

# Corrosion resistance of nanostructured titanium

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## Abstract

The present work reports results of studies of corrosion resistance of pure nano-Ti-Grade 2 after hydrostatic extrusion. The grain size of the examined samples was below 90 nm. Surface analytical technique including AES combined with Ar<sup>+</sup> ion sputtering, were used to investigate the chemical composition and thicknesses of the oxides formed on nano-Ti. It has been found that the grain size of the titanium substrate did not influence the thickness of oxide formed on the titanium. The thickness of the oxide observed on the titanium samples before and after hydrostatic extrusion was about 6 nm. Tests carried out in a NaCl solution revealed a slightly lower corrosion resistance of nano-Ti in comparison with the titanium with micrometric grain size.

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## 1. Introduction

Commercially pure titanium is an excellent implant material because of its high corrosion resistance and outstanding biocompatibility. It is known for not causing allergic reactions and it is preferred when infection is a risk. Its low elastic modulus and flexibility are advantages in many applications. The different grades of titanium and their mechanical properties are specified in ISO and ASTM standards for implant materials. For most implant types the strength level of 680 MPa as it is given for grade 4 cold-worked titanium (Long and Rack, 1998). However, some implants (e.g. certain spin implants, screws) require higher mechanical properties. The mechanical properties of titanium can be modified by chemical composition changes and by work strengthening or by the refinement of the microstructure. Ultrafine grained and nanocrystalline materials exhibit attractive properties such as high strength combined with sufficiently good ductility. The promising technique for significant refinement of the microstructure in bulk materials is severe plastic deformation (SPD) (Horita et al., 1998; Gubicza et al., 2006; Sergueeva et al., 2001). One of the methods which enable high plastic strains is hydrostatic extrusion (HE) (Lewandowska et al., 2005; Kulczyk et al., 2005; Garbacz et al., 2006; Kurzydłowski, 2006). In the present work, HE was used to obtain nano-grained titanium strengthened by grain

boundaries to the level higher than conventional Ti6Al4V. As several properties of nanomaterials dependent on the grain size. Only a few studies have addressed the corrosion resistance of nanocrystalline materials (Zeiger et al., 1995; Erb, 1995; Mishra and Balasubramaniam, 2004; Balyanov et al., 2004). The results obtained by different authors are contradictory and need detailed analysis. This study reports results of the investigations of corrosion resistance of nano-Ti-Grade 2.

## 2. Material

The material investigated in the study was commercially pure titanium Ti-grade2 (Table 1). The microstructure of the titanium in the as-receive state and after HE was examined by light microscopy and scanning microscopy (SEM/STEM Hitachi S 5500). In the as-received state, titanium had coarse-grained (CG) microstructure with the average grain size 21 μm. The nano-grained (NG) titanium was processed by hydrostatic extrusion at room temperature for eight passes. HE process was described in detail by Kurzydłowski (2006). The titanium samples in the form of 20 mm rods were extruded to a diameter of 3 mm, which corresponds to the true strain of 3.8. The as-processed Ti samples had an average grain size of 90 nm and high dislocation density (Fig. 1). The samples contained a large fraction of high-angle grain boundaries. The mechanical properties of the NG Ti were given in Ref. (Garbacz et al., 2006). Hardness of the investigated Ti after and before hydrostatic extrusion are given in Table 2.

## 3. Experimental

Studies of the chemical and physical nature of passive oxide films formed on metals and alloys are a central subject of corrosion research. Passive oxide layers, typically 2–5 nm in thickness, protect many metals (like Ti, Fe, Al, etc.

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Table 1  
Chemical composition of the examined titanium

| Composition (wt.%) | C    | N    | Fe   | O    | H    | Ti   |
|--------------------|------|------|------|------|------|------|
| Ti-grade2          | 0.01 | 0.01 | 0.07 | 0.11 | 0.01 | Base |

(Wołowik and Janik-Czachor, 1999; Janik-Czachor et al., 2003; McCafferty and Wightman, 1999; Santanau et al., 2000)) and alloys from an aggressive influence of the corrosion environment.

Most of present knowledge on the chemical composition of passive films comes from ex-situ surface analytical methods. In particular Auger electron spectroscopy (AES) technique provides fundamental information about the chemical composition and state of components of thin surface layers, and particularly on surface atoms (Werner et al., 2005).

The surface layers composition is often quite different from that of the bulk material due to contamination, oxidation, or processing. These methods give an insight into important problem concerning the nature of passive films.

Many interesting information about structure and chemical composition of passive films one can obtain by using combination of ion sputtering and AES method. Depth profiling is usually accomplished by inert gas ( $\text{Ar}^+$ ) ion bombardment to remove successive layers of materials from the surface. AES composition profiles are particularly useful since they can be acquired fast and with high depth resolution (Briggs and Grant, 2003a). Sputter profiling, however, damages the sputtered oxide films and can lead to composition changes by preferential sputtering and/or ion mixing.

The Ti samples were examined with AES to determine composition and estimate the thickness of the passive film covering their surface. A Microlab 350 (Thermo VG Scientific) analytical instrument was used to determine the composition of the oxide film and chemical state of the components. An  $\text{Ar}^+$  ion gun was used to measure the composition profiles of the film. Discontinuous sputtering (step size of sputtering 6 s) was used to gradually remove the oxide film. The sputtering parameters were: ion energy 3 keV, beam current 1  $\mu\text{A}$ , and the crater size 2 mm  $\times$  2 mm. The Auger spectra were recorded, after each sputtering period at  $E_p = 10$  keV. The Advantage based data system software was used for data acquisition and processing.

The Auger studies give information about the first monolayers of a sample ( $\sim 1$  nm) (Briggs and Grant, 2003b; Watts and Wolstenholme, 2003). Therefore, the high resolution scanning Auger was applied to monitor surface morphology and local chemical composition, utilizing the Auger electron spectroscopy (AES) with the lateral resolution of about 20 nm (Reniers and Tewell, 2005).

The sputtering rate of oxide layers removed by  $\text{Ar}^+$  ions was estimated approximately by ion etching of  $\text{TiO}_2$  oxide layer, grown by oxidation on the Ti substrate (Kim et al., 2000; Liu et al., 2004). The sputtering rate (nm/s) for this material was determined on the basis of measurement of the crater depth after sputtering process. A profilometer (NT1100 Optical Profiling System – Veeco)

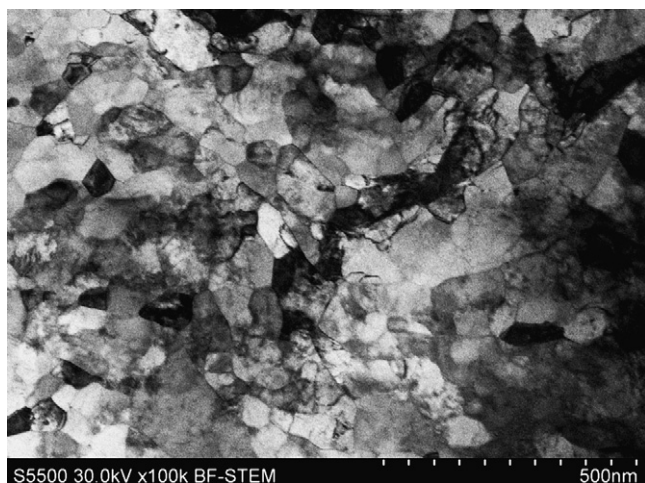


Fig. 1. Microstructure of titanium after HE (transverse section).

Table 2  
Specification of corrosion potentials values ( $E_{\text{corr}}$ ) and corrosion currents density ( $I_{\text{corr}}$ ) for CG and NC Ti

|       | $E_{\text{corr}}$ (mV) | $I_{\text{corr}}$ ( $\mu\text{m}/\text{cm}^2$ ) |
|-------|------------------------|---|
| CG Ti | –152                   | 18  |
| NG Ti | –158                   | 41  |

instrument was used to define the crater depth. The following parameters were used:

1. crater depth: 1490 nm;
2. sputtering ( $t_{\text{sputt}}$ ) time necessary to remove the oxide films: 7500 s;
3. sputtering rate ( $\sim 0.2$  nm/s).

Corrosion tests were carried out in 0.9% NaCl solution in the duration time of 20 h. Changes in the character of the double layer were analysed using the impedance spectroscopy method. The impedance tests were conducted basing on a computerised measurement system Autolab PGSTAT100 (voltage signal amplitude 20 mV, frequency 1 MHz to 0.001 Hz, reference electrode: a saturated calomel electrode (SCE)), while the potentiodynamic tests (also with the application of Autolab PGSTAT100 set) were conducted by polarizing the samples with the potential change rate of 0.2 mV/s; the reference electrode was a saturated calomel electrode (SCE).

The impedance spectra for titanium were analyzed using the equivalent circuits (EC). Fig. 2 represents the EC for two-time-constants model (R(RQ)(RQ)).

#### 4. Results and discussion

For a better understanding of the chemical composition of passive film on the Ti samples before and after HE process the authors used the surface analytical measurements (AES) (Lausma, 1996). Fig. 3 shows examples of survey spectra for Ti sample before (a) and after HE (b). Disappearance of the O (KLL) peak in the course of sputtering is well visible, reflecting analytical results at various depths of the sample: within the passive film and, eventually, within the substrate. After sputtering the oxide film away, the substrate spectra revealed the presence of metallic Ti (LMM).

Fig. 4 presents a typical composition profile for Ti samples before (a) and after HE (b). Three distinct domains can be distinguished within the profile: I – contamination oxide film (zone which is enriched in carbon); II – an anodic oxide film containing a  $\text{Ti}^{\text{ox}}$ ; and III – the substrate containing  $\text{Ti}^{\text{m}}$ . A careful inspection of the composition profiles revealed that the oxide films are very thin. The  $\text{Ti}^{\text{ox}}$

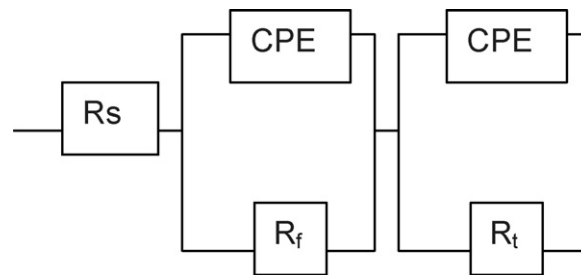


Fig. 2. Equivalent circuits: R(RQ)(RQ). CPE – constant phase element;  $R_s$  – solution resistance;  $R_f$  – resistance of dielectric layer;  $R_t$  – charge transfer resistance through double layer.

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