

Titanium oxidation by pulsed oxygen plasma

M. Z. BALBAG, S. PAT, I. CENIK, N. EKEM, T. AKAN, B. BAKSAN^a, R. VLADOIU^b, G. MUSA^b

Eskisehir Osmangazi University, Physics Department, Eskisehir, Türkiye

^a*Eskisehir Osmangazi University, Metallurgy Institute, Eskisehir, Türkiye*

^b*Ovidius University, Physics Department, Constanta, Romania*

The high oxygen affinity of titanium can be used to improve the surface hardness and wear resistance of titanium. The aim of the present study is controlled preparation and characterization of oxidized titanium surfaces. Such surfaces are of general technological interest. The samples (17 x 4 x 0,3 mm) of commercially pure titanium were oxidized by means of the high voltage pulsed discharge. The discharge chamber was introduced an oven system which reaches the elevated temperature of 900 °C. The oxidation of titanium sample was performed for various oven temperatures (300, 500 and 700 °C) but fixed discharge parameters (interelectrode distance, discharge current and discharge pressure). The microstructure of the oxidated titanium samples was examined by optical metallographic techniques and Scanning Electron Microscopy (SEM). The thickness and the hardness of the samples were measured.

(Received September 25, 2007; accepted March 12, 2008)

Keywords: TiO₂, Pulsed plasma, Oxygen discharge, Anodization, SEM, EDX, Hardness, Thickness

1. Introduction

Oxidation is also form of surface modification [1]. When a metal semiconductor surface is immersed in oxygen/argon plasma, an oxide layer can be formed on top of the surface. When the surface is at “floating potential”, no current flows toward the substrate during the oxide growth, and the process is called “plasma oxidation”. The plasma species (neutrals, electrons, positive and negative ions) can reach the substrate by diffusion, and the formed oxide layer is generally thin, typically less than 10 nm. When a positive bias is applied to the surface, electrons and negative ions are accelerated toward the substrate, and the oxide growth is stimulated. This process is than generally called ‘plasma anodization’, and the oxide layers can reach a thickness of several μm . [2-6]

In some cases, a negative bias is applied to the substrate. The thickness of the oxide layer is then controlled by diffusion, which can be enhanced by the bombardment of positive ions. In this case, equilibrium can be reached between the growth rate and the rate of sputter-removal. By varying the plasma parameters, such as electrical power, pressure and argon/oxygen ratio, the thickness of the oxide layer can be very accurately controlled. [2]

The advantage of plasma oxidation and anodization is that it can be performed at lower temperatures than thermal oxidation. Typically, the plasma oxidation of silicon occurs at a temperature of 300 – 500 °C. Another application of plasma oxidation is the fabrication of high T_c super conductors by ECR reactors [1-2].

2. Experimental Setup

Oxide layers on the titanium surface were produced using pulsed oxygen plasma in a low pressure discharge tube. Experimental design is schematically shown Figure 1. Advantages of the experimental system are very basic and useful.

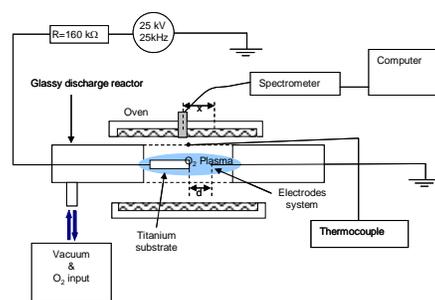


Fig.1. Experimental system of the oxidation pulsed plasma process

3. Experimental Results

Experimental parameters are given in Table 1. Except for these substrates, we keep a sample “0” as a reference probe for comparisons after the plasma treatment following parameters. Probes 1-7 were treatment in approximately 3.4×10^{-1} mbar. Probe 8 was kept in 1.8×10^{-1} mbar for plasma surface treatment.

Table 1. Experimental Parameters.

| Parameter Group (PM) | d(mm) | T(°C) | t(min) | V(kV) |
|----------------------|-------|-------|--------|-------|
| 1 | 6 | 704 | 15 | 20 |
| 2 | 6 | 550 | 15 | 20 |
| 3 | 6 | 550 | 30 | 20 |
| 4 | 6 | 704 | 30 | 20 |
| 5 | 10 | 550 | 15 | 20 |
| 6 | 10 | 704 | 15 | 20 |
| 7 | 6 | 600 | 15 | 20 |
| 8 | 13 | 300 | 20 | 14 |

3.1 Optical microscope image of the samples

For the optical microscope image of samples were used by Metallographic Optic Microscope Olympus Leco

2001. Optical Microscope images of the all samples are shown in Figure 2. These images of substrate were taken from cross section of the samples.

3.2 Thickness Measurement results of titanium substrates

The oxide layer thicknesses were measured by Metallographic Optic Microscope Olympus Leco 2001 and results are listed in Table 2. All thickness measurements were collected from 50 points on the substrate surface layer.

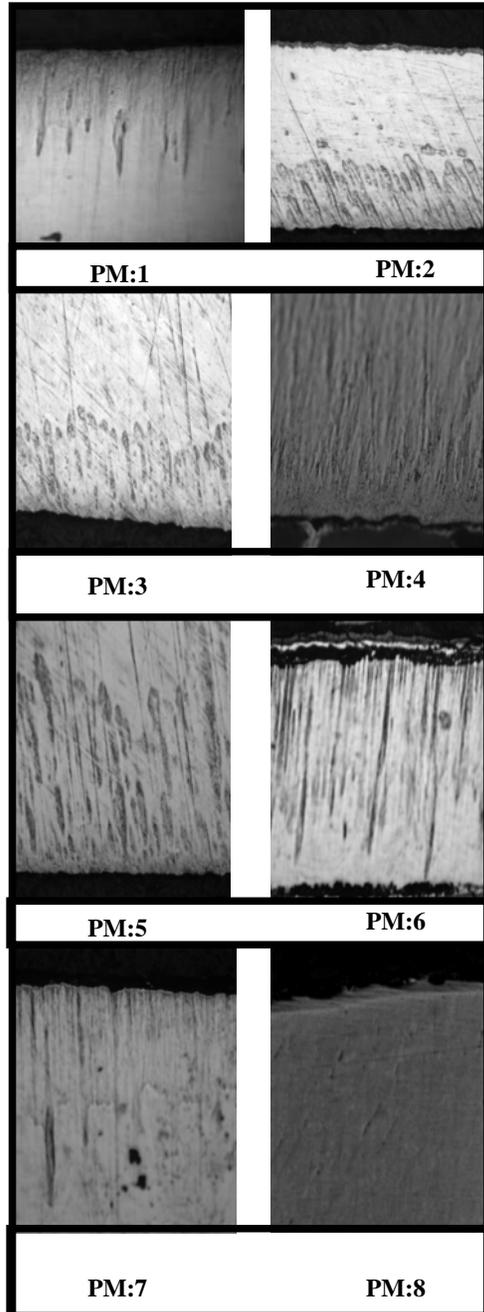


Fig. 2. Optical microscope images at 200 magnifications at various parameters shown in Table 1.

Table.2 The thickness results of the oxide layer

| Parameter Group | Max. Thick. (μm) | Min. Thick. (μm) | Mean Thick. (μm) |
|-----------------|-------------------------------|-------------------------------|-------------------------------|
| 1 | 261.73 | 88.89 | 134.52 |
| 2 | 164.60 | 93.82 | 125.58 |
| 3 | 248.56 | 60.91 | 126.88 |
| 4 | 78.73 | 22.38 | 39.58 |
| 5 | 383.54 | 184.36 | 282.52 |
| 6 | 335.80 | 177.78 | 256.22 |
| 7 | 324.28 | 121.81 | 180.96 |
| 8 | 19.694 | 13.129 | 16.411 |

3.2. Micro hardness measurement results of titanium substrates

The oxide layer micro hardness were measured by HMV-2000 Shimadzu Micro hardness system. Micro hardness results are listed in Table. 3

Table 3. Micro hardness results of the oxide layers

| Parameter Group (PM) | Mean Micro hardness (HV) |
|----------------------|--------------------------|
| 0 | 247,6 |
| 1 | 547.8 |
| 2 | 671.4 |
| 3 | 523.2 |
| 4 | 636.4 |
| 5 | 921.6 |
| 6 | 692.2 |
| 7 | 480.4 |

Parameter Group 0 (zero) is reference prop which is not exposure the pulsed plasma surface treatment. After plasma treatment as can be seen in Table.3, all substrate surfaces are harder than reference titanium sample.

3.3 OES Spectra of O₂ plasma

Optical emission spectra and digital image were realized in process. In addition, Pulsed O₂ plasma digital image and optical emission spectra of pulsed O₂ plasma were shown Fig. 3 and Fig. 4, respectively.

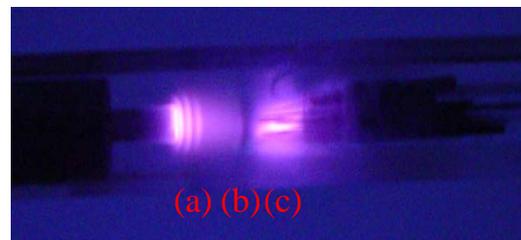


Fig..3 O₂ plasma digital image

In Fig.3, The region correspond to the applied a positive bias high pulsed voltage and c is connected with the negative bias, that is ground.

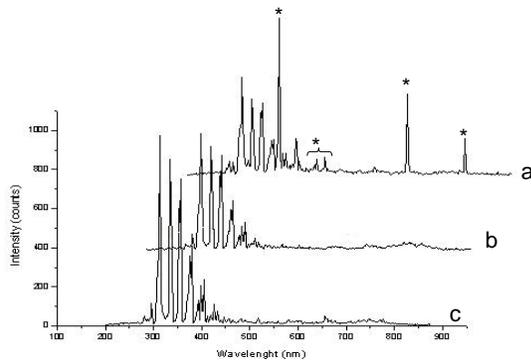


Fig. 4. OES spectra of O₂ pulsed plasma

All Ti substrates were connected to the positive bias of the pulsed power supply. According to OES spectra was taken from positive bias, extra peaks shown clearly, these peaks correspond the as * in Fig. 4 were based on negative oxygen ions.

3.4. EDX Results

EDX micro analyses were measured by using scanning electron microscope which is ZEISS mark Supra 50 VP and results are listed Table 4.

Table.4 EDX results of oxide layers

| Parameter Group (PM) | Ti (Atomic %) | O ₂ (Atomic %) |
|----------------------|---------------|---------------------------|
| 1 | 94.17 | 1.51 |
| 2 | 42.44 | 24.70 |
| 3 | 74.29 | 10.66 |
| 4 | 63.88 | 25.06 |
| 5 | 80.82 | 10.84 |
| 6 | 31.83 | 61.36 |
| 7 | 53.90 | 23.27 |

4. Results and discussion

Oxide layer on the Titanium was produced by using pulsed oxygen plasma. Ions of the oxygen tracks are seen at 200 magnifications in clearly. A linear relation in oxide layer quality with corresponding to experimental parameters but Parameter group 6 is the most optimum value. If oven temperature increases, oxide layer thickness and micro hardness increases. Experimental parameters affect the quality of oxide layers. We have used technical oxygen gas. This system is very basic and economic for other oxide layer producing methods for small titanium pieces.

Acknowledgements

These research activities were realized using device of the Scientific Research Committee of ESKISEHIR OSMANGAZI UNIVERSITY under the project number of **200319009**.

References

- [1] Alfred Grill, Cold Plasma in Materials Fabrication, IEEE Pres, 1993, 257.
- [2] J. Reece Roth, Industrial Plasma Engineering, Vol. II., IOP Publishing, 2001, 645.
- [3] K. Bange, C.R. Ottermann, O. Anderson, U. Jeschkowski, M. Laube, R. Feile, Investigations of TiO₂ films deposited by different techniques, Thin Solid Films, 197, (1991), 279.
- [4] T. Bacci, F. Borgili, B. Tesi, Surf. Eng. **14**(6), 500 (1998).
- [5] T. Bacci, F. Borgili, B. Tesi, Surf. Eng. **16**(1), 37 (2000).
- [6] A. Bogaerts, E. Neyts, R. Gijbels, J. Mullen, Gas Discharge Plasmas and Their Applications, Spectrochimica Acta Part B 57,2002, 609-658.

*Corresponding author: zbalbag@ogu.edu.tr