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Pulsed laser growth and characterization of thin films on titanium substrates

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Abstract

Colored layers were obtained by laser surface treatment of Ti substrates with a pulsed Nd:YAG Q-switched laser. The changes in the morphology, structure and chemical composition of the layers were studied by SEM, EDS, XPS, SIMS and Raman spectroscopy as a function of the laser fluence in the 4–60 J cm^{-2}. For laser fluences lower than 25 J cm^{-2}, the layers are colorless or yellow. Their surface is smooth, but they display cracks which increase when the fluence increases. The O/Ti ratio, determined by XPS analysis, varies from 0.7 (colorless layers) to 1.3 (yellow layer). Moreover, XPS spectra evidence non-negligible amounts of nitrogen and carbon in these layers. Raman spectra show large bands which support the formation of titanium oxy-carbo-nitride.

For laser fluences higher than 25 J cm^{-2}, the layers are purple and blue and very rough sample surfaces were obtained. As a consequence of this, XPS analysis could not be used to obtain quantitative information on the layer composition. Finally, Raman spectra clearly showed the increasing formation of anatase and rutile phases of TiO_2 in these layers when the laser fluence increases.

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Keywords: Laser surface treatments; Titanium oxides; Titanium nitrides; Thin films

1. Introduction

Laser surface treatments are powerful tools for modifying the surface appearance or composition of a material in order to improve their mechanical, chemical and optical properties. The specific thermal characteristics of pulsed laser irradiation can give rise to the formation of unusual microstructures including nanocrystalline and metastable phases.

In this field, many studies have been focused on titanium and its alloys because of their many applications in aeronautical, marine and chemical industries [1,2]. Thermal oxidation of titanium in air leads only to the formation of titanium dioxide in the rutile structure. By contrast, laser irradiation in air allows to obtain surface layers containing different oxides and nitrides, in spite of their lower thermodynamic stability [1,3]. These layers present a wide variety of colors that make them very attractive in jewelry and decorative applications [4,5].

In previous works [6,7], we reported the growth and first characterizations of colored layers formed by pulsed laser irradiation of Ti substrates in air with a Nd:YAG Q-switched laser. The early stage of the laser-induced oxidation of the titanium substrate was mainly studied by X-ray diffraction and discussed with respect to the Ti–O phase diagram.

Here, we analyze the influence of the laser fluence value, varying from 4 to 60 J cm^{-2} range, on the morphology, the structure and the chemical composition of the formed layers. Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and Raman spectroscopy experiments were performed to this end.

2. Experimental details

2.1. Materials

Commercially pure titanium (grade 4) samples of dimensions 15 mm × 10 mm × 1.2 mm were used. Prior to laser treatment, the sample surfaces were mechanically polished

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with 1200-grit SiC before an electrolytic polishing in a perchloric acid with ethylene glycol in methanol solution for 30 s at 24 V and 2 A to obtain a reference surface with very low roughness (Ra < 0.4). Previous SEM observations revealed no features on such prepared samples. XPS analysis showed the formation of a very thin layer of titanium dioxide at the surface of the samples.

2.2. Laser treatments

The laser treatments were performed using a Nd:YAG Q-switched laser with a wavelength $\lambda = 1.064$ μm, a pulse duration $\tau_l = 35$ ns and a repetition rate $f = 5$ kHz. The focused laser spot, with a diameter of about 100 μm, was moved over the titanium substrate surface with a velocity of 50 mm s^{-1} to form parallel straight lines. The laser fluence per pulse, F_{lp} (J cm^{-2}), can be calculated by the relation.

$$F_{lp} = \frac{P_l}{A f}$$

with P_l being the average laser power (in W), A the laser spot area (in cm^2) and f the repetition rate (in s^{-1}). It is worth to note that the overlap between adjacent laser pulses must be taken into account in order to calculate the cumulated fluence on the substrate. An *overlap factor* around 50 can be evaluated by considering a Gaussian distribution of the laser beam energy, which leads to a circular shape spot, and a step of 40 μm between two laser traces.

Table 1 summarizes the laser treatment conditions and the color of the films analyzed in this work.

2.3. Characterization techniques

SEM was used to study the morphology of the films. The apparatus was a JEOL JSM 6400F typically working at 20 keV. The surface elemental composition of the samples was analyzed by energy dispersive spectrometry (EDS-OXFORD-Inca energy software).

XPS measurements were performed with a SIA 100 Riber system. An Al Kα X-ray source was used with 300 W power (accelerating voltage 12 kV and emission current 25 mA). A MAC 2 Riber spectrometer was used with its axis in the direction perpendicular to the surface of the sample. Total resolutions including primary photons and spectrometer, measured from the Ag 3 d$_{5/2}$ line width, were equal to 2.0 eV for global spectra and to 1.3 eV for windows corresponding to selected lines. Argon ion sputtering with 4 kV accelerating voltage and 20 mA emission current was applied for in depth composition analysis. The analysis

chamber pressure was maintained below 10^{-9} mbar during measurements. The Casa software package was used for data treatments including background subtraction with a Shirley routine and quantifications using relative sensitivity factors given in the package.

SIMS measurements were performed using a MIQ 256 Riber. Primary Ar$^+$ ions energy was 10 keV, with a sample current of 5 nA. The incidence angle was 45° and the analyzed area was 95 μm × 134 μm. Micro-Raman spectra were obtained with a Jobin-Yvon T64000 spectrometer. The excitation was provided by an Ar–Kr ion laser. The wavelength was 514.5 nm and the excitation power was kept low enough to avoid heating the samples.

3. Results and discussion

3.1. SEM observations

Fig. 1 displays SEM pictures of the films formed at the surface of Ti substrates with the laser treatment conditions and the colors indicated in Table 1. Quite different surface features are observed as a function of the laser fluence.

For low fluences, $F_{lp} < 25$ J cm^{-2} (colorless and yellow films), the laser treatment induces parallel scars and cracks which increase when the laser fluence increases, but the sample surface appears rather smooth. EDS analyses do not reveal significant differences all over the surface of the layers. Titanium, oxygen and a small content of nitrogen, around 1.6 at.%, are detected. For the colorless film, the detected oxygen content is very low, and the Ti signal mainly comes from the substrate. This effect is certainly reduced in the case of thicker layers, but it cannot be discarded for the yellow ones. Thus, the O/Ti ratio obtained for the yellow layers, which is equal to 0.6, can underestimate the real oxygen content in the layer. Otherwise it suggests the formation of a sub-stoichiometric titanium oxide. For high fluences, $F_{lp} > 25$ J cm^{-2} (purple and blue films), the sample surface is very rough and displays a *plowed field* aspect. The laser passage induces ablation processes and hydro-dynamic phenomena in the melting pool [7]. EDS analyses must be carefully considered in this case due to the roughness of the surface. For both purple and blue layers, different values of the O/Ti ratio were obtained depending on the analyzed area. For the highest areas, the O/Ti ratio varies in the 1.6–2 range, while it clearly decreases to around 0.9 in the lowest areas corresponding to the furrow formed by the laser impacts.

3.2. SIMS observations

The polished cross-section of a blue layer was studied by SIMS in image mode in order to analyze the in-depth composition of the layer. The binarized images corresponding to carbon and oxygen signals are displayed in Fig. 2. Results clearly show that carbon and oxygen are co-localized in the layer. In our conditions, with a lateral resolution of 5 μm, no gradient of composition is visible for carbon or oxygen.

Table 1
Laser treatment conditions and color of the films analyzed in this work

	Colorless	Yellow	Purple	Blue
P_l (W)	1.6	9	11	13–23
F_{lp} (J cm^{-2})	4	23	28	33–60

P_l (W) is the average laser power and F_{lp} (J cm^{-2}) is the laser fluence per pulse.
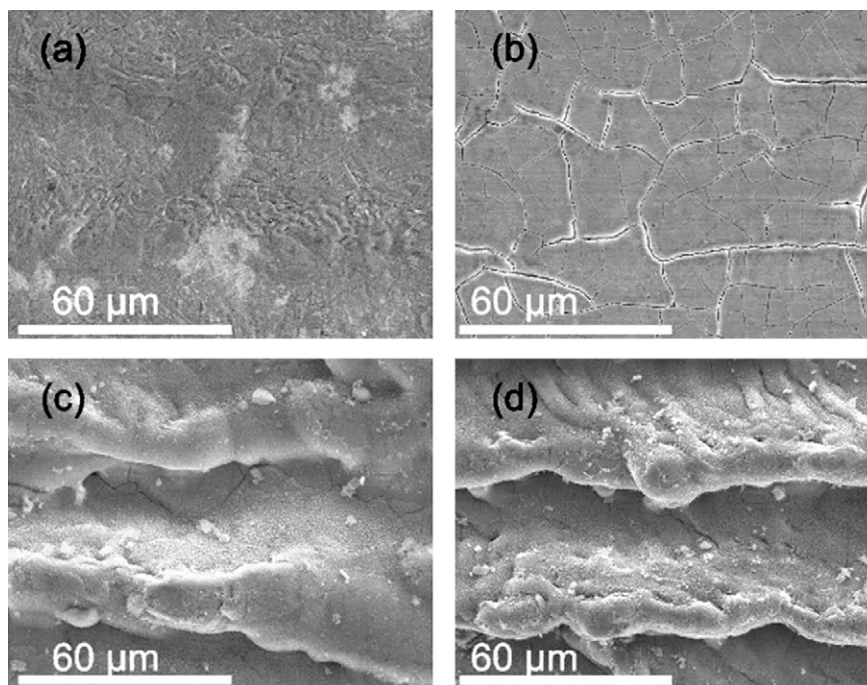
Fig. 1. SEM pictures of the surface of Ti substrates after the laser treatment with increasing laser fluences as indicated in Table 1 and showing the following colors: (a) colorless, (b) yellow, (c) purple and (d) blue.

3.3. XPS observations

Layers obtained after the different kinds of preparations were analyzed by XPS, before and after several ion bombardments, in order to obtain some information on chemical composition of the layers in addition to surface information. However, an important point has to be noticed: as evidenced in the already presented SEM results, layers obtained for low fluences (colorless or yellow) are smooth, while the ones prepared with high laser fluences (purple and blue) appear very rough, with an average roughness of about 10 μm. Information concerning layers with such a high roughness is difficult to obtain with XPS especially after sputtering. Indeed non-uniform sputtering occurs and signals coming from different zones which have been submitted to different treatments are integrated within the same XPS line. This fact makes the XPS results hard to discuss and information concerning low fluences layers will be particularly discussed here.

Before any ion bombardment, whatever the preparation conditions, large amounts of carbon and oxygen are evidenced on the surface as well as the presence of hydroxyl groups: the first ones are revealed by the relative high intensities of the C 1s and O 1s lines while a clear evidence of OH groups is given by the presence in the O 1s line of a shoulder at about 1.8 eV higher binding energy than the main line which corresponds to the oxide. Nitrogen is also present in smaller amounts on the surface. Actually layers preparation takes place in air and this should induce the presence in the layers of carbon, nitrogen and oxygen in addition to titanium. Indeed, this kind of laser processing in the presence of reactive gases is used to obtain composite layers having interesting wear resistance [1,8]. Moreover, the Ti 2p line

has a shape characteristic of pure titanium dioxide with the presence of only the two peaks Ti $2p_{3/2}$ and Ti $2p_{1/2}$ corresponding to Ti^{4+}. Indeed, the stoichiometry of the surfaces is very close to TiO$_2$, whatever the initial stoichiometry of the layers, an oxidation of the topmost layers takes place, certainly during the cooling down of the system which occurs in air.

After sputtering, the amount of hydroxyl groups and of carbon decreases. Concerning the layer stoichiometry, average oxygen versus titanium ratio equal to 0.7 is obtained for the colorless sample, while it is equal to 1.3 for the yellow one. These values are higher than the ones obtained from EDX and previous NRA analysis [7]. Moreover the presence of non-negligible nitrogen amount in addition to carbon is evidenced by XPS in these layers. Actually, in order to fit correctly the Ti 2p line after the sputtering, a special procedure [9] has to be applied which involves the presence in the layer of both titanium oxide and titanium oxy-carbo-nitride. These two kinds of species exhibit different behaviors upon argon ion bombardment and factor analysis of this line allows evidencing the presence of these different compounds inside the layers. These results should be discussed together with those obtained by Raman spectroscopy.

3.4. Raman spectroscopy observations

Fig. 3 shows the Raman spectra obtained for the samples described in Table 1. According to SEM observations, Raman spectra demonstrate the effect of the laser fluence value on the properties of the formed film.

For low fluences (colorless and yellow films), no Raman bands corresponding to crystallized TiO$_2$ phases are detected. In fact, the Raman signal is quite small in the case of the
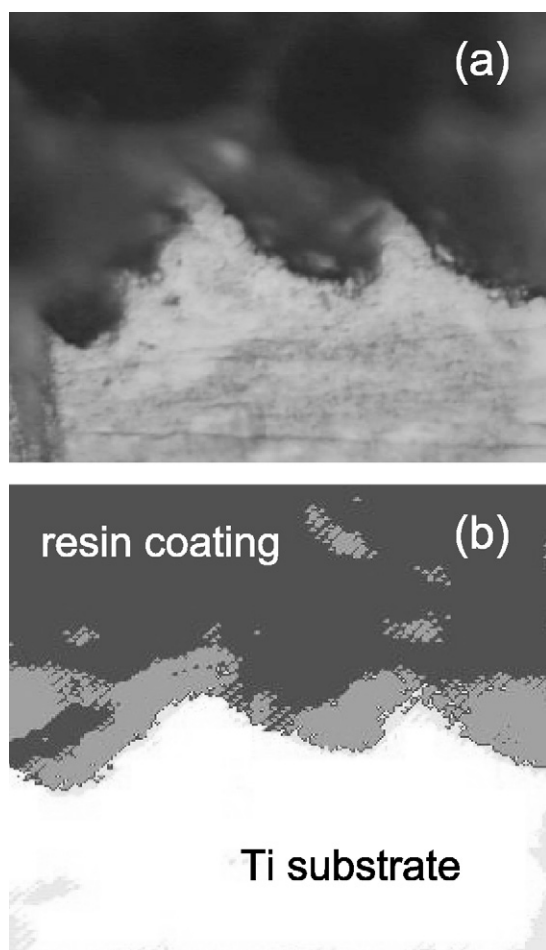
Fig. 2. (a) Optical microscope view of the polished cross-section of a resin coated sample corresponding to a blue layer and (b) image obtained for the same sample area by SIMS experiments in image mode. Only binarized carbon and oxygen signals are depicted in the image. Colors code: (gray) areas where both carbon and oxygen signals were detected, (white) areas where C and O signals were negligible (corresponding to the Ti substrate) and (black) areas where only carbon signal was detected (corresponding mainly to the resin coating).
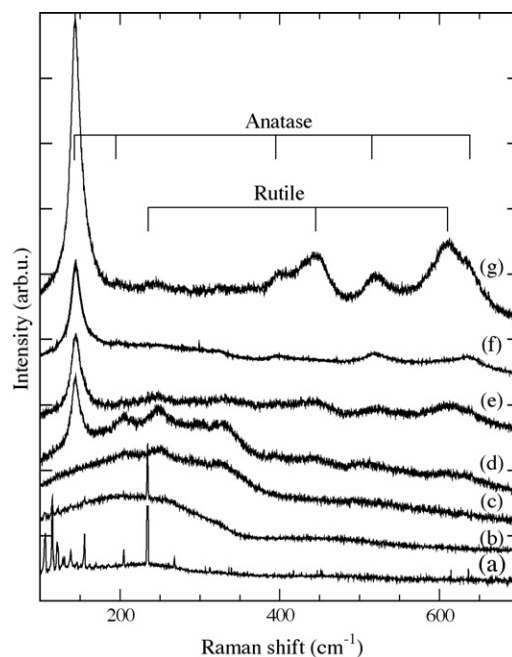

Fig. 3. Raman spectra of the layers formed with the laser treatment conditions indicated in Table 1: colorless layer (a), yellow layer (b), purple layer (lowest area (c), highest areas (d and e)) and blue layer (lowest area (f), highest area (g)). The position of the Raman bands corresponding to TiO_2 anatase and rutile phases are indicated.

colorless sample. Plasma laser lines (and Raman bands of the air) are detected for low frequencies together with a small band in the 175–275 cm^{-1} range. Analogously, a large band dominates the spectra of the yellow layer in the 100–350 cm^{-1} range. A second contribution is observed with a smaller intensity in the 400–550 cm^{-1} range. This spectrum is similar to that reported for titanium or zirconium nitrides [10,11]. The fcc structure of TiN and TiC have no allowed first order Raman modes, thus, the experimental Raman spectra displays only disorder-allowed modes and second order scattering. As previously discussed, XPS results point to the formation of titanium oxy-carbo-nitride in this layer and Raman results support this hypothesis. Amorphous TiO_2 is not revealed by Raman spectra, but its formation cannot be discarded.

For high fluences (purple and blue films), crystallized TiO_2 phases are detected, but the spectra display some differences as a function of the analyzed area and of the laser fluence during the preparation. The anatase phase of TiO_2, with a main band at

145 cm^{-1} [12], is clearly identified in the spectra obtained for both purple and blue layers by focusing on the highest areas. TiO_2 rutile bands can also be observed in these spectra and their relative intensity, with respect to the anatase bands, increases from the purple to the blue layer. On the other hand, the spectra obtained for the lowest areas display a large contribution, similar to that observed in the spectra of the yellow layers. This large band is more intense for the purple layer and it displays additional peaks at 220, 260 and 340 cm^{-1}. This structure could be related to the formation of other titanium oxides, such as Ti_2O_3 [4,13], according to previous X-ray diffraction results [7].

4. Conclusions

Commercially pure titanium substrates were laser treated within a Nd:YAG Q-switched laser giving rise to colored surface layers. The laser fluence was varied from 4 to 60 J cm^{-2}, and the color of the layers changed from colorless and yellow for low laser fluences $F_{1p} < 25$ J cm^{-2}, to purple and blue for higher fluences. Moreover, the morphology, the structure and the chemical composition of the layers were also modified.

For low laser fluences, the laser passage induces scars and cracks, but the surface layer is smooth. After sputtering of native TiO_2 formed on top of the layers, the analysis of XPS spectra allowed to obtain an O/Ti ratio varying from 0.7 for the colorless layers to 1.3 for the yellow ones. Moreover, XPS spectra revealed the presence of non-negligible nitrogen amount in addition to carbon in these layers, pointing to the

formation of titanium oxy-carbo-nitride. Raman spectra displaying large bands in the 100–350 and 400–550 cm^{-1} ranges support this hypothesis.

For high laser fluences, the sample surface is very rough. Thus, XPS analysis could not be used to obtain quantitative information on the layer composition. Raman spectra revealed the formation of crystallized TiO_2 phases, anatase and rutile when increasing the laser fluence.

Acknowledgments

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