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Superficial characterization of a TiO_2 – $TiN_{0.26}$ layer implanted in Titanium

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Samples of pure Titanium were treated by means a PIII process using a dense DC glow discharge with different mixtures of nitrogen–oxygen and oxygen pure. The surface of treated samples was analyzed by means of different techniques such as X-ray diffractometry, Scanning Electron Microscope, Vickers Microhardness tester and profilometer. We conclude that the modified surface is formed by $TiN_{0.26}$ diffused into TiO_2 in rutile phase, forming a uniform layer up to 10 µm in thickness and whose resultant microhardness is almost five times greater than that of untreated titanium. Some control over the superficial parameters is taken by varying the proportion of nitrogen–oxygen at a pressure of 1×10^{-2} Torr (~1.33 Pa), obtaining a thicker layer, a harder surface or a reduced roughness. The identified phases have biocompatible properties, which provide interest in the bioengineering field.

Keywords: Plasma immersion ion implantation; X-ray diffraction; Tribology and hardness; Scanning electron microscopy; Surface modification.

1. Introduction

Titanium and its alloys have attracted attention for a long time as biomaterials thanks to their excellent mechanical properties such as a very high corrosion resistance and good mechanical strength. However, some disadvantages, especially a relatively poor wear resistance, have limited its application [1]. Mechanical properties like wear and hardness can have an important influence on biocompatibility [2] by restricting the use of titanium in mobile parts and joints.

Different methods to improve the superficial parameters of Titanium have been tested: coatings, anodizing, plating, plasma spraying [3], nitrogen plasma immersion ion implantation (N-PIII) [4], [5] and oxygen plasma immersion ion implantation (O-PIII) [5], [6]. PIII-related processes have demonstrated its effective improvement of the surface properties of biomedical titanium alloys with an extended efficiency, since it eliminates the line-of-sight limitations of conventional beam ion implantation [1].

In order to enhance the nitrided layers increasing the superficial hardness of CpTi (commercially pure titanium, grade 1 99.495% CpTi) as well as to develop a spare titanium oxide substrate in the rutile phase intended to increase the biocompatibility, and whereby the osseo-integration of the sample, a low energy PIII process was carried out on CpTi on the basis of several calibrated gas mixtures of nitrogen and oxygen. Some significant microhardness, roughness, scanning electronic microscopy (SEM), X-ray diffractometry (XRD) and Raman spectroscopy diagnosis of this process is reported.

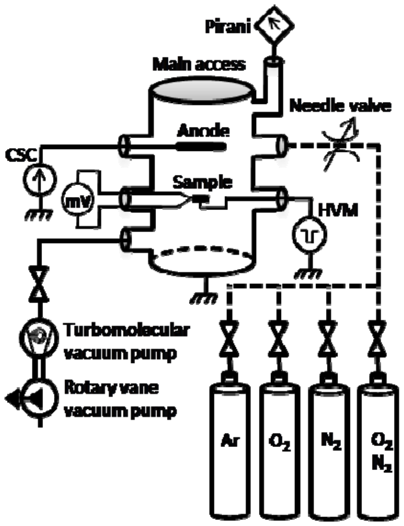


Figure 1. Schematic diagram of the system used for the PIII process.

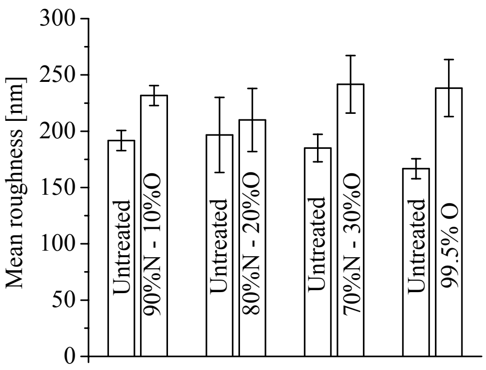
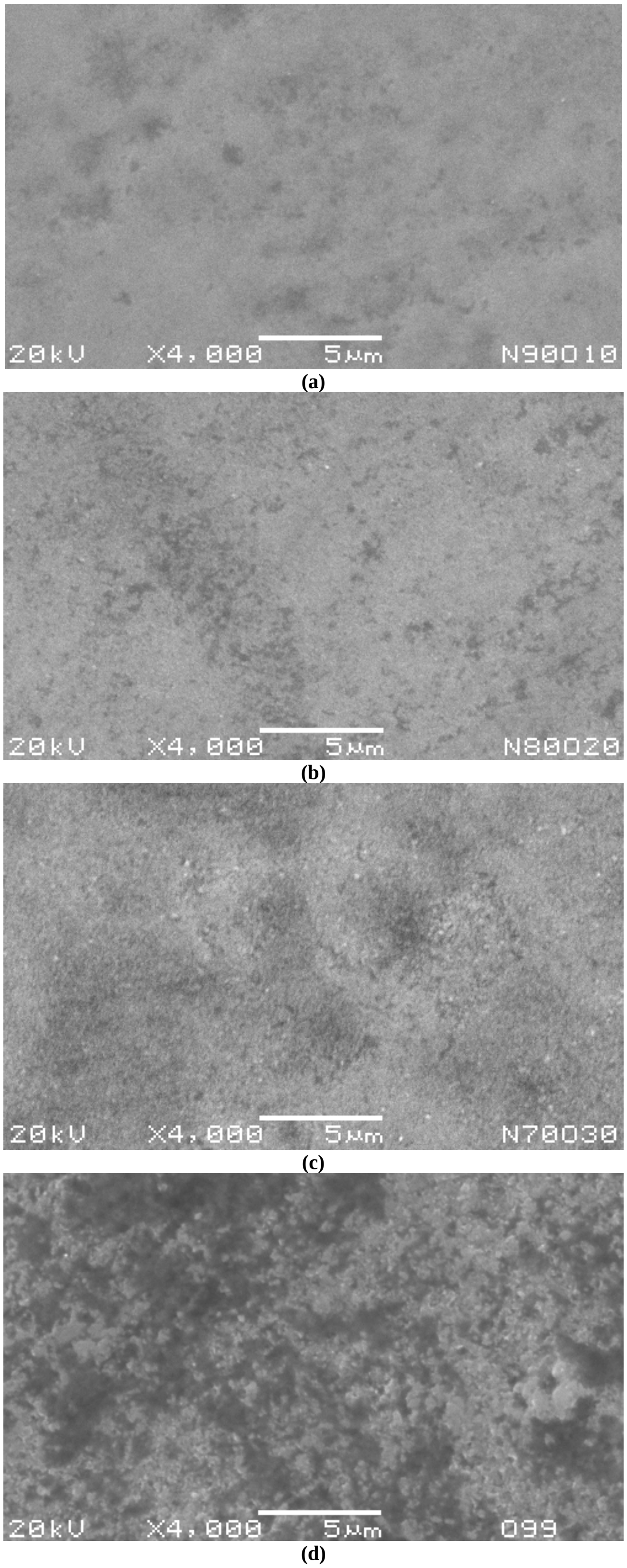


Figure 2. Mean roughness of the samples before and after the treatment.



(a)

(b)

(c)

(d)

Figure 3. Micrographs of the samples surface: microstructure of the modified surface. (a) Sample treated with 90%N–10%O, (b) 80%N–20%O, (c) 70%N–30%O and (d) 99.5% oxygen pure.

2. Experimental set-up

The CpTi was cut in cylindrical pieces with 10 mm in diameter and 5 mm thickness. The samples were mirror polished and ultrasonically cleaned in acetone. Then, they were introduced into the process chamber made of SS-304 stainless which has a cylindrical geometry with a 0.6 m length and a 0.3 m diameter (Figure 1). A base pressure of 10^{-6} Torr (~10^{-4} Pa) was achieved with a turbomolecular vacuum pump, and then the gas pressure established at 1×10^{-2} Torr (~1.33 Pa) by admitting different gas mixtures. The gases used were nitrogen (99.995% pure) and oxygen (99.5% pure) in mixtures of 90%N–10%O, 80%N–20%O, 70%N–30% O and 99.5% pure oxygen.

A plasma discharge was produced using a constant current DC power supply with a maximum output power of 1200W. The DC power supply was specifically designed and constructed, based on a current–source converter (CSC) in a resonant mode [7]. The discharge was established at a constant 2000 mA current leading to an electron plasma density of about 5×10^{16} m^{-3}, which was measured with a 0.98 mm long 0.34 mm diameter double cylindrical probe [8].

After that, the samples were biased by means of a high voltage pulse modulator (HVM) driven to 150 µs pulse width at a repetition rate of 1.6 kHz and 3.5 kV in amplitude. Such conditions intended to maintain the sample temperature around 600 ºC during the treatment duration (4 h for each sample).

With an aim to evaluate the efficiency of the PIII process in the treatment of Titanium, different techniques of superficial analysis were used including: profilometer, Vickers microhardness, X-ray diffractometry, scanning electron microscopy and Raman spectroscopy.

3. Results and discussion

3.1. Roughness

The roughness of a metal surface determines important properties such as reflectivity, lubricant transport, weldability and adhesion of surface layers [9]. In addition, the roughness of the surface is closely related with the friction coefficient, affecting the overall dynamic response of a material [10].

For the above-mentioned, the mean roughness (Ra) of the treated samples was determined by means a Mitutoyo Surftest 402 profilometer and the results are plotted in figure 2 exhibiting the average value and the error bars for the absolute mean deviation of the measurement in six different regions of the sample. For all cases, the roughness was measured before (untreated) and after the treatment with each one of the N–O gas mixtures as well as the sample treated with 99.5% pure oxygen.

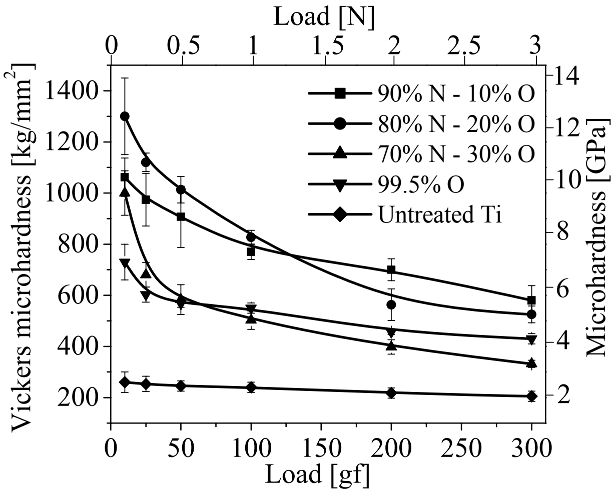


Figure 4. Microhardness as a function of indentation load.

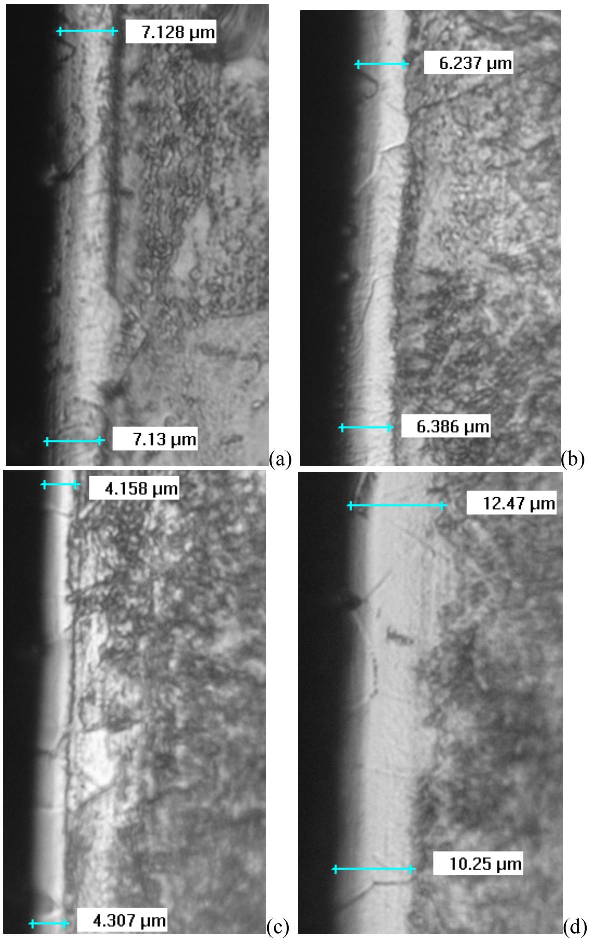


Figure 5. Micrographs of the samples cross-section. The thickness and appearance of the modified layer is observed. (a) Sample treated with 90%N–10%O, (b) 80%N–20%O, (c) 70%N–30%O and (d) 99.5% oxygen pure.

From the figure 2 can be inferred that the sample treated with the mixture of 80%N–20%O had the smaller change in roughness after the treatment, because is noted an increment of only 13 nm in the mean roughness. In contrast, the sample treated with pure oxygen showed an increment of 72 nm in its mean roughness after the implantation process. Therefore, it can be said that a high concentration of oxygen redounds in a marked increment in the roughness of the sample.

With the purpose of support the data obtained from the profilometer, scanning electron microscopy was used to obtain micrographs of the samples, and they are showed in figure 3. In accordance with the results from mean roughness, the surface of the samples treated with the higher oxygen concentrations present a more irregular microstructure when they are compared with the samples treated with the mixtures that are low in oxygen.

3.1. Microhardness

The microhardness of the treated samples was characterized using a Buehler Micromet 5104 Vickers microhardness tester, with loads from 10 to 300 gf (~9.8×10^{-2} to ~2.94 N) applied during 15 s (figure 4). The reported data are the average value taken over six indentations per load, and the error bars represent the mean deviation.

As can be observed in figure 4, the microhardness of the samples treated with mixtures of nitrogen–oxygen is higher than the samples treated with oxygen only, achieving up to 1300 HV (~12.75 GPa) at 10gf (~9.8×10^{-2} N) for the sample treated with 80%N–20%O. This is to say that the superficial hardness of the sample is increased five times with respect to the untreated sample, with the expectative of a better performance in wear.

The best values for microhardness at low loads (100 gf, ~0.98 N, or less) are attained by the sample treated with the 80%N–20%O mixture, but the major values at high loads (more than 100gf) are accomplished with the mixture containing 90%N–10%O. The latter means that the thickness of the modified layer affects the hardness at high loads. So, a harder but thinner layer is expected in the sample treated with 90%N–10%O, and viceversa for the sample treated with the 80%N–20%O mixture.

A similar behaviour is noted for the samples treated with the 70%N–30%O mixture and the treated with oxygen pure. Higher hardness is observed at high loads for the sample treated with the mixture, while, for a high load, the sample treated with oxygen is better. So, a thinner layer is expected for the sample treated with the mixture. The noticeable enhancement of the hardness of the material treated with N–O mixtures is due to the nitrogen-enriched layer caused by diffusion of nitrogen at high-temperature PIII [4].

In order to verify the aforementioned, the samples were cut in their cross-section and then they were mirror polished to

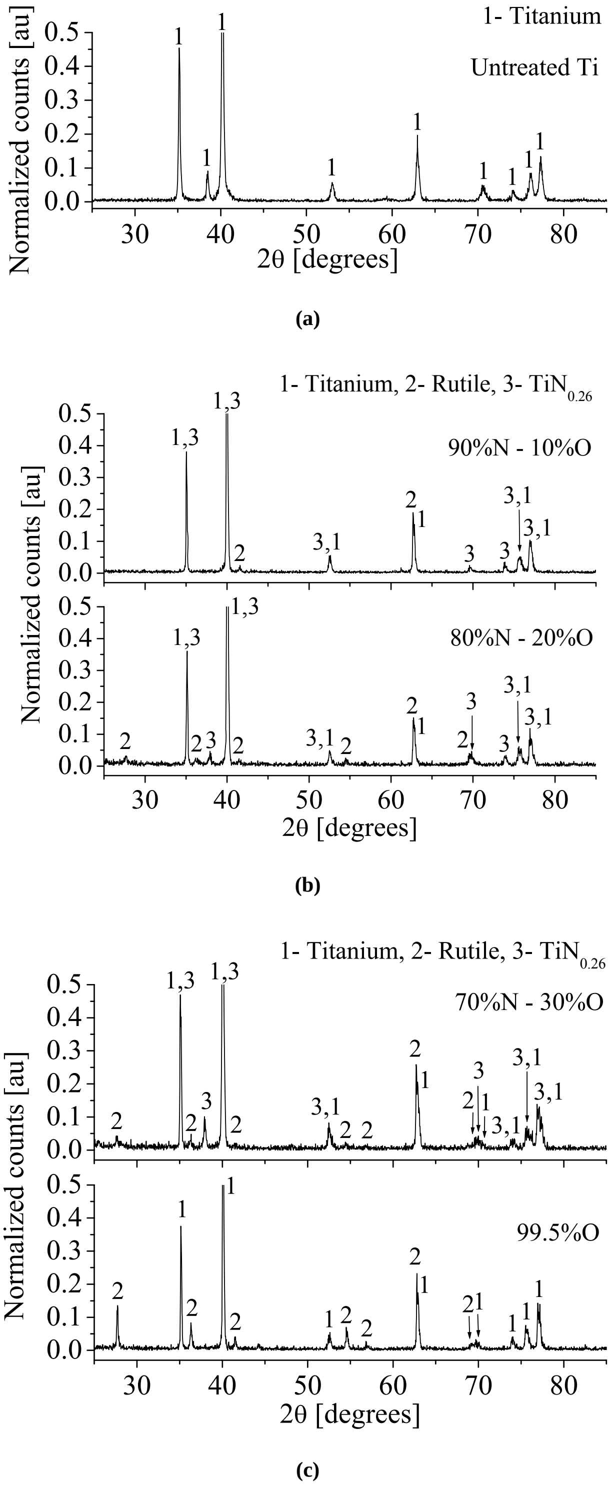


Figure 6. XRD patterns for (a) untreated sample, (b) samples treated with 90%N–10%O and 80%N–20%O, (c) samples treated with 70%N–30%O and 99.5%O pure.

be observed with the microscope; the obtained micrographs are showed in figure 5. The thicker layer corresponds to the sample treated with oxygen pure (figure 5.d) with a layer of about 10 µm (mean deviation of 1 µm).

Furthermore, for the samples treated with a mixture of N–O, the layer's thickness appears directly related with the amount of nitrogen in the mixture. Then, the layer of the sample treated with 90%N–10%O reports 7 µm in average (mean deviation of 0.5 µm), 6.5 µm for the sample treated with 80%N–20%O (mean deviation of 0.4µm) and 4.2 µm for the sample treated with 70%N–30%O (mean deviation of 0.25 µm). All of the above-mentioned is in accordance with the behaviour of the microhardness.

The effect of the treatment with different gas mixtures over the microhardness values is evident when only the low–load interval is observed in Figure 4 (50–10 gf or ~0.49–0.098 N). Then, the hardness of the substrate has a negligible effect in the measurement. The harder layer is obtained with a mixture of 80% N–20% O. The greater nitrogen content entails a catalysing effect on the titanium oxidation although it may also lead to the formation of $TiN_{0.26}$ in the nitrided substrate.

3.2. X-Ray Diffraction

Aiming to assess the formation of biocompatible phases in the processed material, XRD analysis was carried out using a D5000 Siemens X-ray diffractometer. The figure 6(a) exhibits the XRD pattern for untreated titanium where Ti peaks are marked. In figure 6(b), the patterns for the samples treated with 90%N–10%O (up) and 80%N–20%O (down) are plotted. And, in a similar way, the figure 6(c) plots the XRD patterns for the samples treated with 70%N–30%O (up) and 99.5% oxygen pure (down).

The presence of Rutile (mainly at 2θ=27.6°, 41.4° and 54.5°) and $TiN_{0.26}$ (mainly at 2θ=37.9°) is evident for the samples treated with 80%N–20%O and 70%N–30%O mixtures, while the sample treated with 90%N–10%O shows only traces of the mentioned compounds. The latter can be explained by the existence of non-crystalline structures or non-stoichiometric compounds in the modified layer. The sample treated with oxygen pure clearly shows the peaks corresponding to Rutile, and the peaks for $TiN_{0.26}$ are not displayed.

The absence of the Ti peak at 2θ=38.5° (plane 002) and the reduction in the relative height of the Ti peak at 2θ=35.2° (plane 100) must be noted in the spectra of all the treated samples. Plane 100 is the most probable entrance plane for the implanted ions thanks its reduced superficial packaging; so, the change in its diffraction peak's height is because the atoms entered in the crystalline structure of Titanium. On the other hand, the absence of the diffraction peak for the plane 002 (the most saturated external plane) is due to an expected strain in the crystalline structure, which deforms it annulling the diffracted peak.

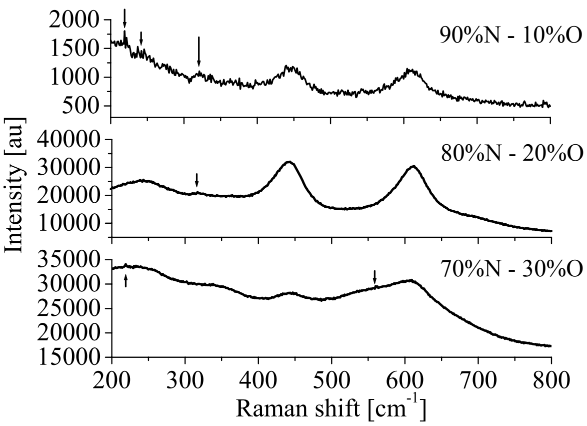


Figure 7. Raman spectra for the samples treated with different nitrogen –oxygen mixtures.

The solid solution that results from substitutions with nitrogen atoms in the titanium lattice often contains the $TiN_{0.26}$ phase without altering the substrate compact hexagonal structure whose parameters are c=4.765Å and a=2.956Å. Consequentially, the maximal (100%) diffraction relative intensities, corresponding to the planes (200), (112) and (201), are respectively given by the 2θ diffraction angles: 73.99º, 75.65º and 77.08º. On its part, titanium 2θ diffraction angles are 74.26º, 76.30º y 77.32º which are very close to those of the $TiN_{0.26}$ phase, although with a much lower relative intensity, whereby the respective peaks appeared broadened. It follows that the three planes of highest intensity in Ti are the same as those of the $TiN_{0.26}$ phase, in other words, the formation of this phase is favoured by being a compact hexagonal structure like that of the α-titanium. The crystalline phase of rutile (TiO_2) increased along with the oxygen concentration (see Fig. 3). It should be noticed that the x ray diffraction pattern from the $TiN_{0.26}$ phase does not give evidence of its spatial group. This fact can be attributed to a considerable deformation of the lattice created by the disproportioned atomic radii of nitrogen (0.74Å) and titanium (1.467Å) [11], in spite of the hexagonal structure of their solid solution. It is also interesting to remark that both, TiO_2 (rutile) and $TiN_{0.26}$ are considerably biocompatible compounds [2], [12].

3.3. Raman Spectroscopy

The samples treated with a mixture of N–O were analyzed by means of Raman Spectroscopy, in order to corroborate the results obtained from XRD (He-Ne laser with 632.8 nm in wavelength). As can be noted in the figure 7, TiO_2 is identified with peaks at 447 and 610 cm^{-1} [13], [14] confirming the existence of Rutile. On the other hand, two bands centred at 242 and 562 cm^{-1} identify TiN [14]. However, the sample treated with 90% N–10% O (figure 7.a) shows two extra peaks at 219 and 321 cm^{-1} which have been attributed to disordered TiO_2 [15]. This fact validates the results from XRD analysis, concluding that stoichiometric TiO_2 cannot be formed from a mixture of 90% N–10% O due a low fluency of Oxygen during the process.

4. Conclusions

Samples of CpTi were treated with mixtures of nitrogen–oxygen and oxygen pure in a PIII process at low pressure. The modified surface was characterized with profilometer, and it was observed that a high concentration of oxygen in the plasma redounds in an increased roughness while the samples treated with a low amount of oxygen are not substantially affected.

The modified layer of the samples treated with N–O is formed by Rutile and $TiN_{0.26}$ (4–8 μm) while the sample treated with oxygen has a layer composed by Rutile only (10 μm). Due to the simultaneous existence of TiO_2 and $TiN_{0.26}$, the hardness of the layer is substantially greater in the mixtures of nitrogen–oxygen than in the treatment with pure oxygen, being up to five times harder than untreated Titanium. The rutile phase developed on the treated samples is sufficient to improve their biocompatibility and potential for osseo-integration. At the same time, the addition of a nitrided layer must increase substantially the wear performance of the treated pieces.

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