

# The influence of laser power and repetition rate on oxygen and nitrogen insertion into titanium using pulsed Nd:YAG laser irradiation

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## Abstract

Oxygen and nitrogen insertion in a titanium substrate is performed in air using a Q-switched Nd-YAG laser. This process modifies the surface by the formation of specific layers on the substrate. These layers show different properties, largely influenced by the insertion of elements in the layers. The treatment conditions, especially the laser parameters (fluence and repetition rate), must be known and controlled. Using nuclear analysis, we demonstrate that oxygen insertion is mainly influenced by repetition rate, and that nitrogen insertion is controlled by laser fluence. The physical phenomena involved in the oxygen and nitrogen insertion are discussed.

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## 1. Introduction

Surface laser treatments are powerful tools for modifying the surface appearance or composition of a substrate in order to improve its mechanical, chemical or optical properties. The specific thermal characteristics of laser irradiation can generate specific microstructures including nanocrystalline and/or metastable phases.

The insertion of light elements (N, O) in titanium targets depends on the interactive conditions between the laser, the substrate and the gaseous environment (air, mixture of N<sub>2</sub> + O<sub>2</sub>, N<sub>2</sub>, ...) [1–7]. Many studies have dealt with the influence of overlapping [8], of the nature of the surrounding gas [9], of the intensity of the laser beam on the morphology of the layers that are created [10], and on the nature of the phases that are formed [11].

The aim of the study presented here is to complete this work with an understanding of the influence of the laser parameters on the insertion of the light elements N and O present in the ambient air.

Work based on elementary analyses conducted through NRA (nuclear reaction analysis) microanalyses demonstrates that the higher the intensity of the laser beam the more nitrogen is inserted, whereas the amount of oxygen inserted depends more on the number of laser impacts.

## 2. Experimental

### 2.1. Titanium substrate

Commercially pure (CP) titanium (grade 4) samples were used. Prior to laser treatment, the sample surfaces were mechanically polished before an electrolytic polishing to obtain a reference surface with very low roughness ( $R_a < 0.4$ ). X-ray photoelectron spectroscopy (XPS) analysis showed the formation of a very thin layer of titanium dioxide at the surface of the samples [12].

### 2.2. Laser treatments

We used a Q-switch Nd:YAG laser from Quantel (Brillant B model). This laser operates at 1064 nm and generates 5 ns pulses at a repetition rate of 10 Hz. We assume that the laser spot is circular with a Gaussian energy distribution. We obtained a spot diameter of about 465  $\mu\text{m}$ . Two samples groups were obtained:

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Table 1

Changes in the area of the impact trace and atomic fraction in nitrogen and oxygen relative to the changes in laser fluence per impulse  $F_{1p}$

Samples	1i2	1i4	1i9	1i15	1i21	1i27	1i33
$F_{1p}$ (J/cm <sup>2</sup> )	2	4	9	15	21	27	33
$A$ ( $\times 10^{-3}$ cm <sup>2</sup> )	5.75	6	10.6	16.6	22.9	36.1	96.1
$x$ (%at O)	0.024	0.022	0.025	0.027	0.027	0.025	0.030
$y$ (%at N)	0	0	0.015	0.026	0.022	0.048	0.048

- A first group of samples was obtained with various laser fluence and laser intensities in the range from 2 to 33 J/cm<sup>2</sup> and from 0.4 to 6.6 GW/cm<sup>2</sup>. These samples are indicated with the value of laser fluence after the letter “i” (Table 1).
- The second group was obtained with different numbers of pulses in the range 1–20 for laser fluence of 9 J/cm<sup>2</sup>. These samples are indicated with the value of the number of impacts before the letter “i” (Table 2).

### 2.3. Observations by 3D microscope

Images of the impacts were created with the use of a three-dimensional *Infinite Focus* microscope from the Alicona company. This microscope uses the technique of Shape from Focus. Using an image-processing program, we were able to reconstitute the profiles of the different zones that were treated (Fig. 1a and b). Two different analysis zones were distinguished in an impact area, the one marked “c” corresponding to the

Table 2

Changes in oxygen composition ( $x(O)$  %at) for different zones (r: ring and c: centre) and in nitrogen composition ( $y(N)_r$  %at) for the ring zone

Samples	1i9	2i9	5i9	10i9	15i9	20i9
$n_i$	1	2	5	10	15	20
$x(O)_r$ %at	0.033	0.039	0.045	0.065	0.073	0.082
$x(O)_c$ %at	0.024	0.026	0.033	0.052	0.067	0.052
$y(N)_r$ %at	0.028	0.035	0.027	0.018	0.028	0.033

centre and the other marked “b” corresponding to a band (Fig. 1d).

### 2.4. Nuclear analysis

To investigate the composition and distribution of the chemical elements, a 2  $\mu\text{m} \times 2 \mu\text{m}$  deuteron micro beam was used with a range of more than 1  $\mu$  [13–15]. This micro beam was delivered by a Van de Graff particle accelerator running at 920 keV. Light elements were measured by nuclear reactions induced by deuterons, mainly  $^{16}\text{O}(d,p)^{17}\text{O}$  for oxygen and  $^{14}\text{N}(d,p)^{15}\text{N}$  for nitrogen.

Light particles induced by nuclear reactions (protons or alphas) were detected by an annular surface barrier detector. Fig. 2a shows the average angular position of 170° (solid angle: 130 msr) that reduces to a minimum the effect of the surface roughness and improves the cross-section [14,15]. A Mylar foil (with a thickness of 26  $\mu\text{m}$ ) was mounted on the collimator to

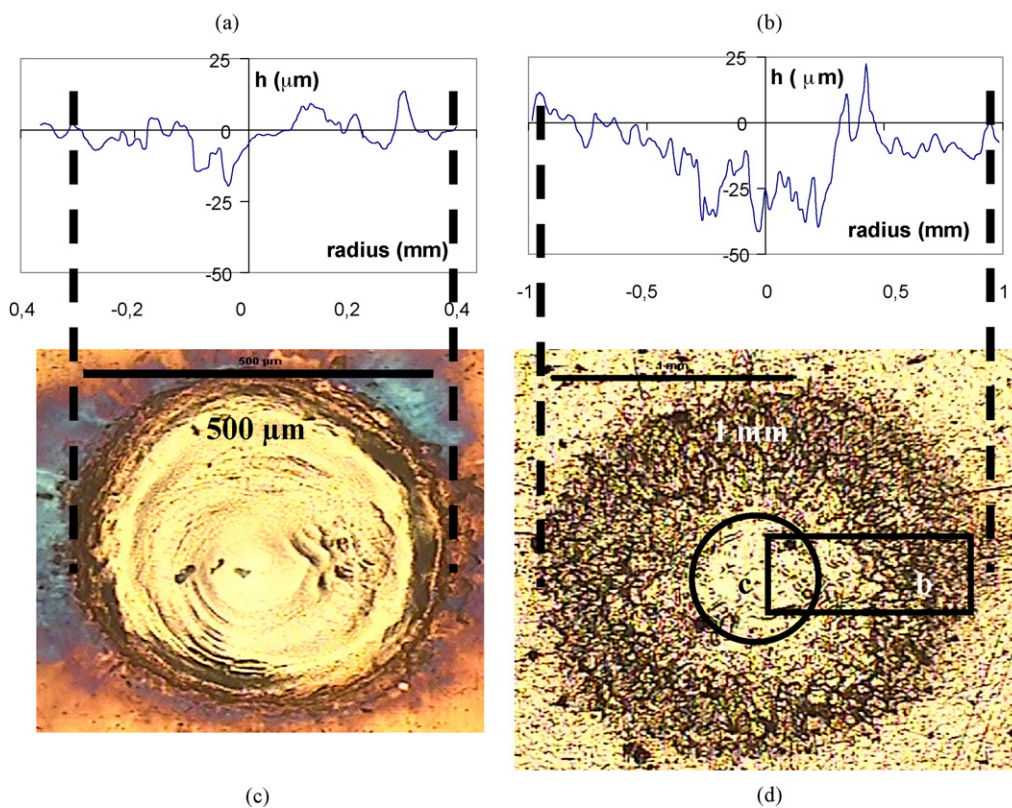


Fig. 1. Profiles, micrography and mapping. The profiles obtained with a 3D image are shown in (a) and (b) corresponding, respectively, to views (c) and (d). Images (c) and (d) were produced with a 3D optical microscope for two zones irradiated by a ND:YAG laser beam. (c) Shows a zone obtained with 20 superimposed impacts at a fluence of 9 J/cm<sup>2</sup>. (d) Relates to the image of an impact zone with a fluence of 33 J/cm<sup>2</sup>.

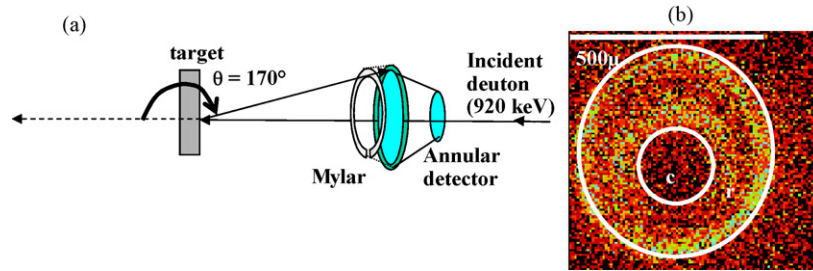


Fig. 2. NRA analysis. (a) Sketch in NRA mode induced by a deuteron beam on a target using an annular barrier detector. Image (b) mapping for oxygen over an area of  $700 \mu\text{m} \times 700 \mu\text{m}$  for zones impacted with fluence per impact of  $9 \text{ J/cm}^2$  for 20 impacts. It was reconstituted on the basis of a NRA spectrum based on the peak Odp1.

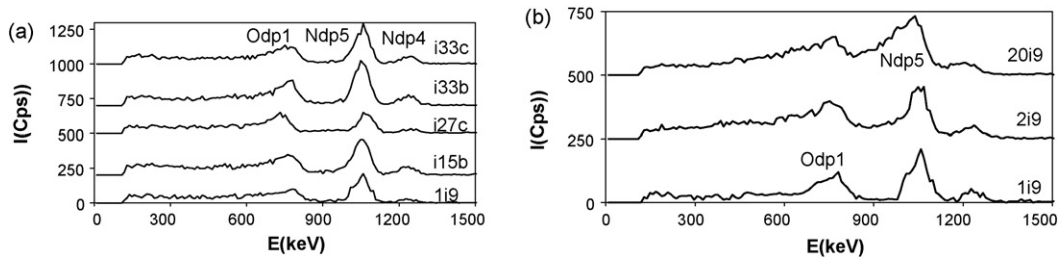


Fig. 3. NRA spectra for different impacts produced with deuteron beams at 920 keV. (a) For impacts at varying fluences (in  $\text{J/cm}^2$ ) indicated by the numbers after the letter “i”. The last letter indicates the type of area rastered under the deuteron beam, ‘c’ for centre and ‘b’ for band. (b) For impacts at  $9 \text{ J/cm}^2$  with varying numbers of impacts indicated by the number in front of the letter “i”.

stop backscattered deuterons (Fig. 2a). With the use of this foil, only high energy particles, induced by nuclear reactions, reach the detector. The concentration of oxygen and nitrogen is deduced from the energy spectrum of the emitted protons. The normalization and the absolute quantification of these analyses need measurement of the number of incident deuterons [14,15].

The same element may produce more than one peak when several nuclear energy levels are involved (Fig. 3a). The intensity of a peak is directly related to the concentration. Quantification of the analyses takes into account the stopping power properties ( $dE/dx$ ) of the targets and cross-sections of the nuclear reactions involved [14,15].

The two reference samples are  $\text{UO}_2$  and TiN (spectra  $\text{UO}_2$  and TiN). The energies can be calibrated in divisions of 10 keV (using the position of the peaks), which leads to a maximum error on the atomic ratios of 1% [15]. The different nuclear reactions induced on these samples are indexed on these two spectra. Peaks corresponding to the following nuclear reactions were used to quantify the nitrogen and the oxygen (Fig. 3a):

- $^{14}\text{N}(d,p)^{15}\text{N}$  (marked Ndp5) for nitrogen in the region of energy 989–1088 keV [14].
- $^{16}\text{O}(d,p)^{17}\text{O}$  (marked Odp1) for oxygen in the region of energy 633–821 keV [15].
- The amount carbon in the layer is less than 0.01 in atomic ratio (peak  $^{12}\text{C}(d,p)^{13}\text{C}$ ). The detected carbon is only due to contamination.

Most of the analyses were done by rastering the beam at the surface of the sample. These data were treated off-line, and the maps (Fig. 2b) and spectra relevant to characterization were extracted by means of the RISMIN code [16].

### 3. Results and discussion

#### 3.1. Observations by the 3D microscope

Fig. 1d illustrates the impacts obtained with laser fluence at  $33 \text{ J/cm}^2$  with one pulse. Table 1 shows that the surface affected by the laser shot increases with laser fluence. This is consistent with previous studies [12], which show the energy deposited to be surface energy.

Fig. 1c illustrates a zone treated with 20 pulses and laser fluence at  $9 \text{ J/cm}^2$ . The profiles obtained for each impact show a centred part more hollowed out than the peripheral part (Fig. 1a and b). We attribute this to the recoil pressure generated by the ejection of matter at the heart of the impact, where laser intensity is greatest [17–19]. It is to be noted that, for the deformation of the surface, the effect of the laser fluence is greater than that of the number of impacts.

#### 3.2. NRA analysis

Fig. 3 represents different NRA normalized spectra according either to zones whose mono impacts were produced with different fluences (Fig. 3a) or to multi-impacted zones (Fig. 3b).

The NRA spectra (Fig. 3a) obtained in relation to laser fluence from one band (spectra i15b and i33b) have peaks Odp1 and Ndp5, from which the oxygen and nitrogen can be quantified. These peaks have a greater area than those deriving from the central zone (spectra i27c and i33c). Finally, the distribution of light elements (N and O) is heterogeneous in the treated zone (see Fig. 2b).

The NRA spectrum (Fig. 3b) obtained in relation with the number impacts shows that:

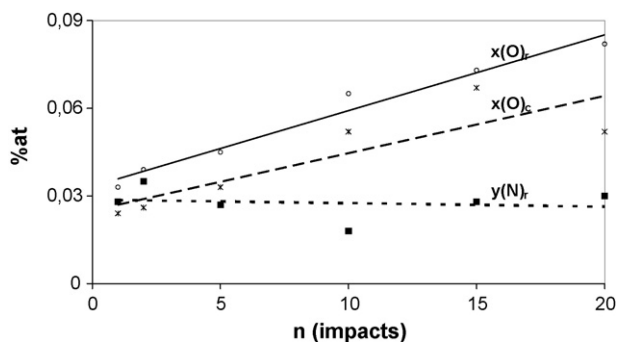


Fig. 4. Changes in the atomic composition,  $x$  in O and  $y$  in N, for a compound of the type  $TiO_xN_y$ . The curves  $x(O)_r$  and  $x(O)_c$  show changes in the oxygen composition in different parts of the impact zones ( $r$  = ring;  $c$  = center). Curve  $y(N)_c$  shows the changes in the atomic composition  $y$  in N.

- The amount of nitrogen remains constant with the peak Ndp5 (Fig. 3b).
- The amount of oxygen rises to a maximum corresponding to about 20 pulses (the peak Odp1 in Fig. 3b).

The NRA spectra realized for the single-impact zones in relation to fluence (Fig. 3a) do not have the same appearance as the multi-impacted one (Fig. 3b), but they are similar to each other in the following respects:

- They show the presence of oxygen and nitrogen.
- The peaks  $^{16}O(d,p)^{17}O$  and  $^{14}N(d,p)^{15}N$  are well separated. The layers are very thin.

As a rule, the quantities of nitrogen and oxygen (Fig. 4) do not vary identically:

- In relation to the number of impacts, the molar fraction of nitrogen remains the same when the number of impacts increases (curve  $y(N)$ ), whereas that of oxygen increases at a regular rate around the impact area (Table 2;  $x(O)_r$ ) and rise to saturation in the impact centre (Fig. 4: curve  $x(O)_c$ ). Further, the oxygen level is greater around the impact than at its centre (curves  $x(O)_r$  and  $x(O)_c$ ).
- In relation to fluence, as is shown in Table 1, laser fluence greater than  $9 J/cm^2$  is needed before nitrogen can be inserted into the titanium lattice. Then, what is inserted seems to vary with fluence. By contrast, oxygen can be inserted starting from the lowest levels of fluence ( $2 J/cm^2$ ) and the amount inserted is affected only slightly by an increase in fluence (Table 1).

Thus, the insertion of oxygen is affected more by an increase in the number of impacts than by an increase in laser fluence, whereas the insertion of nitrogen requires a fluence threshold of  $9 J/cm^2$ . This value corresponds with the threshold for the dissociation energy of nitrogen molecule  $N_2$  in the plume on the target [12,20]. This insertion of nitrogen in a greater quantity is dependent on an increase in laser intensity. Studies on nitriding, carried out in very similar conditions, but with pulses of a longer duration [3,21,22] or with a shorter wavelength [23],

show that the substrate needs to be melted and a plasma created in order for nitrogen to be inserted into the target. We can attest, via the bibliography [16,24], that in our experimental conditions the substrate did melt and that a plasma was created.

A study on the nitriding of iron [5] leads likewise to evidence of a threshold of nitriding, but in a nitrogen atmosphere. This threshold is close to  $1.8 J/cm^2$ . Further, the presence of a plasma above a melted zone assists the insertion of light elements, especially with laser sources emitting near-IR [13].

The oxygen and nitrogen are inserted in the titanium through different processes. The oxygen is reactive enough to combine with the titanium on contact with the titanium liquid and vapour, as is shown by analyses conducted with atomic emission spectroscopy [24]. The nitrogen dioxide in the air needs to be excited, even dissociated, before it can be inserted. That is the role of the plasma created on the surface of the target [5,17].

#### 4. Conclusion

The quantity of light elements inserted using a Q-switched Nd:YAG laser in CP titanium targets in the air was studied with reference to the change in laser fluence per pulse and to the number of impacts. There is a difference in the distribution of these elements in the impact zones relative, on the one hand, to an increase in laser fluence and, on the other, to the number of impacts. Further, it is shown that the quantities of light elements deriving from the surrounding atmosphere do not increase uniformly. The specific ratio increases as follows:

- For oxygen with the number of impacts per unit of area up to a saturation for about 20 impacts.
- For nitrogen with fluence per impulse above a threshold of  $9 J/cm^2$ .

Following similar studies, it emerges that nitrogen is inserted in a significant quantity in melted titanium having a plasma plume above it, which excites, even dissociates, the nitrogen molecule, whereas the very reactive oxygen in the air combines directly with the titanium either on the target or immediately on contact with the titanium vapour present in the plasma plume.

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