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Investigation of the mechanical and chemical characteristics of nanotubular and nano-pitted anodic films on grade 2 titanium dental implant materials

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ABSTRACT

Objective: The objective of this study was to investigate the reproducibility, mechanical integrity, surface characteristics and corrosion behavior of nanotubular (NT) titanium oxide arrays in comparison with a novel nano-pitted (NP) anodic film.

Methods: Surface treatment processes were developed to grow homogenous NT and NP anodic films on the surface of grade 2 titanium discs and dental implants. The effect of process parameters on the surface characteristics and reproducibility of the anodic films was investigated and optimized. The mechanical integrity of the NT and NP anodic films were investigated by scanning electron microscopy, surface roughness measurement, scratch resistance and screwing tests, while the chemical and physicochemical properties were investigated in corrosion tests, contact angle measurement and X-ray photoelectron spectroscopy (XPS).

Results and discussion: The growth of NT anodic films was highly affected by process parameters, especially by temperature, and they were apt to corrosion and exfoliation. In contrast, the anodic growth of NP film showed high reproducibility even on the surface of 3-dimensional screw dental implants and they did not show signs of corrosion and exfoliation. The underlying reason of the difference in the tendency for exfoliation of the NT and NP anodic films is unclear; however the XPS analysis revealed fluorine dopants in a magnitude larger concentration on NT anodic film than on NP surface, which was identified as a possible causative. Concerning other surface characteristics that are supposed to affect the biological behavior of titanium implants, surface roughness values were found to be similar, whereas considerable differences were revealed in the wettability of the NT and NP anodic films.

Conclusion: Our findings suggest that the applicability of NT anodic films on the surface of titanium bone implants may be limited because of mechanical considerations. In contrast, it is worth to consider the applicability of nano-pitted anodic films over nanotubular arrays for the enhancement of the biological properties of titanium implants.

1. Introduction

Self-ordered, vertically oriented nanotubular titanium-dioxide (TiO_2) arrays have the capability of attenuating the attachment of biofilm forming pathogenic bacteria on the surface of medical grade titanium substrates, while mesenchymal stem cells show improved osteogenic differentiation on such surfaces [1–2]. This phenomenon has made nanotubular TiO_2 arrays promising candidates to enhance the biological performance of titanium bone substitutes, such as dental and orthopedic implants [3]. The growing demand for a higher quality of life after joint and tooth replacement has become an essential requirement from the patients side, whereas the survival of those bone implants is compromised by the increasing incidence of implant-associated infections, recently [4–5]. The spread of antibiotic resistance

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among the biofilm forming bacteria exacerbates the problem that may reduce the success rate of implants and implant revisions or even result in life-threatening complications [6,7,8]. Therefore, the development of alternative antibacterial strategies that do not contribute to the spreading of antibiotic resistance, but rather prevent the occurrence of implant-associated infections has become an urgent issue not just for implant manufacturers but also for the world's health care system [9].

It has been suggested that the anodic growth of nanotubular TiO_2 arrays may offer a cost-effective and reliable method for the surface treatment of titanium implants so as to enhance their resistance against infections [10–11]. This idea is driven by the fact that through the precise control of the electrochemical process parameters homogenous nanotubular TiO_2 arrays can be grown on titanium substrates, for instance on titanium foils [12]. The anodic growth of nanotubular TiO_2 arrays can be a reliable method, provided that the process parameters are set in a suitable range that allows the production of uniform surfaces, which can be easily investigated in in vitro experimental settings, e.g. in biocompatibility and microbiology studies [13]. The response of various mammalian and bacterial cells was investigated on nanotubular TiO_2 arrays and correlations have been demonstrated between the survival rate of the cells and the physical, chemical and physicochemical properties of the nanotubes [14–15]. These findings demonstrated the superiority of the anodic nanotubular TiO_2 arrays in terms of osteogenic differentiation rate of mesenchymal stem cells and antibacterial property over micro-rough implant surfaces that were created by etching, sandblasting or by the combinations thereof.

On the other hand, little is known about the mechanical resistance and the reproducibility of the anodic nanotubular TiO_2 arrays on the surface of bulk titanium substrates in comparison to the conventional surface treatment methods, e.g. etching, sandblasting [16–17] or spark anodization [18]. Furthermore, there is limited information in the literature concerning the mechanical performance of the anodic nanotubular TiO_2 arrays on the surface of 3-dimensional implant geometries. As yet, the comparison of the mechanical integrity of the anodic nanotubular TiO_2 arrays from practical point of view with other types of anodic films that exhibit different nanosurfaces has also been a lacking chapter in the art.

The objective of our study was to investigate the characteristics and reproducibility of the anodic growth of homogenous, self-ordered, vertically oriented nanotubular TiO_2 arrays on the surface of bulk titanium substrates, such as discs and dental implants in comparison to a nano-pitted anodic films, which were obtained in a novel two-stage anodizing process. We also investigated the durability of anodic films under mechanical stress that may emerge when a dental implant is driven into the jawbone.

2. Materials and methods

2.1. Surface treatment process

Various electrochemical treatment parameters were applied to Grade 2 titanium (Createch, France) discs ($h = 2$ mm, ∅14 mm) and screw dental implants (Sanatmetal, Hungary) so as to create homogenous anodic films that exhibit either nanotubular (NT) or nano-pitted (NP) TiO_2 features on the surface. Table 1 gives an overview on the sequence of the surface treatment steps and the range of parameters that were systematically optimized. The discs were subjected to a three-sequence surface treatment process. In the first step, the machining marks were removed by electrochemical polishing. In the second step, the polished discs were subjected to acid etching in order to initiate the formation of hydroxide islands on the surface to catalyze nanopore formation [19]. In the third step, nanotubular and nano-pitted anodic films were grown on the surface of the discs. In the following the final parameter and experimental set-ups are further detailed that had been applied for the production of the test samples.

Table 1
shows the sequence of the surface treatment process and the range of tested parameters.

Electrochemical polishing	
Anode-cathode configuration	Anode-cathode distance: 5 mm Cathode geometry: planar, cylindrical mesh
Material of the cathode	316 L stainless steel
Electrolytes	Struers AII solution, and NANOTI EP Electrolyte
Voltage	10 V – 80 V
Temperature	− 40 °C – (+40 °C)
Agitation	Stirring: 100–1000 rpm, or Laminar flow: 0.1–0.5 l/min
Time	10 s – 1200 s
Etching	
Etchants	HCl, H_3PO_4, $(COOH)_2 \times 2H_2O + H_2O_2$, $HF + H_3PO_4 + dH_2O$
Temperature	20 °C – 60 °C
Agitation	Ultrasonic
Time	30 s – 1200 s
Anodization	
Anode-cathode configuration	Anode-cathode distance: 3–65 mm Cathode geometry: planar, cylindrical mesh
Material of the cathode	316 L stainless steel,
Electrolyte	HF, HCl, H_3PO_4, $NH_4F + H_2O + C_2H_4(OH)_2$, $NH_4F + H_2O + C_3H_8O_2$ NANOTI AN I & NANOTI AN II Electrolytes
Voltage	20 V – 100 V
Temperature	− 40 °C – (+ 50 °C)
Agitation	Stirring 100–1000 rpm, laminar flow 0.1–0.5 l/min, no agitation
Time	200 s – 3600 s

2.2. Electrochemical polishing

The electrochemical polishing was carried out in a two-electrode setup (anode-cathode distance was 5 mm) by using a DC power source (Elektro-Automatik, EA-PS8080-40) in a steady electrolyte flow with 0.1 l/min velocity using a thermoplastic mag drive centrifugal pump (HTM6 PP, GemmeCotti), while the temperature of the electrolyte was kept at 15 °C. As electropolishing compound NANOTI EP Electrolyte (NANOTI Ltd., UK) was used (Table 2).

2.3. Chemical etching

The chemical etching of the electropolished workpieces was carried out in the compound of 0.1 wt% HF, 1 wt% H_3PO_4 and distilled water (Molar Chemicals, Hungary) in an ultrasonic bath for 3 min at room temperature. After etching the workpieces were rinsed in distilled water for 4 min in an ultrasonic bath in order to remove residual acid from the surface. After rinsing the workpieces were further cleaned in

Table 2
shows the parameter sets that were suitable to create homogenous NT anodic films.

		NT-1	NT-2	NT-3	NT-4
Electrochemical polishing	Voltage	30 V			
	Electrode	316 L stainless steel			
	Duration	35 s			
	Electrolyte	NANOTI EP Electrolyte			
	Cleaning	Ultrasonic cleaner: 5 min in absolute acetone and 5 min in absolute ethanol			
Chemical etching	Etchant	0.1 wt% HF + 1 wt% H3PO4 + (distilled) H_2O			
	Duration	3 min (in an ultrasonic bath)			
	Cleaning	4 min (in an ultrasonic cleaner)			
Anodization	Voltage	80 V			100 V
	Electrode	316 L stainless steel			
	Duration	600 s	900 s	300 s	300 s
	Electrolyte	0.6 wt% NH_4F + 3 wt% $H_2O + C_2H_4(OH)_2$			0.3 wt% NH_4F + 3 wt% $H_2O + C_2H_4(OH)_2$
	Heat treatment	400 °C for 2 h	–		