SURFACE CHARACTERIZATION OF TITANIUM AFTER ARGON SPUTTER CLEANING

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Abstract

Surface integrity plays a key role in the surface modifications and coating processes that provide high and long-term performance of the treated components. Argon ion bombardment is widely used in many surface modification processes and for surface pre-treatment. The effect of argon sputter cleaning on the residual stress, hardness and surface morphology of commercially pure titanium is investigated in this work. Titanium samples were mechanically polished and then etched by argon ions. The thickness of the sputtered layer was measured by a quartz thickness monitor. The hardness was investigated by nanoindentation, the residual stress was measured by X-ray diffraction, and the surface morphology was monitored by atomic force microscopy. Removal of the surface layer by argon ion bombardment caused a decrease in residual stress and a decrease in hardness. Uneven sputtering of grains resulted in increased surface roughness. The observed changes in surface properties increased with increasing thickness of the removed layer.

Keywords: Ion etching, morphology, residual stress, hardness

1. INTRODUCTION

Titanium and its alloys are used in many engineering applications in the aerospace, automotive, chemical and biomedical industries, due to their high strength, low density and good corrosion resistance in many environments [1-4]. However, a significant disadvantage of titanium alloys is the high coefficient of friction and wear [5]. Advances and innovations in surface engineering have significantly enhanced the performance of commercially available titanium materials. Surface properties can be improved by advanced methods using accelerated ions, such as magnetron sputtering, plasma-assisted chemical vapour deposition, ion implantation and ion beam assisted deposition [6-9]. Surface integrity plays a key role in the surface modifications and coating processes that provide high and long-term performance of the treated components. A major aspect of the structural bonding of coating materials to titanium is the surface pre-treatment of the substrates. The pre-deposition treatment of the substrate has a significant influence on the durability of the adhesion bonds. Ion sputter cleaning in the pre-deposition phase of the coating process is often used to improve the adhesion of coatings [10,11]. Ion etching of the surface leads to the removal of impurities after mechanical polishing and the removal of contaminants from the air. The conditions of the sputter cleaning process (e.g. ion current density, processing time, incidence angle, etc.) influence the amount of material that is removed. Different thickness of the removed layer can have a significant effect on the surface properties of titanium and on the quality of its surface treatment.

This work presents the effect of argon sputter cleaning on the internal stress, hardness and surface morphology of commercially pure titanium grade 2. Hardness was investigated by nanoindentation, residual stress was measured by X-ray diffraction (XRD), and surface morphology was monitored by atomic force microscopy (AFM).

2. EXPERIMENTAL

The substrates were made of commercially pure titanium grade 2 in the form of a cylinder 14 mm in diameter and 3 mm in height. The samples were cut from a titanium bar, and were then ground with a series of waterproof abrasive papers. Final polishing was performed with diamond paste. Before the sputter cleaning process, the samples were ultrasonically degreased in acetone for 20 minutes, and in isopropyl alcohol, also for 20 minutes.

The samples were placed on a sample holder mounted on a rotary manipulator in a vacuum chamber, and were sputter cleaned with 700 eV argon ions to etch and remove the surface layer. The ion beam current density was about 90 μA·cm^{-2}. The sputtering rate and the thickness of the removed layer were measured by a quartz crystal monitor located in the vacuum chamber. An experimental arrangement of the sputter cleaning process is presented in **Figure 1**. The sputter cleaned samples were prepared in two groups. The thickness of the removed layer was 1 μm for the first group and 3 μm for the second group.

The nanoindentation method in continuous measurement mode (CMX) was applied to obtain depth profiles of the surface hardness [8]. The CMX indentation function was prescribed by a quasistatic force (P_{qstat}) in the range from 2 to 10000 mN. The dynamic actuation force (P_{dyn}) was prescribed in the range from 3 to 202.9 mN at a frequency of 200 Hz. For the sputtered sample, average values were obtained from 16 indents in a 4 x 4 matrix with a separation step of 5 μm. The residual stress was investigated by XRD analysis. A PANalytical X'Pert PRO horizontal powder diffractometer was used with a Co anode (λ= 0.178901 nm), a Göbel mirror in the primary beam and a parallel plate collimator in a diffracted beam. The residual stresses were evaluated using the $sin\psi^2$ method. The sputter cleaned surface was analysed by an atomic force microscope (AFM). The AFM was used in tapping mode.

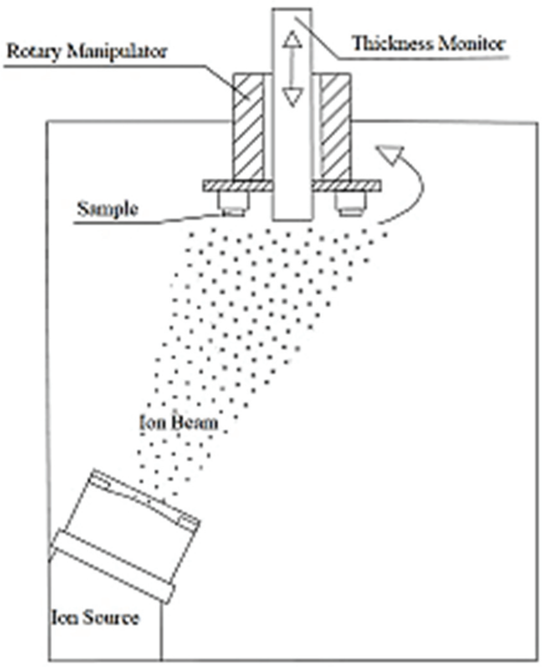

Figure 1 Experimental arrangement of the sputter cleaning process

3. RESULTS AND DISCUSSION

Figure 2 shows the evolution of the macroscopic residual stress with the thickness of the surface layer removed by argon sputter cleaning. The residual stress after polishing was found to be approximately 190 MPa. Argon sputter cleaning reduced the residual stress to approximately 124 MPa for a removed layer 1 μm in thickness, and to approximately 116 MPa for a removed layer 3 μm in thickness. There are two causes for the reduction in stress, both of which act simultaneously. In the first case, the residual stress is reduced by removing the layer in which the stress was induced by polishing. In the second case, the pressure stress induced by argon sputter cleaning counteracts the stress caused by polishing.

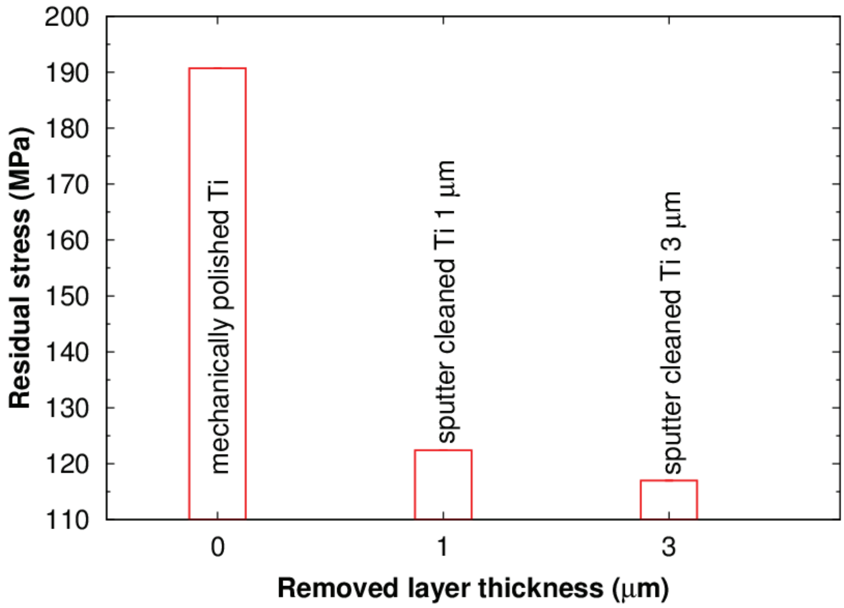

Figure 2 Macroscopic residual stress vs. thickness of surface layer removed by argon sputter cleaning

Figure 3 shows the hardness profiles measured on the polished sample and on the samples sputter claned by argon ions. It can be seen that the course of the surface hardness is not constant. Locally increased surface hardness is probably caused by internal stress after mechanical polishing. The hardness, with the maximum in the near surface region, decreases towards the depth of the sample. The results show that the surface hardness decreases with increasing thickness of the layer removed by argon sputter cleaning. A very flat profile with an almost constant course of hardness was measured on the sample with the removed layer 3 µm in thickness. The results presented here indicate that a reduction in internal stress leads to lower surface hardness values. This phenomenon has also been observed in the strained titanium lattice after ion implantation [8].

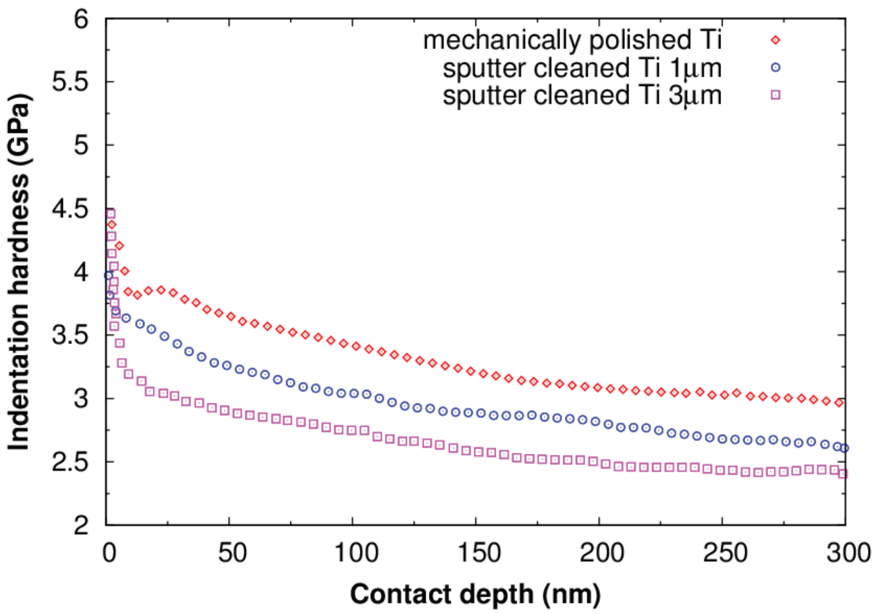

Figure 3 Hardness profiles of mechanically polished titanium and ion sputter cleaned titanium with different thicknesses of the removed surface layer

Representative AFM surface morphology scans are shown in **Figure 4**. The mechanically polished surface is relatively smooth, without major protrusions. However, the surface appears to be wavy. The typical morphology with exposed grain boundaries is observed on the surface sputter cleaned by argon ions (**Figure 4b**). Uneven sputtering of grains with different orientations leads to increasing roughness. The roughness (Ra) increased from 0.006 µm for a mechanically polished sample to 0.135 µm for a sputter cleaned sample with a removed layer 3 µm in thickness. The results show that sputter cleaning of a titanium substrate leads to increased surface roughness and reduced residual stress. These factors play a significant role in the adhesion of coatings [10-12].

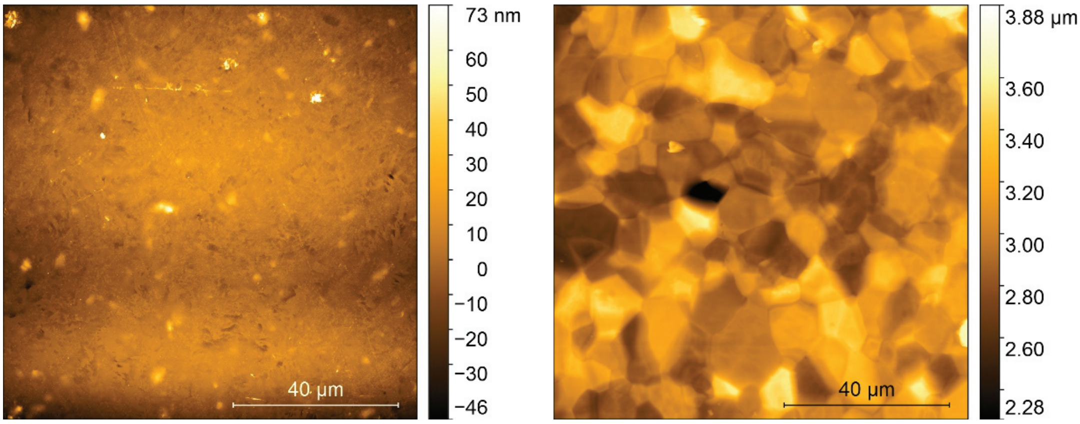

Figure 4 Representative AFM images of a mechanically polished surface (a), and an argon sputter cleaned surface (removed layer 3µm in thickness) (b)

4. CONCLUSION

The influence of the argon sputter cleaning process on the residual stress, the hardness and the surface morphology of commercially pure titanium has been demonstrated. Argon sputter cleaning reduces the residual stress from approximately 190 MPa for a mechanically polished sample to approximately 124 MPa for a removed layer 1 µm in thickness, and to approximately 116 MPa for a removed layer 3 µm in thickness. The reduction in residual stress had an impact on surface hardness. It has been demonstrated that the surface hardness decreases with increasing thickness of the removed layer. Uneven sputtering of grains with a different orientation led to increasing roughness after sputter cleaning.

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REFERENCES

[1] PETERS M., KUMPFERT J., WARD C.H., LEYENS C. Titanium alloys for aerospace applications, Advanced Engineering Materials, Vol. 5, 2003, 419-427.

[2] PODZIMEK S., TOMKA M., NEMETH T., HIMMLOVA L., MATUCHA P., PROCHAZKOVA J. Influence of metals on cytokines production in connection with successful implantation therapy in dentistry, Neuroendocrinology Letters, Vol. 31, No. 5, 2010, pp. 657-662

[3] FOJT J, JOSKA L, MALEK J, SEFL V. Corrosion behavior of Ti-39Nb alloy for dentistry. Materials Science and Engineering C, Vol. 56, 2015, pp.532-537.

[4] VLCAK, P. Evidence of a defect structure in high fluence nitrogen ion implanted titanium and its effect on corrosion, Results in Physics, Vol. 11, 2018, pp. 274-277.

[5] POHRELYUK I.M., SHEYKIN S.E., PADGURSKAS J., LAVRYS S.M. Wear resistance of two-phase titanium alloy after deformation-diffusion treatment, Tribology International, Vol. 127, 2018, pp. 404-411.

[6] CHODUN R., NOWAKOWSKA-LANGIER K., WICHER B., OKRASA S., MINIKAYEV R., ZDUNEK K. Reactive sputtering of titanium compounds using the magnetron system with a grounded cathode, Thin Solid Films, Vol. 640, 2017, pp. 73-80.

[7] MOVASSAGH-ALANAGH F., ABDOLLAH-ZADEH A., ALIOFKHAZRAEI M., ABEDI M. Improving the wear and corrosion resistance of Ti-6Al-4V alloy by deposition of TiSiN nanocomposite coating with pulsed-DC PACVD, Wear, Vol. 390-391, 2017, pp. 93-103.

[8] VLCAK P., DRAHOKOUPIL J., VERTAT P., SEPITKA J., DUCHON J. Hardness response to the stability of a Ti(+N) solid solution in an annealed TiN/Ti(+N)/Ti mixture layer formed by nitrogen ion implantation into titanium. Journal of Alloys and Compounds, Vol. 746, 2018, pp. 490-495.

[9] VLCAK P., JIRKA I. Protective sliding carbon-based nanolayers prepared by argon or nitrogen ion-beam assisted deposition on Ti6Al4V alloy, Journal of Nanomaterials, Vol. 2016, Art. No. 1697090, 2016, pp. 1-9, Doi:10.1155/2016/1697090.

[10] UTRERA O.H., ABUNDIZ-CISNEROS N., SANGINES R., DILIEGROS-GODINES C.J., MACHORRO R. Cleaning level of the target before deposition by reactive direct current magnetron sputtering, Thin Solid Films, Vol. 646, 2018, pp. 98-104.

[11] VLCAK P. The effect of ion irradiation and elevated temperature on the microstructure and the properties of C/W/C/B multilayer coating, Applied Surface Science, Vol. 365, 2016, pp. 306-313.

[12] TOLDE Z., STARY V., CVRCEK L., VANDROVCOVA M., REMSA J., DANIS S., KRCIL J., BACAKOVA L., SPATENKA P. Growth of a TiNb adhesion interlayer for bioactive coatings, Materials Science and Engineering C, Vol. 80, 2017, pp. 652-658.