# Surface effects in pulsed laser beam irradiated shape memory alloys

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The goal of the work is to comparatively assess the effect of laser irradiation on the surface of shape memory alloys for several less common alloy families. The effect of pulsed laser impingement on the composition of NiTi shape memory alloys is analyzed for different compositions and manufacturing paths, with the aim to locally reduce the Ni content and/or to use the laser as a precise selective tool to generate structural reinforcements in a partially sintered shape memory alloy prepared by mechanical alloying. For a Ni-Ti-Hf alloy, the superficial layer formed as a result of the surface re-melting shows major Ni loss. Fe-Mn-Si-Cr shape memory alloys revealed major oxidations that are drastically affecting the properties as a result of interaction with the laser beam, while for the Co-Ni-Ga alloys only minor compositional changes have been detected.

## 1. Introduction

Surface properties are essential for materials to be used in biological or aggressive environments and several surface treatment have been used to improve these properties, among which the surface enrichment or depletion in an element or component, deposition of layers and coatings, generation of particular stresses in the surface by mechanical interactions or surface re-melting using various techniques. Laser melting provides a set of features that can favour the rapid heating of the surface, the easy tuning of the intensity of heating via the pulse duration, power and energy, as well as for rapid cooling or processing by heating in particular environments [1-5]. Ti-based alloys are especially targeted for improvement of the surface properties by melting HVOF coatings [6] assisted nitriding [7] or the analysis of the defects generated in the process [8]. Thus, harder nanocrystalline layers improved biocompatibility, corrosion and/or wear can be obtained by appropriately selecting the laser parameters and the environment for the laser beam-Ti alloy interaction.

Shape memory alloys are materials with special properties, for which the composition plays a key role in the multifunctionality. For such materials, the possibility to modify the composition, structure and properties of only a thin surface layer while keeping unchanged the bulk features appears very attractive especially for the alloys belonging to the Ni-Ti family, for which the Ni content still raises biocompatibility questions. Recent studies showed the effect of laser on Ni-Ti shape memory alloys, inducing a localized austenite to martensite phase conversion within a processing region [9, 10] as well as the enhancement of thermomechanical functionality of hybrid NiTi–NiTiCu shape memory alloy [11]. Although NiTi alloys are the most important shape memory materials other compositions are also interesting to be studied. On the other hand the laser beam can be used to generate controlled structures in partially sintered materials, since it can provide localized melting that can be used to generate complex controlled structures by adapted manufacturing techniques [12].

This work shows results on laser interaction with several less usual shape memory alloys, as well as the effect of localized laser melting on a pre-sintered shape memory alloy. Since surface melting appears to be an interesting solution to control the structural and compositional features of shape memory alloys in view of the possible enhancement of the functionality (e.g. biocompatibility, surface hardening or corrosion protection) as well as for developing new manufacturing techniques for shape memory alloys based on selective laser melting.

## 2. Experimental details

The interaction of the pulsed laser beam has been explored for several shape memory alloys, belonging to the following families: biocompatible NiTi-based alloys manufactured by conventional casting and by powder metallurgy, Fe-based alloys and ferromagnetic Co-Ni-Ga alloys, respectively. A GSI JK300 HP Nd:YAG pulsed

wave laser was used for the surface melting experiments that were made in shielding atmosphere consisting of a 15 l/min flow of a mixture of Argon with 5% Hydrogen and

the spot parameters detailed in Table 1. The beam profile was set using a Spiricon Laser Beam Analyzer, Model LBA-FW-SCOR [13].

*Table 1. Laser spot parameters*

| Beam diameter | . Pulse energy | Peak power | Spot. frequency | Pulse width range | Power density |
|---|---|---|---|---|---|
| (mm) | (J) | (W) | (Hz) | (ms) | (MW/cm$^2$) |
| 0.9 | 10.5 | 700 | 1 | 15 | 0.11 |

A Scanning Electron Microscope (SEM) Zeiss DSM 962 has been used to analyze the compositional changes with an Oxford Instruments model INCAx-sight energy dispersive spectrometer (EDS) and the semi-quantification microanalysis was made using ZAF correction procedure.

The composition of the alloys and several properties of the elements composing the alloys are given in Table 2. Except alloy no. 2, all other alloys have been manufactured by arc melting.

*Table 2 Summary of materials and component properties used in the laser glazing experiments*

| | Ni | Ti | Hf | Fe | Co | Ga | Mn | Cr | Si |
|---|---|---|---|---|---|---|---|---|---|
| Alloy 1, at % | 50 | 30 | 20 | - | - | - | - | - | - |
| Alloy 2, at % | Pre-sintered out of Ni and Ti powders (50:50 at%) | | | | | | | | |
| Alloy 3, at % | - | - | - | 55 | - | - | 25.10 | 5.10 | 14.8 |
| Alloy 4, at % | 23.5 | -- | - | - | 46.5 | 30 | - | - | - |
| Atomic Weight | 58.693 | 47.867 | 178.49 | 55.845 | 58.933 | 69.723 | 54.938 | 51.996 | 28.085 |
| Melting Point, °C | 1455 | 1668 | 2233 | 1538 | 1495 | 29.76 | 1250 | 1907 | 1414 |
| Boiling Point, °C | 2913 | 3287 | 4603 | 2861 | 2927 | 2204 | 2060 | 2670 | 3265 |
| Density, g/cm$^3$ | 8.912 | 4.5 | 13.3 | 7.874 | 8.86 | 5.91 | 7.43 | 7.19 | 2.33 |

The elements composing the alloys and the particular structural features play a role in the surface effects of the pulsed laser melting, with the particularities related to each alloy. In particular, the low Ga melting temperature and the high atomic weight of Hf are expected to have an influence on laser interaction with the surface and the resulting properties.

## 3. Results and discussions

Nd:YAG pulsed laser beam irradiation, in the range of the power densities used in the current experiments, induce very sharp thermal cycles with rapid solidification rates leading to - in some metallic systems - amorphous metallic structures. In alloys where individual components have very distinctive melting and vaporization temperatures, selective depletion of elements that results may be used for specific manufacturing and functionality-enhancement purposes.

On the other hand, shape memory alloy can be manufactured out of elements with various properties and in different compositions as well as by using different manufacturing techniques; therefore the analysis of laser

irradiation effects on different compositions as well as manufacturing paths detailed below provides useful information for both material and manufacturing processes point of view.

### a) Ni-Ti based shape memory alloys *(alloys 1 and 2)*

Ni-Ti-Hf are known as a solution for high temperature shape memory alloys [14], although they are also considered for their stability when thermally cycled and are less affected by aging, compared to Ni-Ti alloys. Low Hf content alloys, below 5at%, do not show a major influence on increasing the transformation temperatures, while the high transformation temperatures are obtained for Hf content in the range of 20%.

The experiments on laser beam interaction with a Ni-rich Ni-Ti-Hf shape memory alloy - exemplified in fig. 1 - show a significant depletion of Ni and an increase in the Hf content. HfO$_2$ also appears to form in a range where the Ti depletion has been detected as well (fig.1).
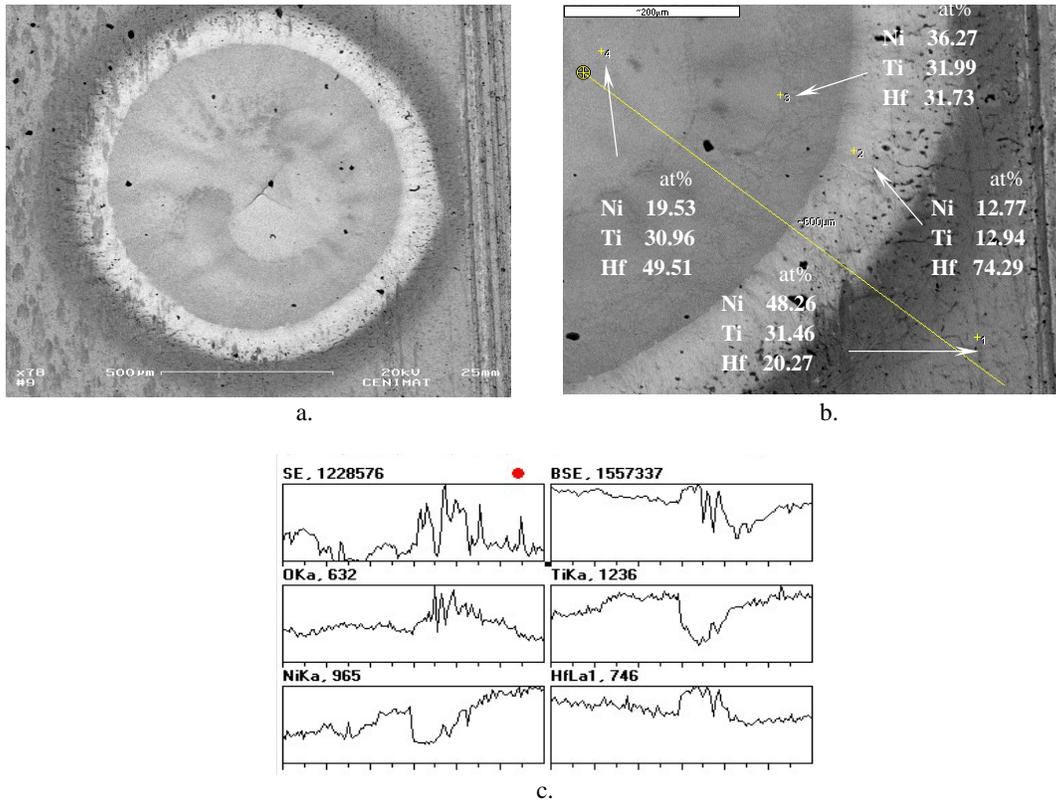
*Fig.1 Surface SEM observation of the pulsed laser spot details and composition; a) Spot BSE image; b) Compositional details c) Compositional gradient for Ni, Ti, Hf and $O_2$, along the line in b.*

This way to locally increase the hafnium content of the surface in NiTi-based shape memory alloy on the expense of Ni content is beneficial for various applications, since Hf is also leading to good biocompatibility and osteoconductivity [15] and provides large neutron capture properties. The excellent properties of Hf – used to increase the creep and tensile strength at high temperature is also beneficial in providing surface protection against oxidation in high temperature environments. The Ni loss has been reported for Ni-Ti alloys as a result of laser melting by Blanco-Pinzon et al. [16] who considered the vaporization of nickel as a major factor.
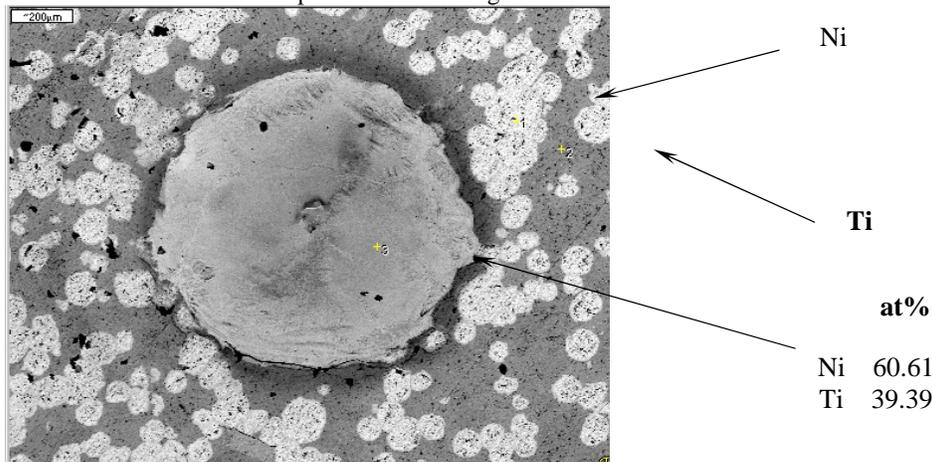


*Fig.2. Effect of pulsed laser on the formation of the spot alloy in NiTi pre-sintered alloy*

The powder metallurgy route for fabrication of Ni-Ti shape memory alloys is used to manufacture graded materials and with controlled porosity, however, the sintering process is difficult to control, leading to the

formation of intermetallic compound that affect the phase transformation. The results of laser beam interaction with a mixture of Ni and Ti pre-sintered powder is presented in Fig. 2.

The experimental result reveals that it is possible to use the laser beam to generate superficial layers embedded in the matrix, starting from pre-sintered elemental powders, by alloying the local melting of the components. This is a step to generate shape memory alloy structures by adequately selecting the laser beam parameters to reach the desired composition.

### b) Fe-Mn-Si-Cr shape memory alloys (alloy 3)

The improvement of Fe based alloy (in particular steels) properties by laser and have been laser surface

hardening, laser surface alloying and cladding. In the surface glazing experiments of the **Fe-Mn-Si-Cr** alloy, with SEM results depicted in fig. 3 the formation of droplets concentrically distributed has been detected. The droplets appear to be related to the formation of Mn and Si oxides.

The formation of Mn and Si oxides (e.g. $MnO \cdot SiO2$) on laser melting of steels has been reported and such type of oxides appear to form in this case also, while the radial distribution may be related to the blowing of the gas premix and the profile of the laser beam.

Thus, for Fe-Mn-Si-Cr alloys, the use of laser glazing may not be an advisable solution since it appears as leading to segregations and compositional and structural inhomogenties that cannot be controlled during the laser melting process.
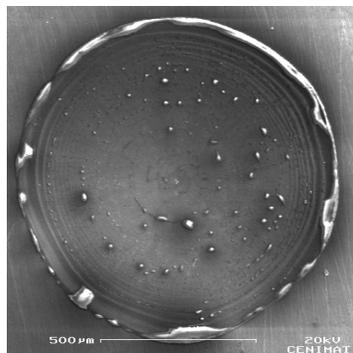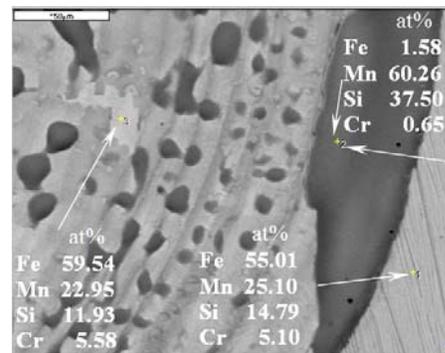


a. SE image of the spot　　　　b. Compositional details of the spot
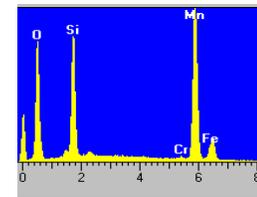
c. EDS peaks showing the oxydes formation

*Fig. 3 Microstructural observations of the Fe-Mn-Si-Cr laser spot*

### c) Co-Ni-Ga ferromagnetic shape memory alloys (alloy 4)

Ferromagnetic shape memory alloys are not only thermally actuated, but their actuation can be also magnetically controlled. Beside Ni-Mn-Ga alloys, the Co-based is another important family of alloys. Up to now the

laser interaction with such materials has been mainly limited to ablation processes.

The effect of the laser beam interaction with the Co-Ni-Ga alloy is shown in fig. 4, with the detail showing a typical martensitic structure in the solidification front with radial distribution
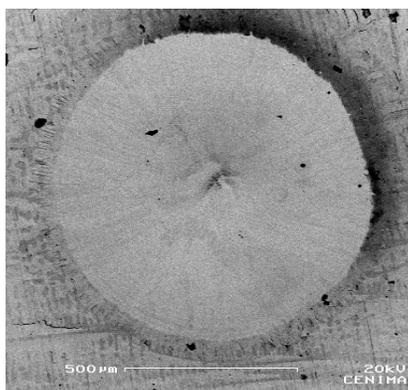


a.　　　　BSE image of the spot　　　　　　b. Radial strips showing martensitc structure
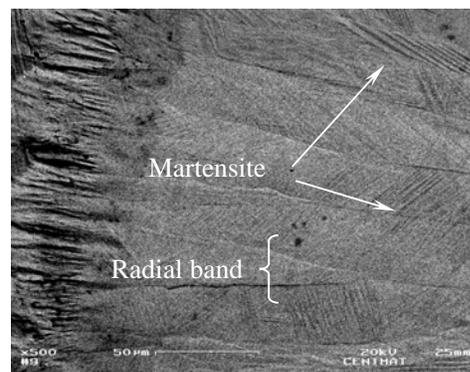
*Fig.4 Details of the laser spot of the Co-Ni-Ga shape memory alloy*

For this alloy, only limited compositional changes have been observed, although the presence of cracks in the vicinity of the spot has been detected. Such cracks have also been observed in the Ni-Mn-Ga alloys and have been attributed to the differences in the thermal properties of the components. By comparison, the laser interaction in the case of Co-Ni-Ga alloy is leading to less severe changes both in composition and the crack occurrence. Beside the formation of particular radial bands with martensitic structure, the interface between the melted zone and the un-melted one is inhomogeneous and may led to crack initiation.

## 4. Conclusions

Pulsed laser irradiations were - performed on four shape memory alloys belonging to the following families: Ni-Ti-Hf, Ni-Ti pre-sintered, Fe-Mn-Si-Cr and Co-Ni-Ga. The experiments showed particularities related to the initial composition and structure.

For Ni-Ti-Hf alloy it was shown the possibility to increase the Hf content of the surface on the expense of the Ni, with potential favourable increase in the biocompatibility and corrosion resistance

In the pre-sintered Ni-Ti shape memory alloy it was revealed the possibility to generate alloy compositions in the powder agglomerated matrix. The technique can be used for further developments in the fabrication of shape memory composites and 3D structures by oriented and/or layered selective laser sintering.

The Fe-Mn-Si-Cr alloys showed very poor behaviour, related to the presence of Si and Mn oxides and leading to the segregations as well as compositional and structural inhomogenity.

By contrast to Ni-Mn-Ga system, the Co-Ni-Ga ferromagnetic shape memory alloys were the least influenced materials by the interaction with the laser beam. Although also showing the risks of cracks in the vicinity of the spot, the tendency is reduced compared to previously studied Ni-Mn-Ga alloys.

It is concluded that the laser irradiation can be an opportunity to increase the functional performance of several shape memory alloys and a solution to use in order to expand the manufacturing options for selective sintering solutions.

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