Fiber Laser Surface Melting of a NiTi Superelastic Alloy: Influence on Structural and Mechanical Properties

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Abstract: The surface melting of a NiTi superelastic alloy using a high-power laser Yb:Fiber was investigated. The influence of this process on the microstructural and mechanical properties was also examined. The reference material was a 3 mm nitinol strip with a homogeneous austenitic B2 phase. For the laser surface melting process, input fluences were applied from 17.5 to 45 J/mm². The morphology of the structure and the chemical composition of several regions were determined by optical microscopy, scanning electron microscopy, dispersive energy spectra, and X-ray diffraction techniques. The mechanical properties, such as modulus of elasticity and hardness, were determined using nanoindentation and microindentation techniques. The greatest surface finishing of the fusion zone was observed for the condition 35 J/mm². Three well-defined regions (fusion zone (FZ), heat-affected zone (HAZ), base metal (BM)) could be observed and dimensions of grain size, width, and depth of the melted pool were directly affected by the laser fluence. The geometry of the molten pool could be controlled by the optimization of the laser parameters. High laser fluence caused preferential volatilization of nickel, dynamic precipitation of intermetallic phases, including Ti₂Ni, Ni₃Ti, and Ni₄Ti₃, as well as solubilization of TiC in the matrix, which led to grain refinement. Thus, high laser fluence is a suitable technique to enhance mechanical properties such as hardness and Young’s modulus.

Keywords: laser; shape memory alloy; nitinol

1. Introduction

Characteristics of NiTi alloy include shape memory, superelasticity, low modulus of elasticity, high corrosion resistance, and biocompatibility [1]. With high shape recovery, up to 10% at 25 °C, which is much larger than the elastic deformation supported by a conventional metallic material (0.2%) [2], shape memory alloys (SMAs) are in demand for many technical and engineering applications, including consumer products and industrial applications [3], structures and composites [4], automotive [5,6], aerospace [7–10], mini-actuators and microelectromechanical systems (MEMS) [11–13], robotics [14,15], biomedicine [1,16–20], and even fashion [21]. In biomedicine, which is a big field for the NiTi alloys, shape memory alloys have been applied for orthodontic wires [16], self-expanding stents for cardiovascular applications [22], treatment of patella fracture by claw-like shape memory alloy [23], and more, due to their unique properties.

According to material requirements for the potential application, the surface of the NiTi alloy can be laser-treated, which can provide improvements, including corrosion resistance, cavitation erosion...
resistance (Re), mechanical properties, electrochemical properties, grain refinement, and correction of defects such as pores and cracks. For a specific modification, parameters such as applied power and interaction time on the surface of the material are essential to produce the desired modifications. The generic term “laser surface treatment” includes treatments with and without the addition of materials [24,25]. The treatments without the addition of materials are laser transformation hardening [26], laser texturing [27], laser surface melting [28,29], and laser glazing [30]. The list of treatments with addition of materials include laser cladding [31,32], laser surface alloying [33], and laser welding processes both similar [34] and dissimilar [35,36].

Examination of the cross-sectional geometry of the melting developed under lower laser fluences [37] found that the depth of the melting gradually increased with increased laser fluence. At a fluence of 6.7 J/mm², a suitable mixture of the molten pool together with the top of the titanium surface was evident, which can be completed with a uniform modulus of elasticity of about 80 to 104 GPa. A high-power laser was used by ZD Cui et al. [28] to melt the surface of NiTi shape memory alloy. The rapid rate of solidification of the fused pool resulted in the formation of a surface layer that consisted of refined and homogenized microstructure. The results indicated that the corrosion resistance of NiTi treated by laser was significantly increased, which was demonstrated by increased passive film-breaking potential and decreased corrosion current. The outer surface of all samples studied was composed of TiO₂, NiTi, and other TiO compounds with increased corrosive resistance and reduced release of nickel ions.

Considered a challenging technique, laser surface modification of NiTi alloy has many obstacles still to overcome to achieve the optimization of the laser parameters and desired properties for application. The behaviors of NiTi SMA under high laser fluence are still unclear. Hence, the present work investigates the effects of high laser fluence surface melting on the structural and mechanical properties of NiTi, which would be of significant interest to those working in the field of laser materials processing.

2. Experimental Details

2.1. Material Preparation

The raw material was obtained by the Brazilian Instituto Tecnológico de Aeronáutica (ITA). The starting material was obtained by vacuum induction melting (VIM) from Villares Metals SA, and was a NiTi ingot with controlled chemical composition as shown in Table 1. The Ni (wt.%), Ti (wt.%), C (wt.%), and O (wt.%) content are global values of each sample measured by X-ray fluorescence (XRF) (LECO, St. Joseph, MI, USA) and direct combustion in LECO CS-444.

Table 1. Nominal composition in atomic percentages and weight of material obtained by vacuum induction melting (VIM).

| Ni (wt.%) | C (wt.%) | O (wt.%) | Ti (wt.%) |
|----------|----------|----------|-----------|
| 55.50    | 0.047    | 0.1132   | 44.66     |

The ingot was heat-treated for 15 min at 900 °C and then hot-rolled in nine rolling passes with a 20% reduction of area (Rₐ) per pass, interspersing and annealing at 900 °C for 10 min, to produce 3 mm thick samples. After the last pass, it was cooled in water, Tₕ₂₀ = 25 °C. The strips were then sanded and immersed in a 5 mL HF(aq) + 20 mL HNO₃(aq) + 75 mL H₂O solution to remove oxides, followed by ultrasonic bath treatment in acetone, and then ultrasonic bath with distilled water to remove superficial impurities. The strips were encapsulated in vacuum glass to prevent contact with an oxygen atmosphere for later homogenization heat treatment at 900 °C/1 h, and then quenched in water. The reference material after this heat treatment is referred to as HT.
2.2. Laser Surface Melting (LSM)

The Yb (fiber) laser used 2.0 kW average power (IPG, Model YLR-2000) with an output fiber 50 µm in diameter and 5.0 m in length with a wavelength (λ) of 1070 nm and 2 mm spot size. A fiber coupling unit connected to a working fiber of 100 µm in diameter and 10 m in length was used in the welding processes. The working fiber was connected to an optical collimator forming the beam coupling system. This laser was housed in an aluminum processing cabin (3.0 m×3) equipped with process auxiliary inert gas systems. The process head was coupled to a computer-controlled XYZ table driven by stepper motors, with a controlled velocity between 1.0 and 160 mm/s; the X-axis at 430 mm and Y-axis at 508 mm both had a resolution of 5.0 µm. A vertical Z-axis with a stroke of 215 mm and a resolution of 1.0 µm was incorporated into the table. The process head, characterized by a focal length of 160 mm, produced a 100 µm diameter laser beam. The welding head was also connected to the cooling-system hoses, the inert process gas system against oxidation, and gases to protect the optics against any splashing. The inert gas used in this project was argon. The configuration and scheme of this process are in Figure 1. Table 2 provides the parameters of the laser surface melting (LSM) processes used in this study on NiTi samples, where the nomenclature LSM 71 means the power used (700 W) and the scan speed (10 mm/s) of the LSM process, for instance. Table 2 also provides the argon flow, focal distance, and laser fluence values.

![Figure 1. (a) Laser surface melting configuration and (b) laser surface melting configuration scheme.](image-url)
Table 2. The parameters of the laser surface melting processes.

| Sample   | Power (W) | Speed Scan (mm/s) | Argon (l/min) | ∆z (mm) | $F_L$ (J/mm$^2$) |
|----------|-----------|-------------------|---------------|---------|------------------|
| LSM71    | 700       | 10                | 18            | 12      | 35.0             |
| LSM72    | 700       | 20                | 18            | 12      | 17.5             |
| LSM91    | 900       | 10                | 18            | 12      | 45.0             |
| LSM92    | 900       | 20                | 18            | 12      | 22.5             |

Figure 2 presents macrostructural images of surface views of the samples before and after the laser surface melting process in all conditions. The best surface finishing of the material was observed for 35 J/mm$^2$.

2.3. Microstructural Characterization

Visible light (optical) and scanning electron microscopy (SEM) were performed to characterize the microstructure of the alloy. Optical microscopy (OM) was performed using an optical microscope (Zeiss model Axio_Imager a2M., Stockholm, Sweden), equipped with Axiocam ICC3 video camera and digitizer board connected to a computer with AxioVision 4.8.2 SP2 software (Stockholm, Sweden). For SEM, an electronic microscope (model VEGA3 TESCAN., Brno, Czech Republic) was used.

Figure 2. Surface finishing view before and after the laser melting process in different conditions.
2.3. Microstructural Characterization

Visible light (optical) and scanning electron microscopy (SEM) were performed to characterize the microstructure of the alloy. Optical microscopy (OM) was performed using an optical microscope (Zeiss model Axio_Imager a2M., Stockholm, Sweden), equipped with Axiocam ICC3 video camera and digitizer board connected to a computer with AxioVision 4.8.2 SP2 software (Stockholm, Sweden). For SEM, an electronic microscope (model VEGA3 TESCAN., Brno, Czech Republic) was used, with secondary electron detectors and microanalysis system by energy dispersive spectroscopy (EDS) from Oxford Instruments (Oxfordshire, Abingdon, UK). The samples were prepared to facilitate observation of their microstructure, making the surface specular for the subsequent chemical attack and revealing the microstructure. The sample preparation procedure involved cutting steps using a low speed ISOMET BUEHLER™ (Lake Bluff, IL, USA) 4000 with a diamond edged disc and cold resin inlay; sanding with grain sizes ranging from 120 to 1200 mesh, and automatic polishing with model METPREP-3ALLIED (Metprep Ltd., Coventry, UK) using 1 \(\mu\)m and 0.3 colloidal silica. X-ray diffraction was carried out using a diffractometer (SEIFERT-RAYFLEX., Nuremberg, Germany) model URD 65, using Cu K\(\alpha\) radiation (\(\lambda = 1.54178\) Å). The acceleration was 20 kV, and the current was 30 mA. In the detector, 1 mm slots were mounted both horizontally and vertically. The reading time was 0.6 s with a pitch of 0.01° in the interval 2\(\theta\) between 20 and 90°.

2.4. Mechanical Tests

A nanoindenter (Anton Paar NHT3., Graz, Austria) was used to provide low loads with depth measurements on the nanometer scale to measure hardness and modulus of elasticity, as well as creep. International standards ASTM E254 and ASTM E384 were used. Diamond tip, Berkovich type, maximum load 25 mN, and 10 s pause were the parameters used to analyze the hardness values and modulus of elasticity. The distances between consecutive indentations varied from 50 to 300 \(\mu\)m depending on different thicknesses of melted zone (MZ), heat-affected zone (HAZ), and base metal (BM). Maps of the hardness distribution in the longitudinal section were obtained through microindentation using an automated Durascal 50 (Emcotest., Kuchl, Austria) to map the hardness distribution in a preselected area. Software controlled the distribution of the indentation points respecting the distance from the edge and the spacing between indentations specified by the operator. The mean microhardness and modulus of elasticity value were calculated by averaging five tested points.

3. Results and Discussions

The micrographs in Figure 3 obtained by SEM illustrate the microstructure of the reference material (HT) with a crystalline structure of austenitic monophasic B2-NiTi. The transformations that occurred in the solid state in the HAZ, such as grain growth, the formation of intermetals and recrystallization are visible in Figure 3b–e. Figure 3a shows the equiaxed grains for the heat-treated (HT) sample with an average size of \(D_{HT} = 35\) \(\mu\)m in diameter and with darker points of titanium carbide (TiC). After the fusion process with pre-established parameters for the laser surface melting (LSM), such as power and scanning speed, the fusion zone (FZ) and the heat-affected zone (HAZ) could be inferred. In Figure 3b–e, the FZ and HAZ are separated by a well-defined fusion boundary. Due to different fluence values and the thermal cycles, the grains exhibited different sizes. Micrographs in Figure 3b–e reveal a dendritic structure in the FZ due to rapid solidification and a recrystallized, equiaxed grain structure in the HAZ. For the fluence of 17.5 J/mm\(^2\), the average grain size was about 15% smaller than those found in the HT samples. For the fluences from 22.5 to 45 J/mm\(^2\), the laser surface melting increased the grain sizes from 3% to 15%. The observed solidification structure can be explained by the fast solidification theory, which establishes four parameters to control the microstructure found in the FZ temperature gradient (\(\Delta T\)), cooling time (t), crystal growth rate (CGR), and alloy composition (wt.%) [34]. The ratio between growth rate and temperature gradient governs the solidification mode. Those results demonstrated that the laser surface melting technique can be suitable for directly changing the morphology. Although
the energy density was large and the cooling procedure was very fast, the low thermal conductivity of the NiTi alloy caused the temperature gradient to spread very little, so that the base metal cooled the HAZ [38,39].

Figure 3. SEM images before (a) and after laser treatment (b) 17.5 J/mm² laser fluence, (c) 22.5 J/mm² laser fluence, (d) 35 J/mm² laser fluence, and (e) 45 J/mm² laser fluence. Highlighting the fusion zone, fusion boundaries, and heat-affected zone.
Figure 4 presents grain growth related to different laser fluence values, and Figure 5 shows the comparative diagram of laser fluence vs. depth and width dimensions of the molten pool. The width and depth of the melted pool were directly affected by the laser fluence. The desired geometry of the molten pool could be achieved by controlling the optimization of the laser parameters.

**Figure 4.** Comparative diagram of grain size with laser fluence.

**Figure 5.** Comparative diagram of laser parameter fluence on the dimensions of width and depth of the melt pool of NiTi.
The geometry of the cross-section of Figure 6a–c exhibits a “U”-shaped molten pool. These semi-spherical shapes, in most cases, indicate proper mixing of all materials in the liquid and semi-viscous states due to the flow forces acting within the molten pool. Under fluence 45 J/mm², shown in Figure 6d, the penetration cord was deeper, indicating a transition regime from conduction to keyhole; therefore, the 45 J/mm² (900 watts by 10 mm/s) was a sufficient condition in which the material would melt, followed by vaporization. The vaporization rebound in the 45 J/mm² formed a depression zone whose dimensions depended on the physical properties of the material and the beam intensity. The vapor channel received multiple reflections of the beam within it, which was associated with higher bead depth, splashing material losses, and preferential volatilizing of some elements.

Figure 6. Microstructures of a cross-section of NiTi samples showing the width and depth of the melted pool: (a) 17.5 J/mm², (b) 22.5 J/mm², (c) 35 J/mm², (d) 45 J/mm².

The EDS analysis, presented in Table 3, revealed the values of chemical composition for the FZ and HAZ. As a consequence the transformation temperature behavior, transformation temperatures are very sensitive to the proportion of Ni and Ti. The superelasticity and shape memory of the resulting material is directly related to Ti/Ni ratio; thus, the Ti/Ni ratio is the key aspect in nitinol manufacture. For most applications, the transformation temperature needs to be controlled at ± 5 °C, which means that the alloy composition should be controlled within ± 0.05%. Therefore, this effect implies a very restrictive chemical tolerance for the alloy production and surface treatment, in which changing the
alloy composition by just 1% results in a 100 °C difference in the transformation temperature of the alloy [40].

Table 3. Chemical composition and Ti/Ni ratio comparison of the material before and after laser surface modification *.

| Fluence (J/mm²) | FZ Ni (wt%) | Ti (wt%) | C (wt%) | O (wt%) | Ti/Ni |
|-----------------|-------------|----------|---------|---------|-------|
| 17.5            | 52.9        | 44.9     | 1.2     | 1.0     | 0.848 |
| HAZ             | 53          | 44.9     | 1.2     | 0.9     | 0.847 |
| 22.5            | 54.8        | 43.3     | 1.1     | 0.8     | 0.790 |
| FZ              | 53.4        | 44.3     | 1.5     | 0.8     | 0.829 |
| HAZ             | 53.2        | 44.3     | 1.8     | 0.8     | 0.833 |
| 35              | 52.9        | 45.1     | 1.1     | 0.9     | 0.853 |
| FZ              | 52.8        | 45.0     | 1.2     | 1.0     | 0.852 |
| HAZ             | 53.3        | 44.6     | 1.1     | 0.9     | 0.837 |

* Ti/Ni ratio 0.804 for base metal or bulk material.

According to Table 3, the lowest Ti/Ni ratio was 0.790 for the FZ of the 22.5 J/mm² fluence and the highest value of Ti/Ni ratio was 0.853 from 35 J/mm². This was related to preferential volatilization of Ni, which results in local changes in functional characteristics. Similar behavior was observed in another study [41] that correlated the laser pulse and preferential Ni volatilization, as well as conduction mode, which appears to be the best choice for processing such material. Figure 7 correlates the Ni content and laser fluence. Other studies [29,34] have confirmed that TiO₂ passive films are directly enhanced by greater Ti/Ni surface ratio because of the high oxidation of titanium. In addition, the formation of intermetallic phases (Ni₄Ti₃, Ni₃Ti₂, Ni₅Ti, Ti₂Ni) is directly related to Ti/Ni ratio and is sensitive to heat treatment [29,34].

Figure 7. Comparative graphic of the correlation between Ni content and laser fluence.

All conditions of laser fluence presented a similar behavior: the reduction of Ni content. However, the FZ of the 22.5 J/mm² exhibited closer chemical composition than the samples without laser treatment, due to precipitation of intermetallic Ni-rich phases (Ni₃Ti), confirmed by X-ray diffractogram as shown in Figure 8.
After the laser surface treatment, intermetallic formation often occurs, such as Ti$_2$Ni, Ni$_4$Ti$_3$, and Ni$_3$Ti, and these formations depend on the chemical composition, the temperature gradient, and the thermomechanical history. The HT condition presented monophasic B2 and TiC. For the fluence values of 22.5 and 35 J/mm$^2$, the respective eutectoid reactions NiTi $\rightarrow$ NiTi + Ni$_3$Ti and NiTi $\rightarrow$ NiTi + Ti$_2$Ni occurred, as illustrated in Figure 8. In studies with low and medium laser fluence [38], martensite phase formation has been observed. However, all samples studied in this present work, with high levels of laser fluence and Ni volatilization (Figure 7), did not present any formation of martensite phases, because this formation not only depends on the chemical composition, but also the temperature gradient and the thermomechanical history.

The mechanical tests of micro- and nanoindentation are fundamentally important to understand the performance of the NiTi material after surface treatment with high laser fluence. Hardness values are calculated in different ways. Figure 9a,b presents Vickers indentations, in which their hardness was calculated after loading, and Figure 9c–f presents the Berkovich nanoindentation, in which their hardness was calculated with the loaded indenter.
Figure 9. Images of the mechanical tests performed in different regions studied in this work. In (a) is the microindentations covering from side to side of the melted zone to the 2D graph, (b) presented a singles Vickers microindentations in surface, (c) Berkovich nanoindentations in base metal, (d) and (e) Berkovich nanoindentations in HAZ and (f) Berkovich nanoindentations in melted zone.
Figure 10 presents the hardness values obtained from the Berkovich nanoindentation tests in the FZ as well as the HAZ and BM for all different conditions of laser fluence. The condition 35 J/mm², in Figure 10d, exhibited the highest values of hardness due to its hard intermetallic Ti₂Ni phases. Other conditions presented behaviors similar to the HT condition, with an average hardness of 370 HV, due to its mixtures of Ni-rich and Ti-rich phases. Although Ti₂Ni precipitation occurred for the 35 J/mm², the TiC precipitation in the FZ decreased as a result of solubilization of carbon from the TiC in the matrix, as shown in Figure 5c. This phenomenon was observed not only for 35 J/mm², but for all conditions of laser fluence, due to the high fluence laser treatment.

Figure 11 presents the two-dimensional (2D) hardness map obtained from Vickers microindentations. Those results are according to the ones presented in Figure 10. Therefore, hard intermetallic precipitated phases, such as Ti₂Ni, enhanced the surface hardness of FZ and HAZ.

Figure 10. Berkovich indentation hardness as a function of the distance from the center of melting in the conditions: (a) Heat Treated, (b) 17.5 J/mm², (c) 22.5 J/mm², (d) 35 J/mm², (e) 45 J/mm².
as well as the surface hardness of BM without grain recrystallization. Despite the agreement of the behavior found by the different hardness measurement techniques, the higher values found for the microindentations tests were directly related to the superelastic effect in the projected area.

![Image of hardness measurements](image-url)

**Figure 11.** 2D surface graphic of Vickers microhardness from all NiTi samples in the conditions: (a) Heat Treated, (b) 17.5 J/mm², (c) 22.5 J/mm², (d) 35 J/mm², (e) 45 J/mm².
The superelastic behavior of distinct zones (WZ, HAZ, and BM) are represented by load–displacement curves in nanoindentation tests as evidenced by the depth recovery rate (Figure 12). The superelastic properties were affected by high laser fluence, noticeably changing the depth recovery ratio due to differences on displacement axis.

Figure 12. The nanoindentation load vs. displacement depth curves for the conditions studied in this work in the conditions: (a) Heat Treated, (b) 17.5 J/mm², (c) 22.5 J/mm², (d) 35 J/mm², (e) 45 J/mm². Blue lines for fusion zone, red lines for HAZ, and black lines for base metal.

Figure 13 presents Young’s modulus of the different regions studied in this paper. Increased average modulus of the FZ tended to increase the laser fluence, and the highest value was obtained
from the condition 35 J/mm² (80 GPa), which was 14.3% higher than the reference sample (HT = 70 GPa). In general, this depends on the chemical composition, as well as the temperature gradient and the thermomechanical history.

Figure 13. Comparative diagram of elasticity modulus from different regions of the NiTi samples.

4. Conclusions

The following conclusions can be made after studying the relationship between laser surface melting treatment with high fluence values in Ni-rich NiTi alloys:

(a) The greatest surface finishing of the fusion zone was observed at the condition of 35 J/mm².
(b) Three well-defined regions (FZ, HAZ, BM) could be observed. The laser fluence directly affected the dimensions of grain size as well as the width and depth of the melted pool. The geometry of the molten pool could be controlled by the optimization of the laser parameters.
(c) High laser fluence values caused preferential volatilization of nickel, dynamic precipitation of intermetallic phases like Ti₂Ni, Ni₃Ti, and Ni₄Ti₃, and solubilization of TiC in the matrix, which leads to grain refinement.
(d) High laser fluence proved to be a suitable technique to enhance mechanical properties like hardness and Young’s modulus.

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