

Scanning tunneling microscopy of oxidized titanium surfaces in air

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Using an STM in air, we have studied three different electropolished Ti surfaces. One sample was analyzed without further treatment. The second was thermally oxidized in air at 500°C. The third was exposed to an argon glow discharge and then oxidized in pure oxygen. The samples were characterized by Auger spectroscopy prior to STM measurements. Electropolished and thermally oxidized samples showed a granular structure, with a low corrugation between 2 and 10 nm. At a larger scale, the glow discharge treated sample showed a high corrugation ~ 100 nm.

1. Introduction

Titanium is a commonly and successfully used biomaterial in dental and orthopaedic applications. The suitability of Ti as an implant material is largely due to the favorable tissue response which can be achieved with this material. It is, however, not known which biological mechanisms or specific surface properties of Ti lead to this tissue compatibility. The properties of the surface oxide on Ti and the surface topography at a level of 1 nm–10 μ m have been suggested to be important factors in this respect [1]. Based on this, we have pursued an extensive program on characterizing the chemical composition and microstructure of surface oxides on Ti and Ti₆Al₄V prepared by different methods (see, e.g., refs. [2–4]) and investigating the interfaces of these materials with different tissues [5].

Scanning tunneling microscopy (STM) [6] has proved to be a valuable tool to investigate these materials. Previous STM studies on titanium oxides have mainly been on single TiO₂ crystals in air [7] or in vacuum [8], but studies from a more biomaterials point of view have also been reported [9–11].

In this contribution, we present an STM study of some differently prepared Ti samples, with the

objective to study the surface topographies at the nanometer scale.

2. Experiment

2.1. STM

The STM used here is described in greater detail elsewhere [12]. The microscope was operated in air and at room temperature. A standard piezo tube scanner assured a maximum scan length of 2.8 μ m. For the coarse motion a commercial inch-worm motor was used (Burleigh Instruments, Inc.). To reduce the mechanical and acoustical noise the tunneling unit was hanging in thin rubber bands inside a closed box. The box was placed on a platform, which was suspended from the ceiling with rubber bands. A Macintosh workstation was used to control the measurements and for the data presentation. All images were measured in the constant-current mode, with an analog feedback system. The tips were commercially available etched tungsten tips (Longreach Scientific Resources). The bias voltage was between 1 and 2 V, and the current set point was 1 nA. The scanning speed was 2 μ m/s.

2.2. Sample preparation

Circular (\varnothing 6 mm \times 0.5 mm) samples were made by machining a rod of 99.6% pure Ti. After mechanical polishing of one of the circular flat surfaces, the samples were ultrasonically cleaned in trichloroethylene (10 min), acetone (5 min), and methanol (5 min). The samples were then electropolished using previously described procedures [13]. After electropolishing, the samples were ultrasonically cleaned in methanol (5 min) and then dried.

Some of the samples were subjected to further preparation steps. Two samples were thermally oxidized in air at 500°C for one 1 h, in order to produce a thick thermal oxide. Two samples were treated in an Ar DC glow-discharge plasma (0.31 mbar, 2 kV, 2.5 mA/cm² for 10 min), in order to remove the surface oxide formed during electropolishing. The plasma-treated samples were reoxidized in a pure (99.9995%) oxygen atmosphere at room temperature before they were removed from the vacuum chamber of the plasma equipment.

2.3. Surface analysis

One sample of each type (electropolished, thermally oxidized, and glow-discharge treated) was analyzed in a scanning Auger microprobe, SAM, (Physical Electronics, model PHI 660). The samples were visually inspected by using the SAM instrument in the SEM mode (lateral resolution \sim 0.1 μ m). AES survey spectra were taken from two points of \varnothing 100 μ m at each sample, and depth profiles were measured using 2 keV Ar ions at a sputtering rate of 10 nm/min (as calibrated for Ta₂O₅).

3. Results

3.1. SEM

The electropolished samples appeared smooth and homogeneous at the SEM level of resolution. Grain boundaries were clearly distinguished, and some particulate contamination could be ob-

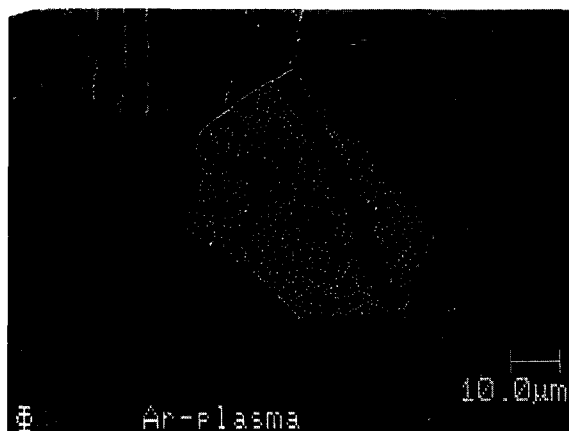


Fig. 1. SEM micrograph of a glow-discharge-treated Ti sample, showing distinct regions with different surface topographies. The regions often correlated with the grains of the metal.

served. The thermally oxidized sample showed a very similar surface topography, with a smooth surface and some particulate contamination.

In contrast, the glow-discharge-treated sample was more heterogeneous, showing distinct regions with different surface topographies (fig. 1). The different types of areas often correlated with the grains of the metal, but different types of areas within each grain were also common. The latter type of areas, were often long and narrow in shape, with a distinctly different surface topography than the surrounding area. Areas which appeared bright in the SEM, at low magnifications, were found to be very rough and consisting of cone-like structures of size 1 μ m distributed in a corrugated surface (fig. 2). Other types of areas exhibited a roughness on a smaller scale (\sim 0.1 μ m), while some areas looked smooth in the SEM.

3.2. Auger spectroscopy

At the surface of the electropolished sample, only Ti, O, and C were detected. The relative concentration of C corresponded to \sim 30 at%, and the shape of the Ti LMV peak at 417 eV indicated a composition close to TiO₂ [2]. The AES depth profiles showed that the C was re-

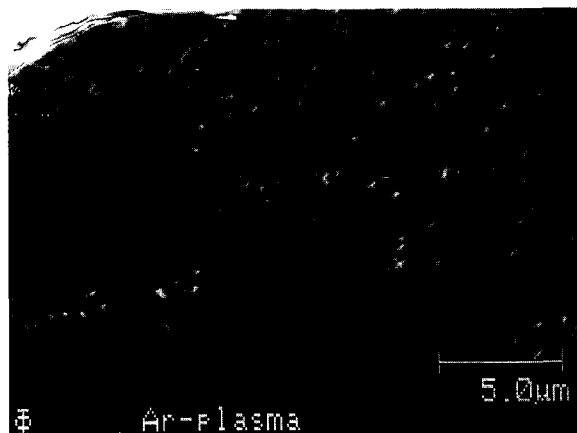


Fig. 2. SEM micrograph with a higher magnification of a glow-discharge-treated Ti sample, showing cone-like structures distributed in a corrugated surface.

stricted to the outermost surface, and an oxide thickness of 4 nm was estimated.

Also the thermally oxidized sample had a TiO_2 surface oxide composition. The carbon contamination level was lower ($\sim 20\%$ relative concentration) than for the electropolishing sample, and in addition a significant potassium (K , $< 5\%$) signal was detected at the surface. The estimated oxide thickness of this sample was 45 nm.

For the plasma-treated sample the surface oxide composition was again TiO_2 , with a carbon surface contamination level of $\sim 20\%$. The depth profile showed that the surface oxide was very thin, ~ 1.5 nm.

3.3. STM

The granular structure of the electropolished sample is visible in fig. 3, which shows a 100 by 100 nm STM top view image. The granular sizes are between 3 and 10 nm. The cross-section also gives an estimate of the corrugation (~ 2 nm). These flat areas were 100–500 nm in size and separated by thin lines (~ 10 nm wide and ~ 10 nm deep). The bias voltage was 1 V (tip negative).

The thermally oxidized Ti sample showed a somewhat higher corrugation (~ 10 nm) (fig. 4). It was more difficult to get a stable tunneling current as compared to electropolished samples. The best results were obtained with a 2 V (tip



Fig. 3. STM top-view image of an electropolished Ti sample, showing the granular structure and the low corrugation ~ 2 nm (image size 100 nm by 100 nm, cross-section at the arrow, the black-to-white z scale is 7 nm).

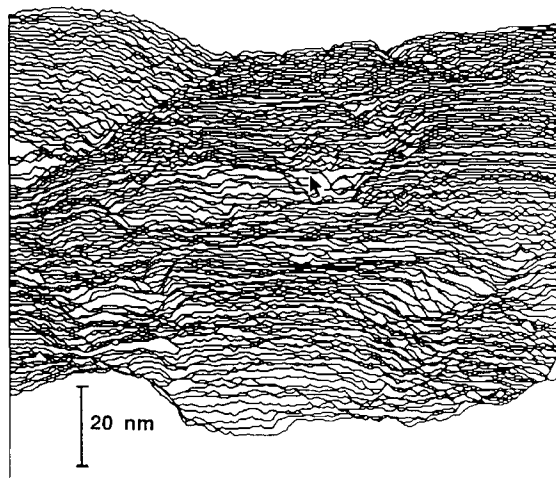


Fig. 4. STM line plot image of a thermally oxidized Ti sample, showing a higher corrugation ~ 10 nm, as compared to the electropolished samples (image size 100 nm by 100 nm).

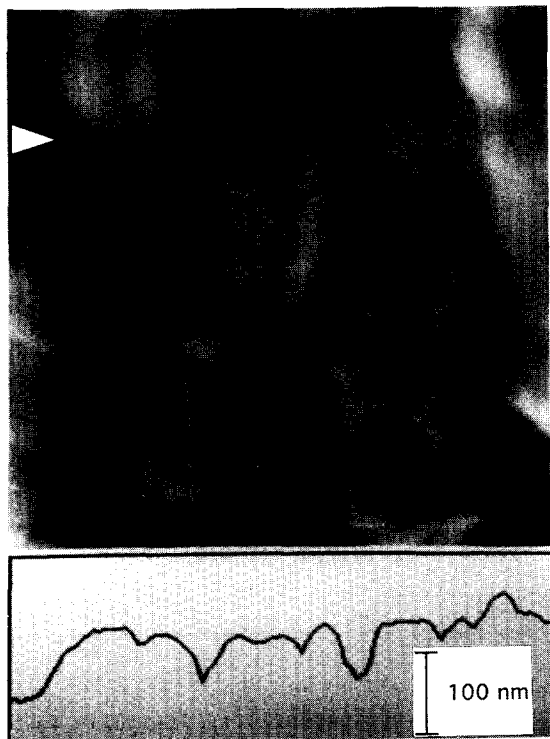


Fig. 5. STM top-view image of a glow-discharge-plasma-treated Ti sample of the corrugated structures visible in the SEM micrograph in fig. 2. From the cross-section curve the height of the structures can be estimated to ~ 80 nm (image size 1400 nm by 1400 nm, cross section at the arrow, the black-to-white z scale is 200 nm).

positive) bias voltage. On a larger scale this sample maintained its flatness; even at a $2 \mu\text{m} \times 2 \mu\text{m}$ scan, the z scale could be as low as 40 nm. The thin deeper lines, that were visible in the electropolished sample, were absent here.

A lower-magnification STM image of a plasma-treated sample is shown in fig. 5. The measured area was probably from a region similar to that in the upper right corner of the SEM micrograph in fig. 2, showing the long-range ordered and corrugated structures. From the cross-section curve the height of the structures can be estimated to ~ 80 nm. At higher magnification (~ 100 nm) the corrugation was similar to the two other samples if a part was chosen that appeared flat at a larger scale. The bias voltage was 1 V (tip negative).

4. Discussion

The topography of the electropolished sample is similar to what has been observed by others [9]. The dimensions of the structures observed on this surface are of the order of the oxide thickness, which makes it difficult to establish whether they represent the roughness of the bulk metal substrate or the morphology of the electropolishing oxide. The dissolution process during electropolishing has the effect of producing a crystalline termination at the surface of each individual metal grain [14]. The electropolished metal surface upon which the oxide forms can therefore be expected to contain facets or steps, rather than being granular at the level we observe. This leads us to believe that the observed surface topography is associated with the oxide, and that a granular surface oxide has grown on individual metal grains. The observed topography of the electropolishing oxide could be due to pores or voids in the oxide, or microcrystallites. The possibility that the observed features are due to surface contamination (e.g. hydrocarbons) cannot, however, be completely ruled out.

Thick thermal oxides have not been studied by STM before. TiO_2 is a semiconductor with a large band gap and a thick oxide, as here, could cause a problem for the STM with insufficient conductivity. However, STM studies have shown [9] that the band gap at the surface is lower (1.3 eV) than the bulk value (3 eV). In our case we had a bias voltage of 2 V, so it should not be any problem with conductivity. Our results indicate that thermal oxidation leads to a significant roughening of the electropolished surface. The moderate temperature used here is not expected to influence the morphology of the bulk metal, which means that the roughening is associated with the growth of the surface oxide. A similar behavior is also observed in TEM [4]: thin thermal oxides (< 10 nm) appear to be essentially amorphous and featureless, while thicker ones (30–40 nm) become more heterogeneous and crystalline with thickness. The heterogeneity is associated with an increase in the size and density of pores and voids in the oxide. It is not unlikely that this heterogeneity, in turn, leads to

the roughening of the surface that is here observed by STM.

At a larger scale, the plasma-treated samples show a dramatically different surface morphology, with one order of magnitude larger roughness. Since the oxide is very thin, the morphology in this case certainly represents the bulk metal substrate. The plasma (glow discharge) treatment is essentially an ion sputtering of the surface. Several examples exist in the literature (see, e.g., ref. [15]) of roughening of, and/or cone formation at, surfaces that have been subjected to ion bombardment. Apparently, grains of different orientation are affected differently by the sputtering process. On some grains cones are formed, while on others a corrugated morphology results.

Neither of the three different surfaces above is well suited as substrate for imaging adsorbed smaller sized proteins, due to the inherent roughness of the substrates. For larger-sized proteins, the electropolished sample would be smooth enough. Problems with insufficient conductivity of the molecules could, however, hamper proper STM work. For larger molecules it would probably be better to use a scanning force microscope.

5. Conclusions

We have studied the topographies of differently prepared TiO₂ surfaces by scanning tunneling microscopy in air.

Electropolished and thermally oxidized samples showed a smooth surface on a larger scale, while at the nanometer scale showed a granular structure with a corrugation ~2–10 nm. In contrast, a glow-discharge-plasma-treated sample showed, on a larger scale, a highly corrugated surface (~100 nm).

Acknowledgement

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