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NANOSTRUCTURED VACUUM ARC DEPOSITED TITANIUM COATINGS

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Abstract. Ti coatings on silicate glass substrates have been produced using a nonfiltered vacuum arc deposition technique. The dependence of the deposition rate on the distance from the cathode both in lateral and transversal directions was investigated. The average roughness, R_a, decreases with the distance, showing a transition area between the microparticle-containing and microparticle-free Ti films. R_a depends strongly on the number of microparticles. A linear dependence of R_a on the discharge current was obtained only for substrates far enough from the cathode. For substrates close to the cathode the dependence is governed by the microparticle density. Transmission electron microscopy (TEM) reveals dense structure with nanograins.

1. INTRODUCTION

Titanium is a transition metal mainly characterized by its high specific modulus and its good resistance to corrosion. Ti coatings are mainly attractive due to their biocompatibility which make them reliable for the design of medical instruments or implants in the human body. The chemical and morphological modification of metallic implant materials has been shown by *in vivo* tests to influence their biocompatibility. The control of the surface roughness is an important factor for the implants [1, 2]. Rougher surfaces have been shown to result in firmer bone fixation [3, 4]. Vacuum arc deposition of titanium, though less documented than sputter deposition, offers a wide range of microstructural and morphological properties for coatings [5, 6]. Particularly, these coatings are dense and nanograined. The cathodic arc plasma deposition process enables to generate a much higher degree of ionization than other ion-plating processes, providing a better film adhesion and higher densities. 30 to 80% of the material that is evaporated from the cathode surface is ionized, including multiply charged states [7, 8]. The kinetic energies of the ions typically are in the 10 to 100 eV range. These features result in deposits of superior quality in comparison to other physical vapour deposition processes. High deposition rates can be achieved with an excellent coating uniformity. As a result of the arc process, microparticles are emitted at a very high velocity towards the substrate and contribute to the film formation. Though often considered as a disadvantage for applications in optics and electronics, the microparticles also represent a good way to create films of a given roughness [9]. The following study presents the main coating characteristics of vacuum arc deposited titanium on silicate glass depending on deposition parameters. It gives a quantitative overview on the deposition rate and roughness values available for widely used titanium coatings.

2. EXPERIMENTAL, SETUP AND CHARACTERIZATION OF SAMPLES

The vacuum arc apparatus used in this work is described elsewhere [10]. The facilities for magnetic

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filtering of the microparticles were not used in this work. Ti was deposited on a 450×470×4 mm silicate glass plate. The glass plate was positioned horizontally, at the middle of the round cathode, perpendicular to the cathode surface plane, 50 mm away from it. The round cathode has a diameter of 180 mm. Before coating, a grid was drawn on the glass surface with the aid of an overhead pen. The grid provided a set of nodes located at a definite position relative to the cathode surface. The grid also acted as a mask and its removal after deposition made it possible to determine of the film thickness at each node. After deposition, the plate was cut to 40×30 mm samples suitable for the measurements. This experimental procedure ensures the similarity of the process conditions for each sample, the absence of sample shadowing and a large quantity of samples through one experiment. All data given in this work were obtained on the top surface of the substrate. The vacuum arc source voltage was maintained constant at U = 22 V while the discharge current I varied (I = 110, 140, 160, 175 and 220 A). No bias was applied to the substrate. The coating time t was the same for all samples (t = 420 s) except for I = 160 A (t = 240 s). To prevent from overheating of the surfaces, the 420 s coating process was divided in two coating periods (210 s each) separated by a 60 s interruption.

The sample surface was observed using a Zeiss *Axiophot* optical microscope and an atomic force microscope (AFM) *Autoprobe CP AFM* from Park Scientific Instruments and transmisison electron microscop (TEM) JEOL FX 2000. The thickness of the coatings d was measured with the aid of both Taylor-Hobson *Polystep* profilometer and AFM. During the thickness determination using profilometry six consecutive measurements of the step height between the coated and non-coated part were averaged. The average roughness R_a also was derived from profilometry measurements. The AFM was operated in the contact mode, using sharpened gold-coated microlevers with a nominal radius of the tip curvature less than 20 nm. For the film thickness measurements 50×50 μm scans were positioned in such a way that the border between coated and uncoated glass was approximately in the middle of the scanned area (Fig. 1). The thickness was then determined as an average from four line scans which were not disturbed by the particles or contaminations at the coated/uncoated glass border. The profilometer thickness measurements were known within a 5% accuracy while the AFM enabled to measure the thickness with an accuracy of 5 nm.

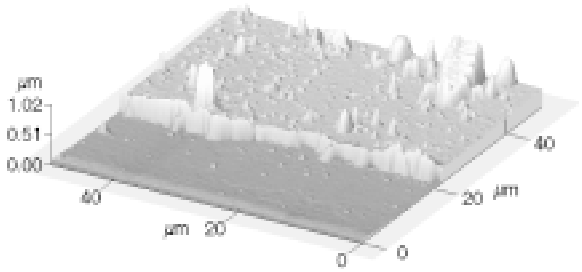

Fig. 1. AFM low magnification micrograph of a vacuum arc deposited Ti coating on the silicate glass substrate (L = 80 mm, I = 160 A, t = 240 s), showing the step between the masked and coated part. Small droplets and the smooth film formed from the ionic flux can be seen.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figs. 1 and 2 display the microstructure of the Ti coatings. During vacuum arc deposition, the flux of material coming from the cathode to the substrate contains multiply charged ions and microdroplets [10]. The microdroplets are ejected from the liquid pool of the cathode (created by the arc impact) and accelerated by the ionic flux towards the target. In our case, the microdroplets fly almost parallel to the substrate plane. Their resulting shape is thus ellipsoidal and can be characterized by their aspect ratio. The surface morphology of the coating is driven mainly by the microparticle density. Close to the cathode, the Ti film has a very rough surface made of overlapping microparticles. Further away from the cathode, both droplets and a homogeneous film formed by the deposition of individual ions can be clearly seen. The microdroplets are still of various size but their shape is more uniform. In the AFM image taken at low magnification (Fig. 1) the „tail“ of a large microdroplet is visible together with some smaller particles on the rather smooth surface of a film formed by the flux of individual ions. High-magnification AFM pictures show the smooth film between the droplets (Fig. 2a) and the surface morphology of the microdroplets (Fig. 2b). The average roughness, R_a, measured profilometrically on the length of 80 μm, includes both big and small droplets and a smooth surface among them and, therefore, is rather high (about 350 nm on the sample shown in Figs. 1 and 2). R_a measured microscopically is much lower (3.7 nm for the location shown in Fig. 1a and 6.2 nm for Fig. 2b). If the deposition time t is high, the microdroplets become an integral part of the coating. At the largest distance from the

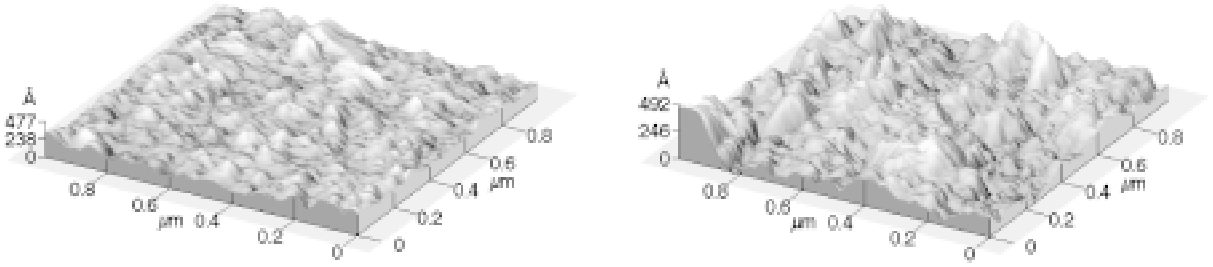

Fig. 2. AFM high magnification micrograph of vacuum arc deposited Ti coating on the silicate glass substrate (L = 80 mm, I = 160 A, t = 240 s). The topography of a film between droplets (a) and the surface topography of a large droplet (b).

cathode, the microdroplets density is very low and the coating consists of a homogeneous film formed by deposition of individual ions and which can be considered as microparticle free. The AFM measurements reveal that the film between the particles is atomically smooth (R_a = 1 nm) at L > 200 mm. Fig. 3 displays the dark-field TEM micrograph of Ti coating. The film contains uniform grains having size from 3 to 10 nm.

The two-dimensional dependence of deposition rate R_d on the distance form the cathode L and transversal distance x is shown in Fig. 4. The curves are symmetric having the maximum at the middle of the substrate. R_d decreases monotonically with increasing L and x. Close to the cathode, the microparticles presence boosts the deposition rate. The decrease of R_d with increasing L and x is rather slow, especially at high I. The low variation of R_d with increasing distance illustrates the high throwing power of the arc process [5]. It allows one to coat effectively the three-dimensional parts having a complicated form. The slow R_d (L) dependence is also advantageous for the coating of planar large-area substrates allowing to transport the frames with substrates at various distances from the cathode. This feature allowed one to simplify the construction of the vacuum arc deposition apparatus for large area substrates [11].

The dependence of R_d on the discharge current I for various values of the distance L from the cathode is shown in Fig. 5. These data were measured along the middle line of the substrate (x = 0). For samples close to the source, R_d sharply decreases with the distance L. At low L values the surface is

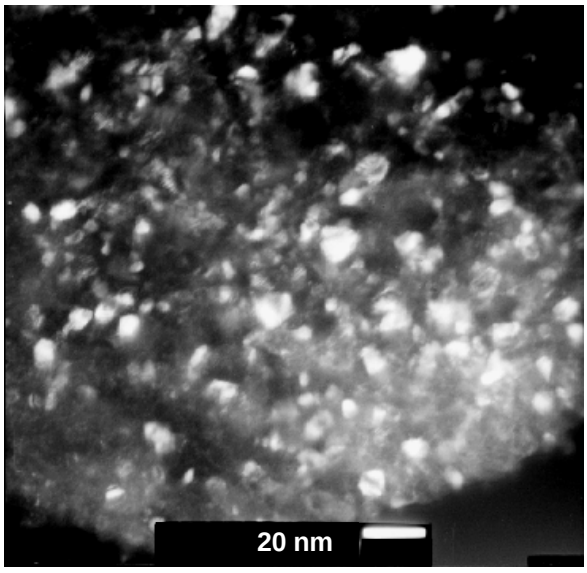

Fig. 3. Dark-field TEM micrograph of the vacuum arc deposited Ti coating on the silicate glass substrate planar view. The film thickness is 110 nm.

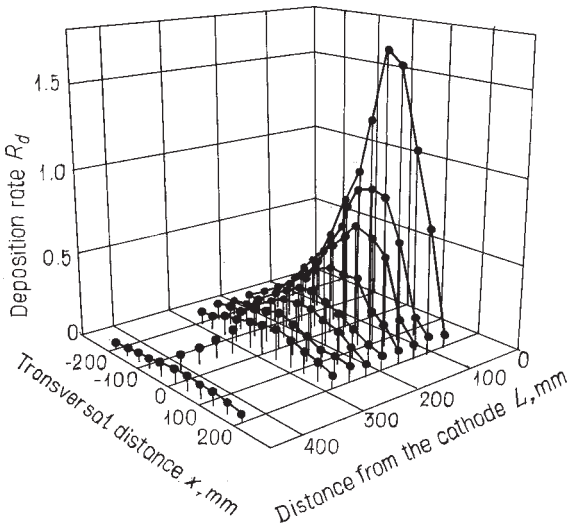

Fig. 4. Dependence of the Ti deposition rate R_d on the distance to the cathode L and transversal distance x from the symmetry axis of the substrate. I = 150 A.

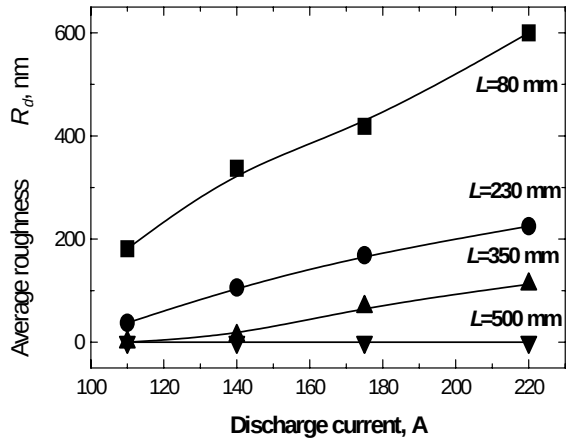

Fig. 5. Dependence of the average roughness R_d on I for different values of L.

built of micron size overlapping particles. Values up to 600 nm are found. Further away, as the film gets free from microparticles, R_d goes down to about 4 nm which is the initial roughness of the glass substrate. An increase of the discharge current I increases the roughness and widens the choice of the available roughnesses. The higher the discharge current, the larger the microparticle-free zone. The deposition time t is the third parameter which enables to produce a given roughness but its influence has not been studied here. Namely, the deposition rate decreases much slower with increasing L and decreasing I than the average roughness. It is very important from the technological point of view, because it allows one to get very smooth coating substrate with a reasonable deposition rate simply increasing the distance from the cathode.

4. CONCLUSIONS

Vacuum arc deposition permits to produce Ti coatings with high deposition rate R_d. The decrease of R_d with increasing distance from the cathode (both in longitudinal and transversal directions) is rather slow, especially at high discharge power. It allows one to coat effectively the three-dimensional parts having a complicated form. The Ti coatings have dense nanostructured grain structure. The roughness of the coatings can be changed in the broad interval.

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