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Investigating dry electro-chemical polishing of titanium structures

Novel polishing methods for the MedTech industry

Abstract: With the introduction of novel automated polishing methods, more attention has recently been paid to post-processing methods of metallic implants. One such method is the polishing process known as *DryLyte*®. The most significant difference to previous electropolishing methods is the use of solid organic polymer particles activated with sulfonic acid acting as the electrolyte. The solid particle electrolyte raises new question in terms of polishing results for small features as well as overall polishing quality of metallic surfaces. The aim of this study was to determine the quality of the polishing process for titanium rods with different initial surface roughness and with tapped holes in three different orientations (0°, 45°, 90°) by subjecting them to the *DryLyte*® polishing process for 30 min. In addition, the influence of the process parameters *voltage* and the *anodic time T2* during the treatment on the resulting surface quality and the polishing efficiency was determined. In conclusion, the dry electro-chemical finishing process has shown great smoothing capabilities for titanium even with small, tapped holes. The R_a values were lowered significantly throughout all titanium samples after 30 min polishing time.

Keywords: Dry electro-chemical polishing, titanium

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1 Introduction

The interest in novel automated polishing methods has steadily increased over the past few years due to rise of additive manufacturing (AM) in general [1]. The development for a subsequent post processing method of AM structures with the ability to produce satisfying polishing results on complex-shaped structures is seen as a future requirement. One such method was developed by the company GPAInnova (Barcelona, Spain [2]) which is known as their automated polishing process *DryLyte*®. A notable difference compared to traditional electropolishing methods is the usage of porous solid styrene polymer particles containing sulfonic acid derivatives which are acting as the electrolyte in the polishing process. It is already known that the achievable final surface quality depends on the initial roughness and the treatment times [3].

In this study, the polishing quality of Ti samples was investigated after 30 min treatment time in the solid electrolyte as a function of the initial roughness, orientation of the sample and cavities and process parameters such as applied *voltage* or *anodic time T2*.

2 Theory of electro-chemical polishing of titanium

Compared to other metals the electro-chemical polishing of titanium surfaces is rather challenging due to the fast formation of a passive titanium oxide layer. Specific chemical properties of the electrolyte, *voltage* and process time, as well as stirring modes are required to give the material dissolution with surface flattening the advantage over oxide formation. Theoretically, it means that the electro-chemical process must run in the potentiodynamic or potentiostatic transpassive regime [4]. Two mass-transport mechanisms are discussed in the literature to understand the polishing rate: a) the product-mass transport-limiting “salt film mechanism” and b) the acceptor-mass transport-limiting “acceptor mechanism” [1]. In the first case, the titanium ions generated on the anode cannot diffuse fast enough into the electrolyte and therefore dissolution occurs preferred on the surface peaks.

For the second mechanism, an acceptor molecule is required to chelate the titanium ions and remove them from the surface. The transport of the acceptor towards the anode is rate-limiting. Regarding the shape change of the sample during electropolishing, one must consider the geometrical current density distribution on the surface which depends on the orientation of the sample to the cathodic net insert (see Figure 2) as well as on the surface topography at the beginning of the process [1].

2.1 Process parameters

To understand the *DryLyte*® process, all these mentioned mechanisms play a role, however, at a different extent. According to the manufacture process receipt the electropolishing is run in an alternating pulse mode with four phases:

Phase T1 = no applied voltage; The system chemically equilibrates – formation of wet layers on the sample surface (anode) and the „dry"-particles of the electrolyte. The particles are not completely dry but contain water, sulfuric acid and sulfonic acid species [5] which act as acceptor for titanium ions produced during Phase T2.

Phase T2 = applied positive voltage; Anodic formation and dissolution of the titanium oxide species as well as metallic titanium. The voltage must be high enough to reach the transpassive region (> 20 V). $Ti \rightarrow Ti^{4+} + 4e^-$. Because the electrolyte consists of porous particles which slide tangentially against the sample surface, the product-mass transfer mechanism seems not to be relevant. However, the rate of the acceptor-mass transport is strongly enhanced.

Phase T3 = no applied voltage; The system chemically re-equilibrates: re-formation of wet layers on the sample surface (anode) and the „dry"-particles of the electrolyte.

Phase T4 = applied negative voltage, alternating the electrical polarization – reduction of oxidized titanium species as well crystal reorganization of the species on the surface including titanium „plating ".

The total process time is given by the number *n* of cycles of the phase pattern (T1-T2-T3-T4). The anodic dissolution time T2 (10, 20 and 30 µs used here) is therefore only part of the total process time (n·T2/(T1+T2+T3+T4). For a total process time of 30 min and our selected values for T1-T4, the number of cycles is between 18 and 22.5 million.

2.2 Sulfonic acid activated polymer particle electrolyte

The "dry" particles consist of macro-porous solid styrene divinylbenzene copolymer matrix functionalized with sulfonic acid. It acts as acid cation exchanger (i.e. Amberlite-252RF-H-L) [5]. To achieve conductivity during the electro-chemical process small amounts of sulphuric acid and water are needed [6]. The macro-porous particles have a sufficient retention capability for water and sulphuric acid which guaranties that the sample becomes wet during the mechanical stirring, controlled by the humidity sensor. By sliding over the surface of the anodic sample the porous particles bring the acid cation exchanger in contact with the formed titanium ion species ("acceptor mechanism"). Mechanical abrasion from the titanium certainly plays only a subordinate role for the polishing effect since the solid particles are not hard enough.

3 Materials and Methods

The aim of this study was to determine the polishing efficiency (PE, decrease of R_a [%]) of the process on titanium rods (supplied by Bibus Metals AG, Switzerland) processed with the DryLyte® system (DLyte 10H + Ti). The surface of the titanium rods was sub-sectioned into four regions which were beforehand mechanically modified. Specifically, the sections were either roughened, rough machined, fine machined or mechanically polished by hand in order to achieve a different starting surface roughness, see Figure 1.

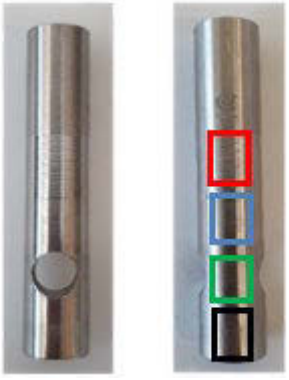

Figure 1 Titanium rod with roughened (red), rough machined (blue), mechanically polished (green) and **fine machined** (black) subsections. Graphics from [3].

Samples of four different initial surface roughness were then subjected to 30 min of polishing in the dry-electro-chemical machine operated with the "dry" electrolyte DLyte MIX MSA-S S10 by systematically varying the orientation of the sample and cavities (0°, 45°, 90°, see Figure 2), cavity type (ø8 mm, through hole in radial direction and blind hole in axial direction), process parameters such as applied *voltage* (20 V, 30 V and 40 V) and *anodic time T2* (10 µs, 20 µs and 30 µs). T1, T3 and T4 were kept constant (10 µs, 10 µs and 50 µs, respectively).

After the polishing process, the samples were cleaned with compressed air to remove any residual polymer particles. Afterwards, the obtained surface roughness was determined through tactile measurement (Tesa Rugosurf 90). Each measurement was carried out three times.

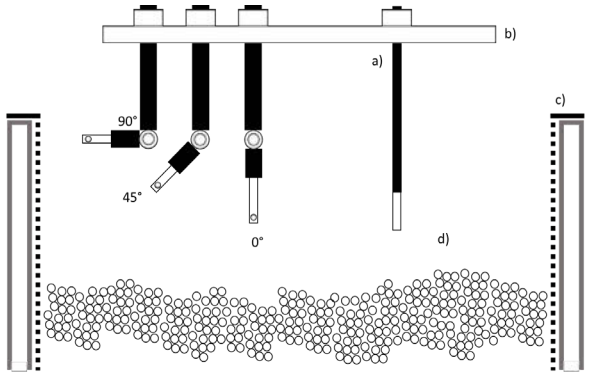

Figure 2 Scheme of the mounted titanium rods in 90°, 45° and 0° orientation. Additionally, the humidity sensor (a), the anode sample holder (b), the container with the cathodic net insert (c) and the polymer particles (d) are indicated.

4 Results

First, the PE was studied as a function of the applied voltage. Its increase from 20 V to 40 V led to a significantly lowered R_a value of all the surfaces as seen in Table 1.

Table 1: R_a values before and after the *DryLyte*® process and achieved PE as a function of the *voltage* (T2 = 10 µs, n = 3).

Subsection	Voltage [V]	R_a start [µm]	R_a 30 min [µm]	PE [%]
Mech polished	20	0.19 ± 0.01	0.11 ± 0.01	42.1
Mech polished	30	0.29 ± 0.01	0.14 ± 0.02	51.7
Mech polished	40	0.17 ± 0.01	0.07 ± 0.00	58.8
Fine machined	20	0.43 ± 0.01	0.22 ± 0.03	48.8
Fine machined	30	0.40 ± 0.02	0.18 ± 0.02	55.0
Fine machined	40	0.44 ± 0.01	0.16 ± 0.02	63.6
Rough machined	20	0.64 ± 0.00	0.36 ± 0.01	43.8

Continuation of Table 1

Subsection	Voltage [V]	R_a start [µm]	R_a 30 min [µm]	PE [%]
Rough machined	30	0.60 ± 0.01	0.28 ± 0.01	53.3
Rough machined	40	0.50 ± 0.01	0.12 ± 0.01	76.0
Roughened	20	1.27 ± 0.04	1.16 ± 0.02	8.7
Roughened	30	1.18 ± 0.01	1.03 ± 0.01	12.7
Roughened	40	1.24 ± 0.00	1.05 ± 0.01	15.3

This decrease of R_a value was observed in all four initial roughness sections with the largest PE being observed for surface with low initial R_a values such as mechanically polished or fine machined surfaces. The second process parameter examined was the *anodic time T2*. Table 2 shows that the PE of mechanically polished and fine machined surfaces increases drastically with *anodic time T2* = 20 µs. Whereas in comparison, the roughened surface displays diverging results as seen in Table 2.

Table 2: R_a values before and after the *DryLyte*® process and resulting PE as a function of *anodic time T2* (V = 35 V, n = 3).

Subsection	T2 [µs]	R_a start [µm]	R_a 30 min [µm]	PE [%]
Mech polished	10	0.15 ± 0.02	0.08 ± 0.02	46.7
Mech Polished	20	0.21 ± 0.02	0.08 ± 0.01	61.9
Mech Polished	30	0.27 ± 0.02	0.07 ± 0.01	74.1
Fine Machined	10	0.39 ± 0.05	0.17 ± 0.01	56.4
Fine Machined	20	0.40 ± 0.03	0.10 ± 0.03	75.0
Fine Machined	30	0.30 ± 0.01	0.08 ± 0.01	73.3
Rough machined	10	0.53 ± 0.01	0.20 ± 0.03	62.3
Rough machined	20	0.50 ± 0.00	0.12 ± 0.05	76.0
Rough Machined	30	0.39 ± 0.01	0.08 ± 0.02	79.5
Roughened	10	1.24 ± 0.03	1.03 ± 0.02	16.9
Roughened	20	1.22 ± 0.01	0.99 ± 0.02	18.9
Roughened	30	1.26 ± 0.02	0.86 ± 0.01	31.7

The results of the orientational study for cavities (see Figure 2) are displayed in Table 3.

Table 3: Angle-dependent R_a values inside cavities before and after the *DryLyte*® process and resulting PE (V =35 V, T2 = 10 µs, n = 3).

Hole type	Angle [°]	R_a start [µm]	R_a 30 min [µm]	PE [%]
Through	0	1.42 ± 0.05	1.41 ± 0.06	0.7
Blind	0	3.83 ± 0.23	2.74 ± 0.17	28.5
Through	45	0.73 ± 0.06	0.77 ± 0.17	-5.5
Blind	45	5.85 ± 1.71	3.09 ± 0.27	47.2
Through	90	1.24 ± 0.20	1.18 ± 0.09	4.8
Blind	90	2.69 ± 0.08	2.23 ± 0.05	17.1

Independent of the sample orientation, the through boring exhibits a low PE. In contrast, the blind holes seemed to be considerably more affected by the orientation, with a maximum of 47.1 % PE at 45° indicating that Faraday electric field distribution plays a role.

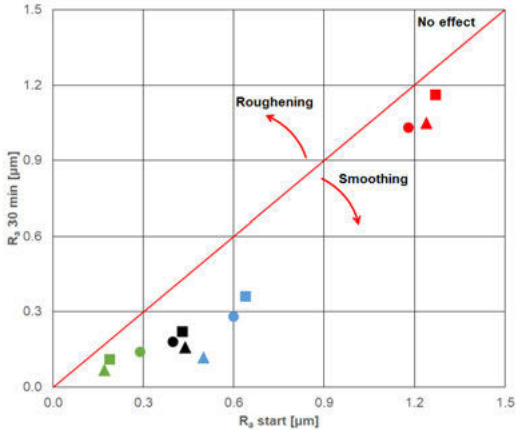

Figure 3 Effect of *voltage* on the polishing efficiency for the mech. polished, **fine machined**, rough machined and roughened surfaces (rectangles = 20 V, circles = 30 V and triangles = 40 V). An increased deviation to the red line corresponds to a high PE.

The influence of the parameter *voltage* on the polishing efficiency is displayed in Figure 3 for mechanically polished and rough machined surfaces. The increase in *voltage* for the 30-minute process leads to an increased polishing efficiency for both surface qualities.

The influence of the parameter *anodic time T2* on the polishing efficiency is displayed in Figure 4 for a mechanically polished and rough machined surfaces. A prolonged *anodic time T2* of the process increases the polishing efficiency likewise.

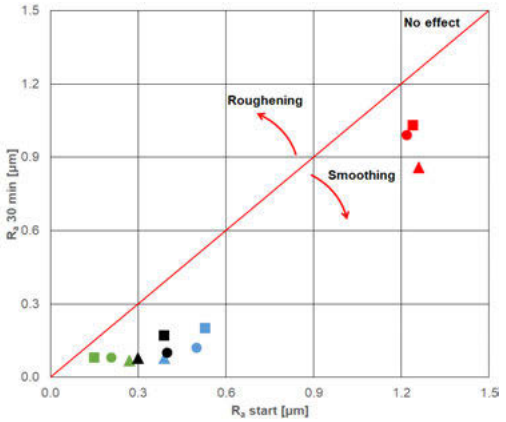

Figure 4 Effect of *anodic time T2* on the polishing efficiency for the mech. polished, **fine machined**, rough machined and roughened surfaces (rectangles = 10 µs, circles = 20 µs and triangles = 30 µs). An increased deviation to the red line corresponds to a high PE.

5 Conclusion

In conclusion, the "dry" electro-chemical polishing process has shown great smoothing capabilities for titanium even with small, tapped holes. The R_a values were lowered significantly throughout all titanium samples after 30 min polishing time.

The processing *voltage* and the *anodic time T2* play a crucial role. The process has shown good PE for blind hole oriented in a 45° angle while the roughness for the through holes remained unaffected regardless of the orientation.

Author Statement

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