Applied Surface Science 278 (2013) 245–249

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Wavelength influence on nitrogen insertion into titanium by nanosecond pulsed laser irradiation in air

F. Torrent[a], L. Lavisse[a], P. Berger[b,c], J.-M. Jouvard[a], H. Andrzejewski[a], G. Pillon[a], S. Bourgeois[a], M.C. Marco de Lucas[a,*]

[a] Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB), UMR 6303 CNRS-Université de Bourgogne, 9 Av. A. Savary, BP 47 870, F-21078 Dijon Cedex, France
[b] CEA/DSM/IRAMIS/SIS2M, CEA-Saclay, F-91191 Gif sur Yvette, France
[c] SIS2M, UMR CEA-CNRS 3299, CEA-Saclay, F-91191 Gif sur Yvette, France

ARTICLE INFO

Article history:
Received 15 June 2012
Received in revised form
20 November 2012
Accepted 21 November 2012
Available online 29 November 2012

Keywords:
Laser nitriding
Light elements insertion
Surface functionalization
NRA
Raman spectroscopy

ABSTRACT

We studied in this work the influence of the wavelength (532 vs. 1064 nm) on the insertion of nitrogen in titanium targets by surface laser treatments in air. The laser pulses were of 5 ns and the irradiance was lower than 25×10^{12} W/m^2. Results obtained using a frequency-doubled Nd:YAG laser at 532 nm were compared with those previously reported for laser treatments at 1064 nm. Nuclear reaction analysis and micro-Raman spectroscopy were used for determining the composition and the structure of the surface layers, respectively.

Results showed the lower efficiency of irradiation at 532 nm for nitrogen insertion, which is possible only above threshold conditions depending on both the laser irradiance and the number of cumulated impacts per point. This was explained as being due to a higher ablative effect in the visible range. The insertion of oxygen giving rise to the growth of titanium oxynitrides was also discussed.

1. Introduction

Titanium and its alloys are widely used in aeronautical, marine and chemical industries for their good mechanical properties, high resistance to corrosion and low density. However, the tribological properties of titanium are poor (highly unstable friction coefficients, poor abrasive wear resistance and poor fretting behavior) [1,2] and they must be improved for many mechanical engineering applications. Different types of surface treatments can be used with this end. Nitriding and carburizing are the most popular thermochemical treatments, but they must be done in highly oxygen-free atmospheres to avoid titanium oxidation [2]. This rules out the possibility of in situ treatments.

Laser treatments are powerful tools for modifying the surface composition of metals. Light elements (oxygen, nitrogen, and carbon) of the reactive atmosphere can be inserted in a surface layer whose composition and microstructure depend on the irradiation conditions and on the thermal properties of the target [3–5]. Thus, surface nitriding of titanium by processes using lasers in nitrogen atmosphere has been widely reported [3,6]. On the other hand, the insertion of nitrogen by laser treatments in air is also of interest for technological applications.

In previous studies [7,8], we reported surface laser treatments of titanium substrates in air with a near infrared Nd:YAG laser emitting in the nanosecond regime at 1064 nm. For the shortest pulse durations, 5 ns, titanium oxynitride surface layers containing about 40 at.% of nitrogen and 6 at.% of oxygen were obtained with a laser irradiance of 15×10^{12} W/m^2 and cumulating 70 impacts per point. For longer pulse durations, 35 ns, the insertion of nitrogen was negligible and the surface layers were mainly composed of titanium oxides. In fact, the ablative effect of the laser increases for short pulse durations [8,9] and gives rise to the insertion of a higher amount of nitrogen on a shorter depth.

Here, we study the influence of the laser wavelength in the insertion of nitrogen by laser treatment of titanium in air. With this end a frequency-doubled Nd:YAG laser emitting pulses of 5 ns at 532 nm was used. The composition of the surface layers was studied by nuclear reaction analysis (NRA), whereas micro-Raman spectroscopy was used for characterizing their microsctructure. The results are compared with those previously reported for laser treatments at 1064 nm, with the same pulse duration, in order to show the influence of the laser wavelength on the nitrogen insertion into titanium.

* Corresponding author.

0169-4332/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2012.11.110

Table 1
Laser treatment conditions used in this work: laser repetition rate (f), laser power (P), laser scanning velocity (v), number of cumulated impacts per point (n_p) and laser irradiance. Oxygen and nitrogen concentrations (at.%) in the surface layers were determined by NRA experiments.

Sample number	f (kHz)	P (W)	v (mm/s)	n_p	Irradiance (10^{12} W/m^2)	O (at.%)	N (at.%)
L1	10	1.05	20	100	11	43	3.7
L2	10	0.82	20	100	8	43	3.2
L3	10	0.52	20	100	5	43	2.4
L4	10	0.52	30	65	5	33	–
L5	10	0.32	30	65	3	22	–
L6	10	0.32	15	130	3	30	0.4
L7	5	1.25	20	50	25	38	4.3
L8	5	1.25	25	40	25	28	0.4
L9	5	1.10	20	50	22	27	0.5
L10	5	1.0	30	35	20	12	–
L11	5	0.9	20	50	18	11	–
L12	2	0.4	5	80	20	38	4.0

2. Experimental details

2.1. Laser treatments

Commercially pure titanium plates (10 mm × 10 mm × 1 mm) were used for surface laser treatments in air. The substrates were mechanically polished with a diamond paste and then washed with ethanol. The laser treatments were performed using a frequency-doubled Q-switched Nd:YAG laser emitting pulses of $\tau = 5$ ns at 532 nm. The laser spot (about 50 μm in diameter) was moved over the sample surface with a constant velocity (v) to form parallel straight lines with an interline spacing of 10 μm.

Table 1 summarizes the different treatment conditions used in this work. Three experimental parameters, i.e. the laser repetition rate (f), the laser power (P) and the scanning velocity of the laser (v), were varied in order to cover a large range of values of both the irradiance and the number of cumulated impacts per point (n_p). These conditions include the ones used in previous works with a Nd:YAG laser emitting pulses of 5 ns at 1064 nm [7,8].

2.2. Characterization techniques

The composition and the distribution of light elements in the layers were analyzed by NRA which allows quantitative analysis of oxygen, nitrogen and carbon without the influence of the chemical environment and a low influence of the roughness.

Two beam conditions were chosen, either 920 keV, an optimum for oxygen quantification from $^{16}O(d,p_1)^{17}O$ nuclear reaction, or 1900 keV, for nitrogen signals, especially $^{14}N(d,\alpha_1)^{12}C$ nuclear reaction [8]. In the first case, for 920 keV deuterons, the detector was covered with a 23 μm thick Mylar foil to stop backscattered deuterons and thus to have access to the whole oxygen depth profile without interferences. At 1900 keV, the detector was let uncovered to benefit from better depth resolutions for nitrogen profiles. The analysis of NRA spectra was done as described in [8]. The oxygen and nitrogen insertion depths were determined taking into account the experimental lowest energy value for an NRA peak assigned to a nuclear reaction involving the selected element (oxygen or nitrogen). Indeed, the lowest energy particles are those coming from the deepest area of the sample. Firstly, the incident beam is slowed down by the interaction with the sample. Then, the particles produced by the nuclear reaction in the deepest areas loose a part of their energy traveling up to the surface before reaching the detector. The PYROLE software [10] was used for calculating the energy loss of the particles through the analyzed material as a function of the incident beam conditions and the nature of the sample. The calculated value was then compared to the experimental energy width of the corresponding NRA peak.

The structure of the films was characterized by micro-Raman spectroscopy by using an InVia Renishaw set-up. The spectra were obtained in back-scattering configuration. The excitation wavelength was 532 nm and the excitation power focused on the sample was about 0.5 mW to avoid heating the samples.

A NT9000 VEECO optical profiler was used for measuring the difference of height between laser treated and untreated areas.

3. Results and discussion

The insertion of nitrogen and oxygen in the surface layers formed by laser treatment of Ti substrates was analyzed by NRA. Fig. 1 shows NRA spectra of layers L1–L4 recorded with optimal conditions for nitrogen detection. Layers L1–L3 were obtained with the same number of cumulated impacts ($n_p = 100$) and a decreasing irradiance (from 11 to 5×10^{12} W/m^2), whereas layer L4 was obtained with the same irradiance as L3 (5×10^{12} W/m^2), but with a smaller number of cumulated impacts ($n_p = 65$). Fig. 2 presents NRA spectra of layers L1–L4 recorded with optimal conditions for oxygen detection.

In Fig. 1, the peak corresponding to the nuclear reaction $^{14}N(d,\alpha_1)^{12}C$ shows the insertion of nitrogen in layers L1–L3, whereas the amount of nitrogen in layer L4 is negligible (Table 1). The height of this peak increases from L3 to L1, showing that the amount of nitrogen in the surface layer increases with the irradiance. The nitrogen concentration calculated from NRA spectra [8] increases from 2.4 at.%(L3) to 3.7 at.% (L1). Moreover, the width of this peak increases in the low energy side from layer L3–L1. This can be explained by the increase of the nitrogen insertion depth because the lowest energy particles are those coming from the deepest area of the sample. The experimental width of the NRA peak was compared to the energy loss calculation given by the PYROLE software. Thus, the nitrogen insertion depths were found to be ~0.3 μm for L3 and ~1.5 μm for L1. The influence of the number of cumulated impacts is shown in Fig. 1 for an irradiance of 5×10^{12} W/m^2. Decreasing the number of impacts from 100 (L3) to 65 (L4) leads to a negligible insertion of nitrogen in layer L4.

The insertion of nitrogen was checked by NRA experiments for all the layers presented in Table 1. The results summarized in Fig. 3 show the treatment conditions for which NRA spectra reveal nitrogen insertion in the surface layer.

NRA spectra reveal also the insertion of oxygen in the surface layers (Fig. 2). The height of the peak $^{16}O(d,p_1)^{17}O$ is almost the same for layers L1–L3, which indicates that the amount of oxygen is almost the same for these three layers (Table 1). This concentration was calculated to be ~43 at.%. For layer L3, obtained with the lowest irradiance, the width of this peak is smaller, which can be explained by a smaller insertion depth. The calculated values are ~0.2 μm for L3, and ~0.6 μm for L1. For layer L4, obtained with the same irradiance than L3 and a smaller number of impacts, both the height and the width of the $^{16}O(d,p_1)^{17}O$ peak are slightly smaller.