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The effect of grain size on the surface properties of titanium grade 2 after different treatments

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ABSTRACT

This paper presents findings concerning the influence of the grain size of titanium on its surface properties and on the efficiency of surface treatments. The investigations were performed on titanium grade 2 of two grain sizes. The chemical composition and chemical state of the surface were analyzed by X-ray photoelectron spectroscopy. Different types of surface treatment were applied: plasma nitriding, and a combination of chemical and mechanical modifications using etching with hydrofluoric acid and shot peening. The effect of the grain size on surface treatments was evaluated through roughness quantification, hardness measurements, and observations of the surface and microstructure.

The investigations showed that grain size influences the wettability and surface free energy of titanium grade 2. A reduction in grain size is beneficial for the effectiveness of plasma nitriding. The results also indicate that the grain size of titanium grade 2 affects the surface morphology after shot peening and chemical etching with HF acid; these various methods make it possible to modify the surface roughness of titanium over a wide range. The present paper demonstrates that grain size affects the surface properties of titanium grade 2 and can be used as an additional parameter in optimizing the microstructure and properties of surface layers and coatings.

1. Introduction

In recent years, tremendous progress has been made in the development of nanometals, i.e., metals and alloys with a grain size of less than 100 nm. They exhibit superior mechanical properties, particularly exceptionally high strength, when compared with their microcrystalline counterparts. This development of nanometals involves titanium directly. Nanostructured titanium can be obtained by severe plastic deformation (SPD) methods [1–6], among others, where unusually high strains are applied. A high density of dislocations is generated during SPD processing. Under greater strains, the dislocations rearrange to form new grain boundaries, dividing the microcrystalline grains into even smaller parts. The spacing between grain boundaries decreases, while their misorientation angle increases. Titanium after SPD shows a unique nanostructure and outstanding mechanical properties. The question is whether its surface properties can also be improved, as is achievable with microstructural titanium. Research into improving the surface properties of nanometals produced by SPD methods is in its infancy at the time of writing this paper. The crystalline lattice of polycrystalline materials contains imperfections, such as grain boundaries, stacking faults, dislocations, and point defects. In their vicinity, the frequency of atom jumps is much higher than in an ideal crystal lattice, and hence the defected regions present easy paths of diffusion, along which the diffusion rate is markedly higher. Research shows that a decrease in grain size decreases the activation energy of diffusion, which leads to an increase in the diffusion coefficient according to the Arrhenius law [7–9]. Grain boundary diffusion is a complex phenomenon, even in the case of standard coarse-grained materials, since the character of the grain boundaries can determine the diffusion properties. The general rule is that increasing grain boundary energy (related to the degree of atomic mismatch) decreases the activation energy of diffusion and leads to a higher diffusion coefficient and diffusion rate. It has also been concluded that the structure and energy of the grain boundaries are determined by the nanomaterial production method. For example, nanometals obtained by SPD methods are characterized by grain boundaries of high energy and high density of dislocation (non-equilibrium grain boundaries), which are favourable for diffusion processes [10,11].

Titanium and its alloys are extensively used as materials for implants and biomedical devices due to their high corrosion resistance in body fluid, their desirable biological properties, and their low density and Young's modulus. However, alloying elements in titanium alloys,

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such as vanadium and aluminium, have been proved to have a toxic influence on the human body due to ion release. On the other hand, pure titanium has weaker mechanical properties compared to its alloys, which limits its application. However, nanometals have come to the fore in the context of biomaterials because their improved strength is sufficient for this type of application. Therefore, nanostructured titanium is a very promising material for biomedical implants, especially dental implants. Moreover, its properties can be further improved by means of surface treatments, as in the case of microcrystalline titanium and its alloys, in order to mediate biological response.

In the case of nanostructured titanium, well-known surface engineering methods employed for metals with a conventional structure (microcrystalline) can be used. The criteria selecting what methods are suitable for improving the surface properties of nanostructured titanium should take account of the thermal stability of those methods and how they affect the processes which occur on its surface.

In light of the potential application of nanocrystalline titanium, it is especially important to check whether its tribological (nitride layers) and biological (passive layer, nitride layers, surface roughness) properties can also be improved, as is achievable with surface-treated microstructural titanium. Thus, the aim of this work was to investigate the impact of the grain size of titanium grade 2 on passive layer formation, and the results of plasma nitriding, chemical etching and shot peening. Concerning the physicochemical properties of the titanium, measurements were made of the wettability and surface free energy of a titanium surface with passive layers. Conventional DC (Direct Current) and RF (Radio Frequency) plasma nitriding of both microcrystalline and nanocrystalline titanium were performed in order to analyze the possibility of improving the hemocompatibility of nanocrystalline titanium and of decreasing process parameters (temperature and time) during plasma nitriding. Prior to nitriding, the thermal stability of the nanotitanium was determined in order to determine the plasma nitriding temperature range that is safe for a nanocrystalline structure. In the last stage, chemical etching and shot peening were applied to modify the morphology of the surface and to control the surface roughness of the nanocrystalline and microcrystalline titanium.

2. Experimental

The experiments were performed on commercially pure titanium grade 2 with a grain size of 65 μm in the initial state and 60 nm after hydrostatic extrusion with a true strain of 3.8 [6]. Because grain size after hydrostatic extrusion was under 100 nm, the titanium was named nanocrystalline. The extrusion process was performed at the Institute of High Pressure Physics, Polish Academy of Sciences in Warsaw. 1 mm thick samples were cut from bars with diameters of 5 mm; these were mechanically polished with an SiO_2 suspension, followed by ultrasonic cleaning. The same procedure of surface preparation was applied for all the investigations performed.

Nanocrystalline and microcrystalline titanium samples were exposed to RF plasma nitriding processes. The plasma nitriding processes were performed within a temperature range where the nanocrystalline structure of titanium is stable, at 250 °C and 400 °C. The time duration of both processes was 5 h. The process parameters of the RF plasma nitriding are presented in Table 1. The temperature of the processes was measured with an ICRON Modeline Plus pyrometer which had a measuring range of from 200 °C to 600 °C. The RF plasma nitriding was performed using a WU-2 M device with an adopted RF generator.

Wettability and surface energy were obtained using a Theta Lite Optical Tensiometer TL100. Double-distilled water, formamide and diiodomethane were used as standard liquids. Surface energy was determined by the Oss-Chaudhury-Good method.

The titanium surfaces were etched using a 3% hydrofluoric HF acid solution at room temperature for 3 min. The shot peening process was performed using glass balls of a diameter of 125 μm and a hardness of 57.5 HRC, which were ejected from the nozzle at a pressure of 4 bars and hit the surface at an angle of 90°. The shot peening process was conducted according to SAE J2277 Standards. The time of shot peening was selected so as to obtain 90% coverage of the surface. The degree of coverage was determined using a light microscope.

Table 1
Process parameters of RF plasma nitriding of nano- and micro-Ti.

Parameter	RF plasma nitriding
Temperature, T [°C]	250; 400
Heating	Plasma RF (− 900 V)
Pressure during heating, p [mbar]	0.01
Atmosphere during heating [%]	Residual
Nitriding pressure, p [mbar]	0.2
Nitriding atmosphere [%]	100% N_2
Nitriding time, t_c [h]	5
U_{bias} [V], I_{bias} [A]	− 500 V
Frequency, f [MHz]	13.56
Power delivered, W_F [W]	400
Power reflected, W_R [W]	50

Roughness quantification was performed using a Wyko NT9300 optical profilometer with approximately 1 nm resolution in the Z direction. Surface observations were conducted with a SEM Hitachi SU 3500 (SE detector, acceleration voltage 10 kV). The microstructure investigations were performed using a SEM Hitachi S 5500 (BF and DF imaging modes, 30 kV with probe size 0.4 nm) and a STEM Hitachi HD-2700 (BF and HAADF, 200 kV, 0.14 nm resolution) equipped with an Energy Dispersive Spectrometer (EDS) for the chemical analysis. The samples for the observations were prepared using a focused ion beam (FIB) system Hitachi FB2100 (40 kV, standard beam current 0.06–0.15 nA). The thickness of the STEM thin foils was about 100 nm. The thin foils were cut from the surface of each sample and were oriented perpendicular to the surface of samples. The mechanical properties were evaluated on the basis of a microhardness and nanoindentation test using a Berkovich indenter. The Vickers microhardness was used with an applied load of 200 G (HV02). Nanoindentation tests were performed using an HSITRON Triboindenter Ti 900 and a displacement control mode in which the maximum indentation depth was 500 nm. For such depths, the indentation loads were about 30 mN.

The chemical composition and chemical states of the surface were characterized by X-ray photoelectron spectroscopy (XPS - Microlab 350 Thermo Elektron) using $Al_{k\alpha}$ non-monochromated radiation (hv = 1486.6 eV). The binding energy of the target elements (Ti2p, O1s, C1s, N1 s, Na1s, P2p, Cl2p) was determined at a pass energy of 40 eV, using the binding energy of carbon as the reference (C1s: 285 eV). The chemical states of the components were identified over a representative 2x5mm surface area, and appropriate standards for XPS reference spectra were also used. A linear or Shirley background subtraction was applied to obtain the XPS signal intensity. The peaks were fitted using the asymmetric Gaussian/Lorentzian mixed function.

3. Results and discussion

3.1. X-ray photoelectron spectroscopy - chemical composition analysis

In the first stage of the work, the surface properties of titanium with different grain sizes were investigated. In order to evaluate the chemical state and composition of the nano- and microcrystalline samples, XPS measurements were performed. The XPS studies confirmed that oxygen and carbon were present on both the nano- and microcrystalline titanium. The detection of carbon was attributed to standard pollution from the laboratory atmosphere. The presence of oxygen was attributed to the spontaneous formation of a passive layer of titanium oxides on the substrate.

For a detailed analysis of the stoichiometry of the oxides on the titanium surface, high resolution Ti2p spectra were measured. The