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Influence of the composition of titanium oxynitride layers on the fretting behavior of functionalized titanium substrates: PVD films versus surface laser treatments

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ABSTRACT

In this work we compared the fretting behavior of pure titanium plates functionalized with titanium oxynitride surface layers, obtained by two methods: a Physical Vapor Deposition (PVD) method, reactive magnetron sputtering, and Surface Laser Treatments (SLT), under different mixtures of oxygen and nitrogen. The composition of the layers was determined by nuclear reaction analysis (NRA) and their structure was analyzed by Raman spectroscopy. PVD layers were TiN-like fcc layers, with an oxygen concentration going from 36 to 50 at.%. Three SLT layers were studied. The first one was a TiN-like layer containing ~28 at.% of oxygen. The second one was formed of different titanium oxide phases containing ~5 at.% of nitrogen. The third one was a titanium dioxide layer with a negligible concentration of nitrogen.
It was found that the steady friction coefficient was similar for all the layers and quite lower than that measured for uncoated Ti. The study of the fretting scars revealed a higher resistance of SLT layers to fretting wear, which can be due to the smooth layer-substrate interface. The detachment of coating particles was observed in some PVD layers.
Finally, the transfer of matter between the first bodies was studied by micro-Raman spectroscopy and nuclear reaction techniques: NRA and Particle Induced X-ray Emission.

1. Introduction

Good mechanical properties, high resistance to corrosion and low density make titanium and its alloys the materials of choice for many applications in the aeronautical, marine and chemical industries. Moreover, power generation, including nuclear, is perhaps the most important growth area for titanium. However, titanium displays poor tribological properties (highly unstable friction coefficients and low wear rate) [1,2] which must be improved for some technological applications. Nitriding and carburizing are the most popular thermochemical treatments [3], but they must be done in highly pure nitrogen or carbon containing atmosphere to avoid titanium oxidation [2]. This rules out the possibility of in-situ treatments and it can also lead to deformation of the treated parts. Another possibility is to coat titanium parts [3], mainly by physical vapor deposition (PVD), but the adhesion and the corrosion resistance of the coatings must be optimized. Modeling and stress simulation have been developed with the aim of predicting the performance of this kind of coating [4,5]. However, the possibility of in-situ treatments is also ruled out in this case.

Laser treatments are powerful tools for modifying the surface composition of metals. Light elements (oxygen, nitrogen, carbon) in the reactive atmosphere can be inserted in a surface layer whose composition and microstructure depend on the irradiation conditions, the atmosphere and on the thermal properties of the target [6–10]. Surface nitriding of titanium using lasers in nitrogen-rich atmospheres has been widely reported [8,11,9,12]. Moreover, the improvement of the titanium tribological properties by laser treatments has also been reported [13–15]. The use of fiber lasers allows considering in-situ treatments.

In this work, we compare the fretting behavior of commercially pure titanium plates functionalized with titanium oxynitride films obtained by two methods: a physical vapor deposition (PVD) method, reactive magnetron sputtering, and surface laser treatments (SLT) within a reactive atmosphere with different mixtures of oxygen and nitrogen. The fretting behavior of both kinds of surface layers will be compared by using the friction coefficient and the morphology of the fretting scars. The microphases present in the layers and the scars were mainly

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studied by micro-Raman spectroscopy. Nuclear Reaction Analysis (NRA) was used to quantify the concentration of light elements in the surface layers and to map their spatial distribution. Particle induced X-ray emission (PIXE) was used to study the matter transfer from the fretting ball to the layers.

2. Experimental details

Commercially pure titanium plates (10 mm × 10 mm × 1 mm) were used for surface laser treatments and as substrates for PVD layers. The substrates were mechanically polished with a diamond paste and then washed with ethanol. The surface roughness of the substrates was $R_a = 0.1$ μm.

2.1. Laser treatments

The laser treatments were performed using an infrared Nd:YAG laser (KALUTI) emitting pulses of $\tau = 40$ ns at 1064 nm with a repetition rate of 10 kHz. The laser spot (about 50 μm in diameter) was moved over the sample surface with a constant velocity to form parallel straight lines with a fixed interline spacing (Table 1). The laser power and the irradiance value used for each SLT are given in Table 1. The irradiance was the same range as that used in previous works [9,16]. SLT was performed in a laboratory-sized chamber, under a reactive gas mixture of oxygen and nitrogen (Table 1). The goal was to obtain different concentrations of both elements in the SLT layers.

2.2. PVD films

Polished titanium substrates were coated with oxynitride films, TiO_xN_y by reactive DC magnetron sputtering in a laboratory-sized deposition system. The deposition system is formed by two vertically opposed rectangular magnetrons (unbalanced of type 2), in a closed field configuration. The films were prepared with the substrate holder positioned at 70 mm from the target in all runs, using a DC current density of 100 A m^{-2} on the titanium target (99.6 at.%). A gas atmosphere composed of argon and a reactive N_2+O_2 gas mixture (17:3 ratio) was used [17]. The Ar flow was kept constant at 60 sccm (3.10^{-1} Pa) for all depositions. The mixed reactive gas flow ($N_2 + O_2$) was 6 sccm for layer P3, 12.5 sccm for layer P2 and 20 sccm for layer P1 (corresponding to partial pressures of 8.10^{-2}, 1.10^{-1} and 2.10^{-1} Pa, respectively). The working pressure was approximately constant during the depositions (varying slightly between 0.4 and 0.5 Pa). The substrates were grounded and no external heating was used. A delay time of five minutes was used before positioning the surface of the samples in front of the Ti target in order to avoid target poisoning resulting from previous depositions and also to assure a practically constant deposition temperature of the substrates during film growth.

2.3. Fretting tests

The tribometer used is based on a piezoelectric actuator APA 120 ML from Cedrat technologies. The contact geometry was a ball on a plane. The ball was made of bearing steel (100Cr6 steel, hardness HRC 60) with a diameter of 24 mm. The Ti plates were stuck with glue to a steel bulk. The ball sample was subjected to alternating movement with an amplitude $\delta = \pm 50$ μm and a frequency of 10 Hz. The normal force, P, on the ball was kept to 11 ± 1N leading to a contact pressure of 450 ± 15 MPa. Fretting tests were done with 20,000 cycles. The measured values of the normal force, P, the tangential force, Q, and the displacement amplitude, δ, were acquired and processed by a specific software [18]. The ball movement was perpendicular to the laser scanning direction in the SLT samples for a better accommodation of the ball-layer contact. Some anisotropy can be expected in the fretting behavior of SLT layers as a function of the ball movement direction. All the fretting tests were done at 22 °C. The humidity in the room was not controlled.

Table 1
Laser treatment parameters: laser scanning velocity (v), interline spacing (p), number of accumulated impacts (Np), laser power (P), irradiance (I), composition of the $O_2 + N_2$ gaz mixture.

SLT layers	v (mm s^{1-})	p (μm)	N_p	P (W)	I (10^{12} W m^{-2})	O_2 (vol.%)	N_2 (vol.%)
L1	40	10	49	10	25	20	80
L2	40	10	49	10	25	5	95
L3	10	50	39	14	35	2	98

2.4. Characterization techniques

The composition and the distribution of light elements in the layers were analyzed by NRA, which allows quantitative analysis of oxygen and nitrogen without influence of the chemical environment and a low influence of the roughness [9]. 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 [9]. Note that the same element may produce more than one peak when several nuclear energy levels are involved. The atomic concentrations of oxygen and nitrogen were determined by using SiO_2 (bulk) and a TiN layer as standards. The accuracy of the method was about 2 at.%. 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 [19] 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 accuracy of the method was about 100 μm.

The distribution of titanium and iron in the fretting scars was studied by PIXE, whereas NRA was used for mapping the oxygen spatial distribution.

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. Grazing-incidence X-ray diffraction (XRD) experiments (not shown here) were also done in order to complete the structural characterization of the surface layers.

A field emission SEM JSM-7600F (JEOL) was used to obtain surface images of the samples. Cross-section observations of PVD films deposited on Si substrates were done for determining the film thickness.

A Veeco Wyko NT9100 optical profiler was used for obtaining non-contact 3-D surface measurements of the layers, the fretting scars and the corresponding ball counterparts using vertical scanning interferometry.

3. Results and discussion

3.1. Surface layer composition and structure

The composition of both PVD and SLT layers was determined by NRA. Fig. 1 shows NRA spectra obtained with optimal conditions for nitrogen detection. NRA spectra (not shown here) were also obtained with optimal conditions for oxygen detection (see Experimental details).

Spectra in Fig. 1 show two peaks corresponding to nuclear reactions involving nitrogen, the most intense peak corresponds to the $^{14}N(d,p_0)$

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