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# Structural characterisation of oxygen diffusion hardened alpha-tantalum PVD-coatings on titanium

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ABSTRACT

Titanium substrates were coated with tantalum layers of 5 μm thickness using physical vapour deposition (PVD). The tantalum layers showed a (110)-preferred orientation. The coated samples were hardened by oxygen diffusion. Using X-ray diffraction the crystallographic structure of the tantalum coatings was characterised, comparing untreated and diffusion hardened specimen conditions. Oxygen depth profiles were determined by glow discharge spectrometry. The hardening effect of the heat treatment was examined by Vickers microhardness testing. The increase of surface hardness caused by oxygen diffusion was at least 50%.



## 1. Introduction

Due to the combination of favourable mechanical properties and high biocompatibility, titanium and its alloys are standard materials for implant applications, which are in contact with hard or soft tissue [1]. A low elastic modulus combined with high fatigue strength of the bulk material make these alloys a preferred choice, particularly for the replacement of hard tissue, e.g. as anchoring parts in total hip and knee arthroplasty [2], as supportive devices for fracture healing [3] and as enossal implants [4]. The reason for the high biocompatibility of titanium is that it is not recognised as a foreign material by the cellular environment. Biomolecules, adsorbed on the surface of these materials, generally undergo only few structural changes [5,6]. Sometimes an aseptic loosening of titanium based prostheses can be observed after short implant duration. Due to this aseptic loosening along with a relative movement between hard tissue/bone cement and implant, the formation of abrasion debris from the prosthesis surface can be provoked. These particles stem from the native oxide layer that is only a few nanometers thick and shows low mechanical stability and hence does not withstand these movements [7,8]. In the worst case, small abrasive particles are generated that cause inflammatory reactions of the surrounding tissue which leads unavoidably to a loss of bone [9,10].

The improvement of the tribological properties of the titanium surface was investigated in several studies. Especially different coating technologies such as chemical (CVD) and physical vapour deposition (PVD) [11–14] as well as thermal and electrochemical oxidation techniques [15,16] were assessed. Although hard material layers consisting of metal oxides and nitrides can improve the abrasion resistance of the bulk material, a considerable disadvantage of these material systems is the abrupt transition from the brittle/hard surface coating to the ductile/softer substrate. A gradient-like transition in mechanical properties from the hard coating to the soft substrate would be more suitable to avoid delamination of the coating when mechanical loads are applied. In case of bulk titanium and Ti-alloys the enhancement of surface hardness can be achieved by oxygen diffusion hardening (ODH) [17–20].

The aim of the present study is to develop this technique further in order to generate gradient-like hard coatings on titanium (Fig. 1). For this purpose the titanium substrate is coated with a thin tantalum layer of approx. 5 μm using radio frequency (RF) magnetron sputtering. The refractory metal tantalum is chosen since its reaction with oxygen occurs much faster compared to titanium. This reaction is also accompanied by a volume increase which will result in self-induced crack healing of the damaged surface [21]. Finally, ODH is applied to the tantalum coatings to achieve both, a hardened surface with high abrasion resistance and a smooth transition zone between the surface layer and the bulk material. Scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), glow discharge spectrometry (GDS) and Vickers microhardness testing are used to distinguish the coatings regarding

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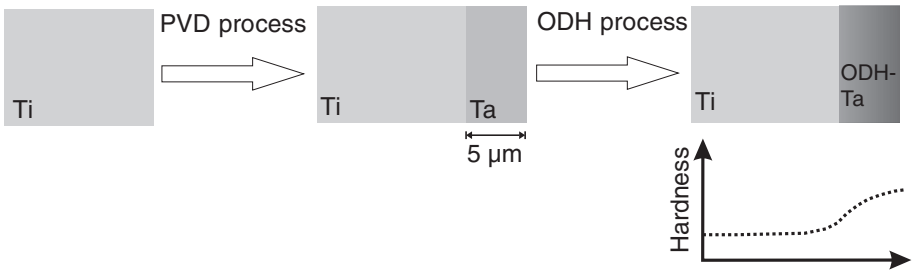


**Fig. 1.** Schematic illustration of the production of oxygen diffusion hardened Ta layers on Ti substrates and expected depth profile of hardness.

their morphology, structure, near-surface oxygen content and surface hardness.

## 2. Materials and experimental methods

### 2.1. Substrate preparation and coating process

As substrate, discs of 15.5 mm diameter were die-cut from commercially pure titanium (grade 2) rolled sheet metal. The discs were cleaned in an ultrasonic bath (first with acetone for 10 min, then with ethanol for 10 min) and finally dried in air. Up to six titanium discs were attached to the substrate holder in the chamber of a physical vapour deposition-system (PVD) of type PLS 570 (Pfeiffer Vacuum) and heated by a pair of internally installed halogen lamps. The substrate temperature was measured using a thermocouple being embedded between the samples. A base pressure of $1 \cdot 10^{-6}$ mbar was adjusted by evacuating the chamber for 15 h at a temperature of 40 °C followed by cooling down within 1 h to 15 °C. Both, heating and cooling were achieved by means of temperature-stabilized water circulation. 30 min before layer deposition, the substrate holder was heated up to process temperature. Prior to deposition of tantalum, the titanium substrates were sputter-cleaned in argon plasma (300 W, 180 sccm, $1.6 \cdot 10^{-2}$ mbar) for 10 to 15 min. Tantalum films were coated by RF magnetron sputtering using a Ta target (120 mm diameter, 10 mm height) with a target-to-substrate distance of 120 mm.

In the course of process development, a wide range of parameters for physical vapour deposition has been explored [22], such as deposition time (180 to 300 min), working pressure (6.7 to $9.9 \cdot 10^{-3}$ mbar), negative substrate bias voltage (−300 to 0 V) and substrate temperatures up to 550 °C. The coatings analysed in this study were produced with a set of fixed parameters: a deposition duration of 180 min, a working pressure of $7.0 \cdot 10^{-3}$ mbar (100 sccm argon) and a substrate bias voltage of 0 V, while the substrate temperature was held constant at 350 °C.

### 2.2. Oxygen diffusion hardening

Oxygen diffusion hardening was performed as metallurgical heat treatment outside the PVD-system. During the heat treatment, the tantalum coated specimens were placed into a quartz recipient, which was connected to a vacuum system. The recipient was positioned in a tube furnace. The specimens' temperature was monitored by a thermocouple positioned close to them. A needle valve was used for injection of the process gases argon or oxygen.

In preliminary studies [20] the ODH-process was developed as a two step procedure. First, the thickness of the native oxide layer of tantalum was increased by annealing the specimens between 350 °C and 650 °C for 30–120 min using an oxygen pressure of $5 \cdot 10^{-3}$ mbar. The diffusion step followed after rinsing the recipient with argon gas and setting-up ultra high vacuum conditions without cooling down. The diffusion of oxygen was activated by annealing the oxidised specimens for up to 120 min at oxidation temperature in a vacuum better than $10^{-7}$ mbar. Subsequently, the specimens were cooled down to room temperature outside the furnace, but still under vacuum conditions.

### 2.3. Coating characterisation

The surface morphology of untreated tantalum coatings was determined by scanning electron microscopy (SEM) using the microscope JEOL JSM 7600F. The lattice structure of the tantalum layers was examined by X-ray diffraction (XRD) in Bragg–Brentano geometry with a Bruker AXS D8 Advanced X-ray diffractometer using Cu-Kα radiation at an acceleration voltage of 35 kV and a tube current of 40 mA. The diffraction patterns were analysed using DiffracPlus EVA software. The positions of the diffraction peaks were determined using the gravity centre method. From the diffraction patterns the lattice plane spacing $d_{hkl}$ and the lattice parameter $a$ were calculated. The angular position of diffraction peaks is related to the lattice spacing via Bragg's law:

$$n\lambda = 2d_{hkl}sin\theta_{hkl}, \tag{1}$$

where $d_{hkl}$ is the lattice plane spacing of the diffracting lattice planes, $\theta_{hkl}$ is the scattering angle, λ is the wavelength of the X-rays and $n$ is an integer [23]. The elastic strain $\varepsilon_{hkl}$ originating from a shift in lattice spacing $\Delta d_{hkl}$ can be calculated from the scattering angle $\theta$ of a specimen with lattice deformation and that of an undistorted reference sample (scattering angle $\theta_0$)

$$\varepsilon_{hkl} = \frac{\Delta d_{hkl}}{d_{0,hkl}} = \frac{d_{hkl} - d_{0,hkl}}{d_{0,hkl}} = \frac{sin\theta_0}{sin\theta} - 1. \tag{2}$$

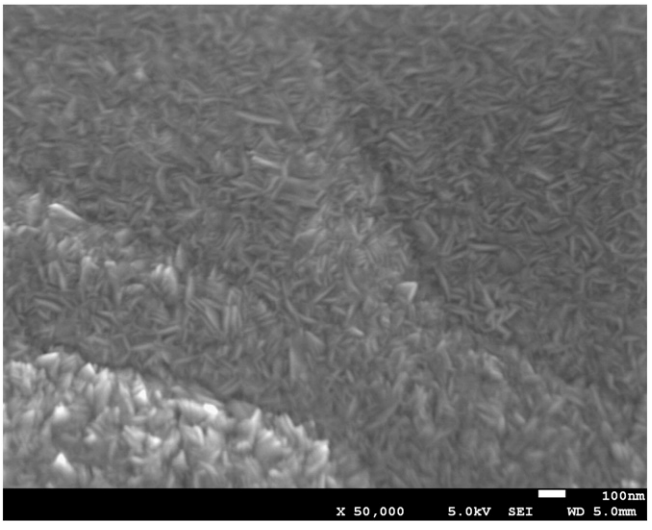


**Fig. 2.** Surface topography of the untreated tantalum layer deposited on titanium, top view normal to the specimen's surface, SEM micrograph, SE-detector.