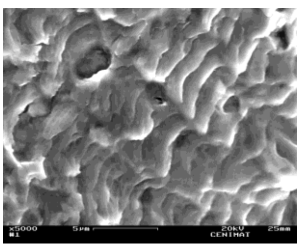
Workshop on Shape Memory Alloys
Processing, Properties and Applications
CENIMAT, 23/07/2015

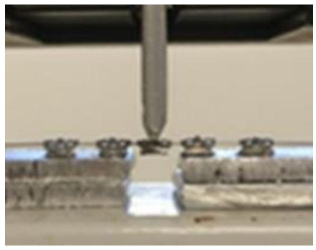












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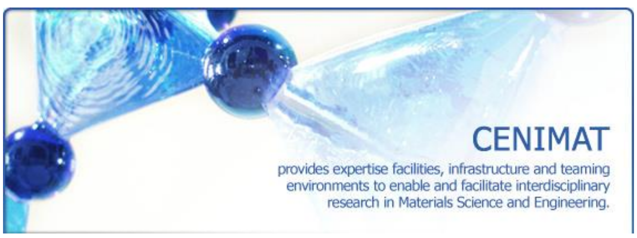
MIDAS
Micro and Nanoscale Design of Thermally Actuating Systems



SEVENTH FRAMEWORK
PROGRAMME

Abstracts

SMAs at CENIMAT

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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.

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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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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Spa da boca - Clínica Médica Dentária

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

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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

Fernando Ferreira, Telmo Gomes dos Santos, João Pedro Oliveira, FM Braz Fernandes
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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).

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.

Structural and mechanical characterization of orthodontic wires

Joana Cruz, Barbey Harold, Rafaella Magalhães, João Pedro Oliveira, FM Braz Fernandes
CENIMAT/I3N, Department of Materials Science, FCT, UNL

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.

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 (≈ 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.

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.

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).

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.