

How is wettability of titanium surfaces influenced by their preparation and storage conditions?

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Abstract The effect of two different etching procedures with inorganic acids (HSE and CSE)—one using additionally strongly oxidising conditions due to the presence of CrO_3 (CSE)—and consecutive storage conditions (dry methanol and air) for previous corundum blasted titanium surfaces is compared with respect to their wettability behaviour and the potential of the etching processes for removing remaining blasting material. The etching procedures result in distinct different surface morphologies. Whereas the HSE surface shows sub-mm to sub- μm structures but neither porosity nor undercuts, the CSE surface is extremely rugged and porous with structures protruding the more homogeneously attacked areas by several micrometers. By EDX analysis both remaining blasting material and chromium and sulphur from the etching treatment has been detected on the CSE surfaces only. Both surfaces states show super-hydrophilic behaviour immediately after etching and storage up to 28 days in dry methanol. Whereas contact with air does not change super-hydrophilicity for the CSE samples, wettings angles of the HSE samples increase within minutes and reach about angles of about 60° and 90° after one and 2 days exposure to air, respectively. The increasing hydrophobicity is discussed with respect to the formation of

a surface coverage from hydrocarbons originating from aromatic compounds present in traces in air.

1 Introduction

In biomaterials research, based on investigations of a number of groups it is well accepted that surface energy and with this wettability of implant materials play an important role in protein adsorption [1–4], resulting protein conformation [1, 2, 4], and in vitro biological response to these surfaces [5–10]. For load bearing implants it could be shown that surface morphology too influences strongly the functional capacity of the implant surface in vivo [11, 12].

In recent years numerous techniques have been developed to produce defined surface morphologies. Besides depositing methods like plasma spray [13, 14] mechanically and chemically based ablation techniques like blasting with corundum [9, 10, 14, 15], glass beads [9, 14], zirconia [10], and titania [16] and chemical etching in mixtures of inorganic acids [16, 17] either alone or in combination are widely used especially for treatment of titanium based materials.

In parallel it has been shown for blasted surfaces, that without a very serious post-treatment these surfaces contain remaining particles from the blasting material even in their final commercial status [15, 18]. And there are indications that these particles are associated with early loosening of implant in the sense of third body wear [15] thus giving an etching treatment following the blasting step two associated combined effects. First is to remove mentioned blasting material particles completely from the materials surface. Besides, as the second effect the etching treatment results in the formation of an additional sub- μm surface morphology which has been shown to give only little

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biological effect in vitro [19, 20] but to significantly enhance bone response in vivo [19, 21–23].

In this work, the effect of two different etching procedures and consecutive storage conditions for titanium surfaces will be compared with respect to their wettability behaviour. It will be analysed how both, the etching process and the storage conditions influence the stability of the super-hydrophilic surfaces resulting from both etching processes. Besides the effect of both etching procedures on removing remaining blasting material will be investigated. Results will be discussed with respect to surface chemistry and morphology of the samples after the etching process.

2 Materials and methods

Corundum blasted samples from c.p. titanium grade 4 underwent two different etching processes as described in brief in the following.

The first process (HSE) was only one etching step in a solution from 50% HCl (32%), 25% H₂SO₄ (95–97%) and 25% of distilled water. Treatment was performed for 300 s at a temperature of 108°C (±3°). Following samples were immediately transferred to a bath from distilled water with three washing steps in total.

The second process (CSE) as already used by Jennissen et al. [17, 24] is a two step method, consisting in an etching step in diluted nitric acid and a consecutive oxidation step using a chromic oxide containing sulphuric acid. In short the process consists of an etching treatment in 5% HNO₃ at 80°C for 2 h, followed by washing steps in distilled water. Finally samples are washed and stored in dry methanol until the oxidation treatment. For this, first 1.3% CrO₃ are dissolved by stirring in hot 92% H₂SO₄. After heating to 235°C (±5°) the samples were stored for 1 h in this solution. Subsequent washing steps in distilled water are followed by a boiling step in 2% EDTA (pH 7.0) for 30 min. The EDTA-treatment is followed by boiling in distilled water for 30 min, washing with distilled water, drying with dry methanol.

Finally both sample types were stored either in dry methanol or in a desiccator.

Dynamic contact angle measurements were performed with distilled water using an OCA 30 system (dataphysics, Filderstadt, Germany) at room temperature.

Surfaces were investigated using scanning electron microscopy (SEM) (DSM 982 Gemini, Carl Zeiss, Oberkochen, Germany) with 1 keV acceleration voltage to visualise the real topography of the outermost surface for imaging and by energy dispersive X-ray spectroscopy (EDX) using an acceleration voltage of 15 keV with a Noran Voyager 3000 System (Noran Instruments, Middleton, USA). For element specific imaging the K α lines of Cr, S, and Al were used.

XPS measurements were carried out at a PHI 5600 CI system (Physical Electronics) equipped with a hemispheric electron energy analyser. Both monochromatic (Al–K α) and non-monochromatic (Mg–K α) radiation and an analyser pass energy of 29 eV was used. Binding energy identification was done by handbook data [25] and some recent investigations on Cr-states in battery material [26].

3 Results

3.1 Surface morphology and chemistry

Surface morphologies of the titanium samples resulting from the etching processes have been investigated by scanning electron microscopy. Figures 1 and 2 give morphologies for the treatments HSE (Fig. 1) and CSE (Fig. 2) in two different magnifications each. The HSE treatment (Fig. 1a and b) results in a surface morphology which can be described as an overlay of irregularly shaped groves, the larger being in the range between 10 and 40 μ m and the smaller being around 2 μ m in diameter. Additionally the morphology is shaped by numerous flat groves of even smaller diameter (Fig. 1b).

For the CSE treatment (Fig. 2) a highly rugged surface, showing additionally irregularly shaped wholes (ranging from sub- μ m to about 10 μ m in diameter) is obtained. Clearly two types of surfaces can be distinguished with the extremely rugged, more dark shining in SEM being protruding the more homogeneously attacked (see lower left part in Fig. 2b) by several micrometers. Furthermore, a number of particles as the one in the upper right part of Fig. 2a have been detected.

To analyze the chemical composition of the surfaces, EDX-mapping and XPS analysis have been performed. For the HSE treated samples no elements besides titanium could be detected (data not shown). However for the CSE treatment an enrichment of both chromium and sulphur could be shown (Fig. 3) with both elements being clearly co-located as follows from Fig. 3b and c. The measured XPS spectral shapes (Fig. 3e) point to sulphur in mainly S⁶⁺ (sulfate) state and some residuals of S⁰ (elemental or sulphide). Chromium (Fig. 3f) is mainly in Cr³⁺; some parts of Cr⁶⁺ maybe found in the high energetic peak shoulder. Quantification of the XPS spectra result in 4.4 (±0.3) atom-% chromium and 0.8 (±0.1) atom-% sulphur, respectively.

Besides these elements a local enrichment of aluminium was detected too for this surface. Figure 4 gives a SEM image for a CSE sample with a particle which can be identified as a remaining from the blasting treatment because of its shape and elemental composition (Fig. 4b) rich in aluminium. Non comparable particles could be detected for the HSE samples.

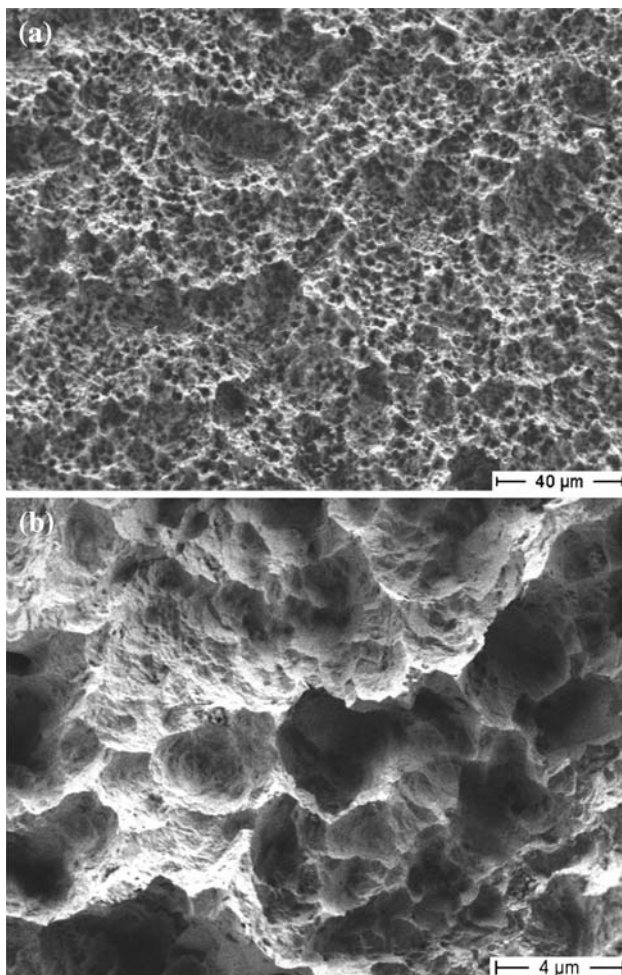


Fig. 1 SEM images of the surface state HSE: **a** magnification 500 \times ; **b** magnification 5000 \times

3.2 Wetting angle measurements

After the etching treatment the titanium samples have been stored in dry methanol or in a desiccator in air, both at room temperature for up to 28 days. Wetting angles measured for these samples as a function of storage time are given in Fig. 5. For both storage types the two etching procedures result in distinct differences in the wetting angles. Whereas for the process CSE irrespective on the storage type values clearly below 5° are measured for all exposure times, HSE samples show wetting angles above 20° for all time points and both storage types. Besides, for these samples the wetting angles strongly depend both on storage type and exposure time. For storage in dry methanol wetting angles of 34.4° (SD 9.3°) and 52.1° (SD 20.4°) are determined for 1 and 7 days of exposure, respectively. Sample storage air resulted in an even faster increase of the wetting angles reaching a plateau in the range between 120° and 130° after about 4 days of exposure.

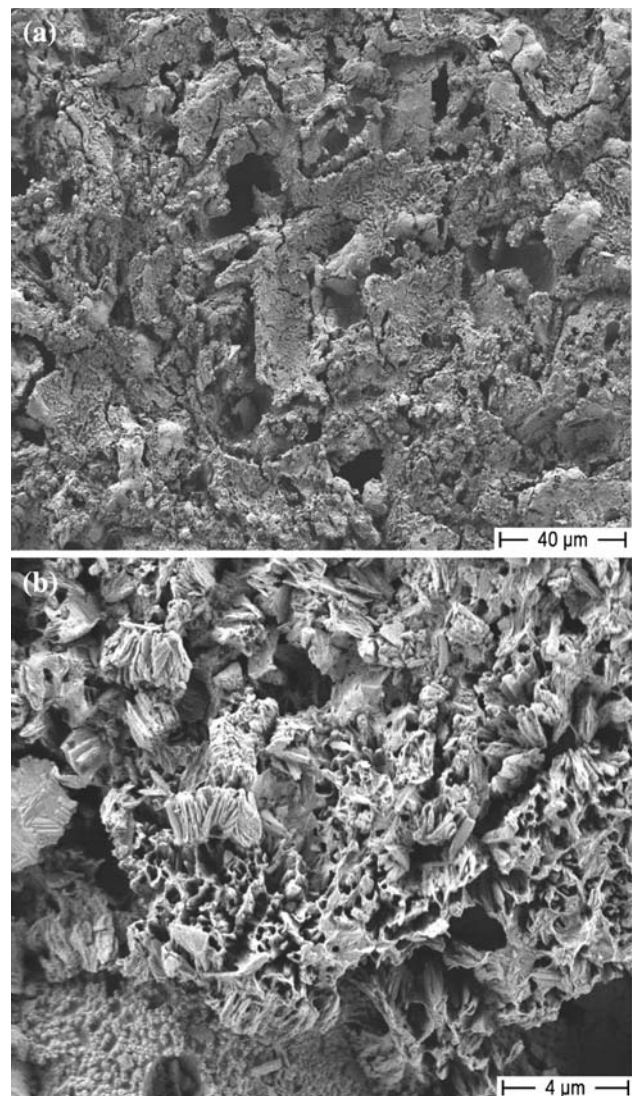
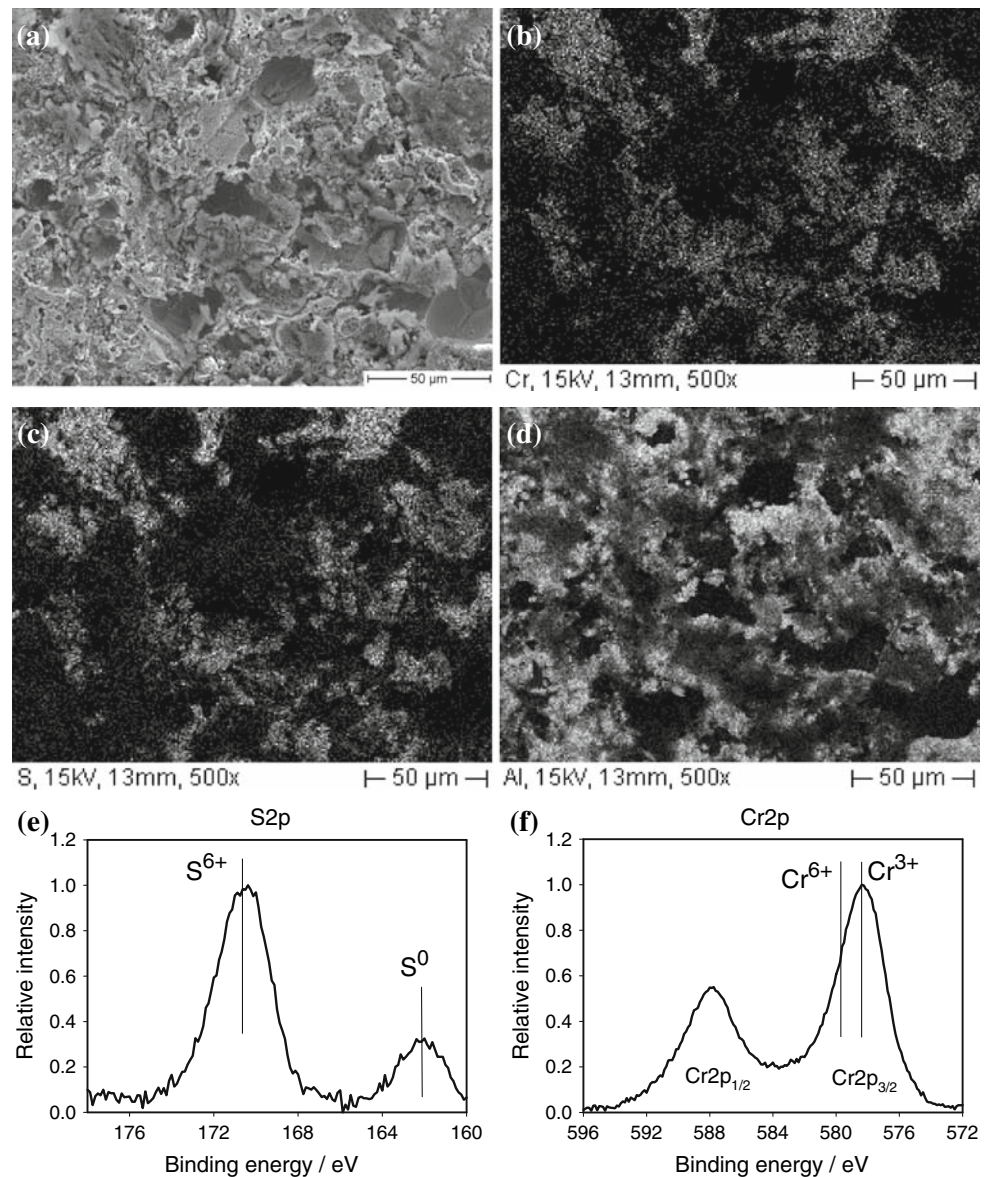


Fig. 2 SEM images of the surface state CSE: **a** magnification 500 \times ; **b** magnification 5000 \times

Due to the high scattering of the wetting angles for the HSE samples after storage in dry methanol this sample type has additionally been investigated as a function of exposure time to air after storage in dry methanol (for 28 days) with special attention to short exposure times in air (Fig. 6). As indicated in the graph in Fig. 6b the wetting angles increase rapidly within the first 100 min of exposure to air to values of about 25°. Following the constant increase in the wetting angle is less steep, however for an exposure time of 1 day (1440 min) values in the range of about 60° are already measured. Another day of exposure to air results in a further increase of the wetting angle of about 30° to values around 90°. It has to be pointed out however, that for extreme short exposure times to air (up to 5 min) wetting angles close to 0° are detected.

Fig. 3 SEM image (a) and EDX images for chromium (b), sulphur (c), and aluminium (d) (magnification 500 \times) together with XPS S2p (e), and Cr2p-spectra (f) for the surface state CSE



4 Discussion

4.1 Surface morphology and chemistry

The aim of this study was to analyse the stability of the super-hydrophilic behaviour of titanium surfaces resulting from two different etching processes as a function of time for two different storage conditions (in dry methanol and in dry air (desiccator)) and to investigate the effectivity of both etching procedures to remove remaining blasting material. Influencing factors to be analysed are the samples surface morphology and chemistry after the etching step.

As shown in Figs. 1 and 2 the etching procedures CSE and HSE give distinct differences in the surface morphology of the samples.

The morphology resulting from the one step HSE treatment (Fig. 1) resembles clearly to the superposition of two material removing processes with the corundum blasting process being mostly responsible for the sub-mm to μm morphology and the etching treatment creating a morphology mostly at the μm to sub- μm level. Clearly the process is effective in removing remaining corundum particles from the blasting treatment, because the EDX investigations gave no signals for aluminium. Very similar morphologies are reported for comparable etching processes [4, 27].

Because a treatment of titanium in 5% HNO_3 at 80 $^\circ\text{C}$ for 2 h does not seriously attack the material (data not shown) the highly rugged surface resulting from the two step CSE treatment (Fig. 2) is mainly caused by the second, strongly

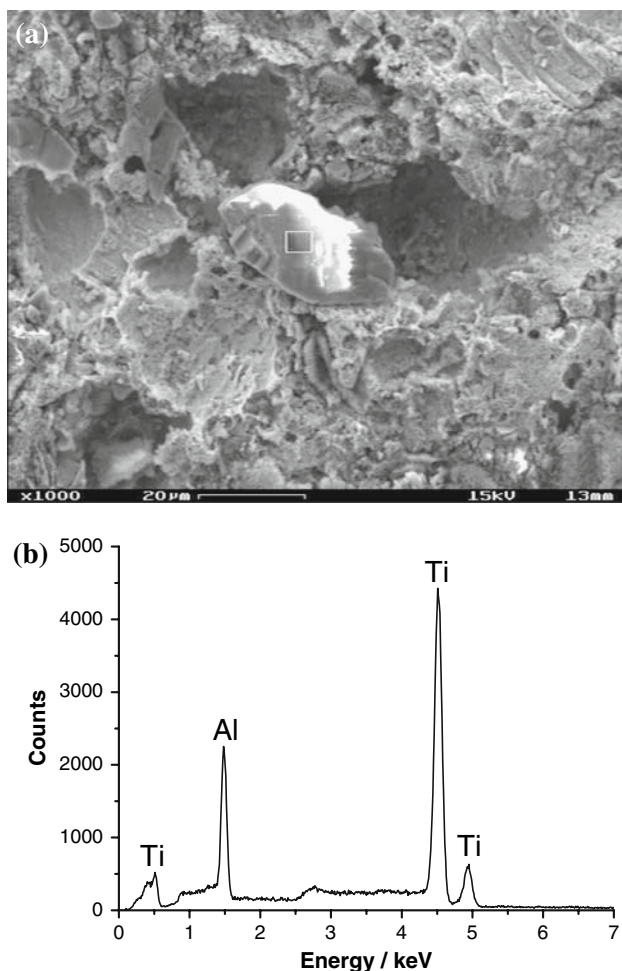


Fig. 4 SEM image with Al_2O_3 particle (a) and respective EDX spectrum (b) for the surface state CSE

oxidising step, i.e. the exposure to 92% H_2SO_4 containing 1.3% CrO_3 at a temperature of 235°C ($\pm 5^\circ$) for 1 h. The morphology together with the EDX and XPS results (Fig. 3) indicates that in this step a severe attack of the titanium material is accompanied by a deposition process. This process obviously results in very stable mainly chromium in the oxidation state 3+ and sulphur in the oxidation state 6+ containing products, i.e. a mixture from chromium (3+) oxide and sulphate (see Fig. 3b, c, e, f) that are at least not completely removed during the boiling step in 2% EDTA (pH 7.0) for 30 min. The additional detection of aluminium (Fig. 3d—in a few cases clearly particles could be detected by SEM (Fig. 4)) indicates that the total CSE process is not effective in removing alumina particles remaining from the corundum blasting process. These results are difficult to compare with former ones using this etching procedure [17, 24] because in [17] only poorly resolved light microscopic images are given and in even in [24] the resolution of the SEM images is low. Neither in [17] nor in [24] any surface analytical investigations have been performed.

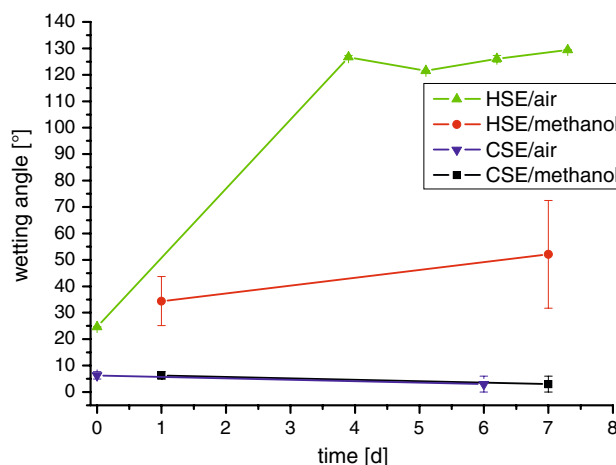


Fig. 5 Water contact angle of the surfaces states HSE and CSE after storage in dry methanol or in contact with air as a function of exposure time

4.2 Wetting angle measurements

The wetting behaviour of the surfaces resulting from the etching processes CSE and HSE in Figs. 5 and 6 shows significant differences with respect to the stability of the super-hydrophilic behaviour. For the CSE samples, in agreement with former investigations [24] both storage conditions (dry methanol and air) give very similar wetting angles below 10° irrespective of the exposure time with a slight tendency for lower angles with increasing exposure time for both storage conditions in the present investigation. Contrarily for HSE samples wetting angles strongly increase with time for both storage conditions with the exposure to air giving much higher values than measured for storage in dry methanol.

Following Fig. 6 the values measured in Fig. 5 for the surface state HSE/methanol however have to be discussed as a function of the exposure time to air between the storage in dry methanol and the start of the wetting angle measurement. The result from Fig. 6, that even a storage time of 28 days in dry methanol still gives super-hydrophilic behaviour within the first few minutes of contact with air, together with the large error bars for the surface state HSE/methanol in Fig. 5 can be explained with varying (short) exposure time to air prior to these wetting angle measurements. In the experiments for Fig. 5 samples were removed from storage in methanol in the chemistry lab and after drying in a work bench transported to the surfaces science lab in a closed box. Thus following wetting angle measurements started at a not exactly defined time point with respect to a fully dry sample surface after evaporation of the methanol. Consequently the experiments for Fig. 6 followed an alternative scheme, where samples were dried already at the stage of the contact angle measurement

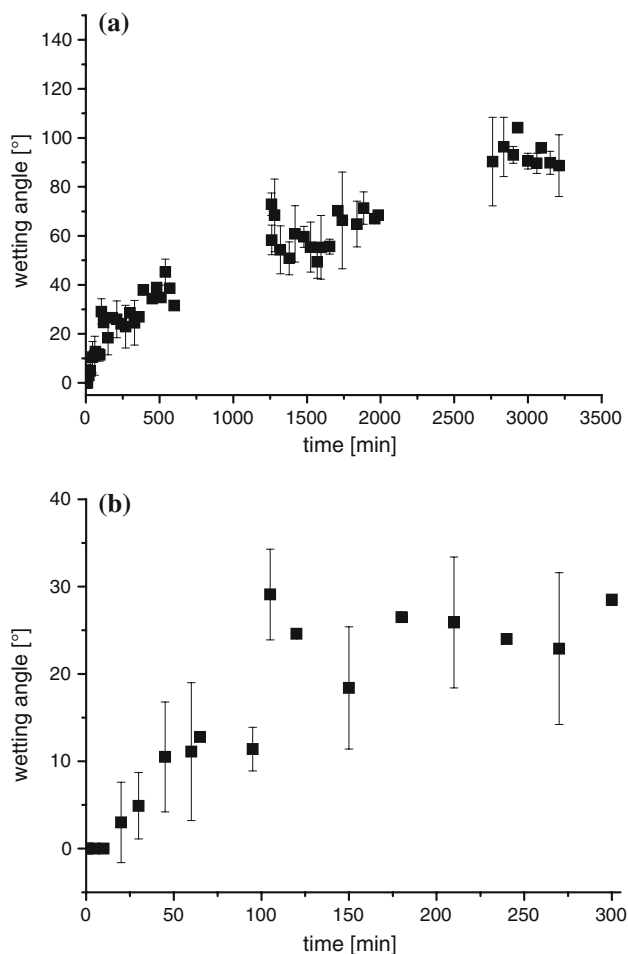


Fig. 6 Water contact angle of the surface state HSE as a function of the contact time with air after storage in dry methanol for 28 days: **a** for contact time up to 3500 min; **b** short term exposure in higher magnification

system OCA 30. The change in the surface colour due the complete evaporation of the methanol was exactly determined and taken for time zero with respect to the measurements presented in Fig. 6.

With the results from Figs. 5 and 6, i.e. the ultra-hydrophilic behaviour of both sample types after storage in dry methanol, can be concluded that the contact of titanium oxide surfaces with methanol does not result in the formation of stable methoxy-groups under room temperature conditions. These groups have been observed by Farfan-Arribas et al. [28] as intermediate product for dehydrogenation and deoxygenation of methanol on different types of TiO_2 surfaces. Depending on the surface type and temperature the methoxy-groups either recombined with OH-groups to methanol or converted to formaldehyde or methane.

Thus samples from the HSE etching procedure are stable with respect to ultra-hydrophobic behaviour when stored in methanol, however form very rapidly a hydrophobic

coating from hydrocarbons when exposed to lab atmosphere in agreement with [29].

The first effect is observed for samples prepared by the CSE etching procedure too, however exposure to lab atmosphere does not change the ultra-hydrophilic behaviour of these samples neither. This different behaviour can be addressed to two major reasons. Firstly, the morphologies resulting from the two etching procedures are very different with the CSE morphology being extremely cliffy and thus promoting wettability due to capillary effects. Secondly, as indicated by the EDX results, the surface chemistry of the CSE samples is at least not pure titanium dioxide but contains chromium, sulphur and aluminium derived species. It seems obvious that these species are much less active than TiO_2 with respect to the formation of a hydrophobic coating from hydrocarbons when in contact with air.

Discussing the differences in the behaviour of both surfaces when in contact with dry methanol and air respectively, results from Augugliaro et al. [30] have to be taken into consideration. These authors compared the photocatalytic oxidation behaviour of aromatic and aliphatic alcohols when in contact with surfaces from TiO_2 . For solely aromatic alcohols they found two parallel pathways corresponding to partial oxidation to an aldehyde and mineralization. In a mixture form aliphatic and aromatic alcohols the aliphatic competed with the aromatic for the mineralization pathway and did not show aldehyde formation. Thus, besides differences in the surface chemistry, differences in the oxidation behaviour of methanol and aromatic compounds present in traces in air are expected to contribute to the different wetting behaviour of the samples. Investigations of Farfan-Arribas et al. [31] however, which compare the catalytic activity of the rutile (110) surface with that of TiO_2 nanoparticles point out that the oxidation behaviour of methanol depends on the coordination of the titanium ions too, i.e. the three-dimensional, local structure. While they found formation of methane for the nanoparticles this was not observed for the rutile (110) surface. However this does not contradict to the results of our investigations.

5 Conclusions

The two etching processes applied in this work result in both, distinct differences of the surface morphology and chemistry of the samples. While the morphology resulting from the CSE treatment, due to the highly rugged surface and the wholes of different diameters reaching up to more than 10 μm , offers potential to immobilise and/or store bioactive components within these surfaces, the chemical status of this surface state together with the low potential

of this treatment to remove particles from the blasting material contradict the biological potential of this etching process.

Both chemical and morphological surface properties determine the different wetting behaviour resulting from the two etching processes. Here again the lower activity of surfaces resulting from the CSE process for the formation of a hydrophobic coating from hydrocarbons when in contact with air is accompanied by the chromium oxide and sulphur/sulphate containing surface composition.

The stability of super-hydrophilicity for the HSE surface state when in contact with dry methanol together with the fast increase of the wetting angle of these samples when in contact with air clearly point to the importance of aromatic compounds for the formation of hydrophobic coatings from hydrocarbons for surfaces from TiO₂ under these conditions.

References

- MacDonald DE, Deo N, Markovic B, Stranick M, Somasundaran P. Adsorption and dissolution behavior of human plasma fibronectin on thermally and chemically modified titanium dioxide particles. *Biomaterials*. 2002;23:1269–79.
- MacDonald DE, Rapuano BE, Deo N, Stranick M, Somasundaran P, Boskey AL. Thermal and chemical modification of titanium-aluminum-vanadium implant materials: effects on surface properties, glycoprotein adsorption, and MG63 cell attachment. *Biomaterials*. 2004;25:3135–46.
- Rupp F, Scheideler L, Olshanska N, de Wild M, Wieland M, Geis-Gerstorfer J. Enhancing surface free energy and hydrophilicity through chemical modification of microstructured titanium implant surfaces. *J Biomed Mater Res A*. 2006;76:323–34.
- Rupp F, Scheideler L, Rehbein D, Axmann D, Geis-Gerstorfer J. Roughness induced dynamic changes of wettability of acid etched titanium implant modifications. *Biomaterials*. 2004;25:1429–38.
- Postiglione L, Di Domenico G, Ramaglia L, Montagnani S, Salzano S, Di Meglio F, et al. Behavior of SaOS-2 cells cultured on different titanium surfaces. *J Dent Res*. 2003;82:692–6.
- Boyan BD, Batzer R, Kieswetter K, Liu Y, Cochran DL, Szmuckler-Moncler S, et al. Titanium surface roughness alters responsiveness of MG63 osteoblast-like cells to 1 alpha, 25-(OH)2D3. *J Biomed Mater Res*. 1998;39:77–85.
- Kieswetter K, Schwartz Z, Hummert TW, Cochran DL, Simpson J, Dean DD, et al. Surface roughness modulates the local production of growth factors and cytokines by osteoblast-like MG-63 cells. *J Biomed Mater Res*. 1996;32:55–63.
- Schneider GB, Perinpanayagam H, Clegg M, Zaharias R, Seabold D, Keller J, et al. Implant surface roughness affects osteoblast gene expression. *J Dent Res*. 2003;82:372–6.
- Luthen F, Lange R, Becker P, Rychly J, Beck U, Nebe JG. The influence of surface roughness of titanium on beta1- and beta3-integrin adhesion and the organization of fibronectin in human osteoblastic cells. *Biomaterials*. 2005;26:2423–40.
- Guizzardi S, Galli C, Martini D, Belletti S, Tinti A, Raspanti M, et al. Different titanium surface treatment influences human mandibular osteoblast response. *J Periodontol*. 2004;75:273–82.
- Hutzschenreuter P, Claes L, Pohler O. Loosening capacity of corticalis tension screws with varying surfaces and their histological correlations. *Helv Chir Acta*. 1976;43:765–8.
- Ferguson SJ, Broggin N, Wieland M, de Wild M, Rupp F, Geis-Gerstorfer J, et al. Biomechanical evaluation of the interfacial strength of a chemically modified sandblasted and acid-etched titanium surface. *J Biomed Mater Res A*. 2006;78:291–7.
- Upasani VV, Farnsworth CL, Tomlinson T, Chambers RC, Tsutsui S, Slivka MA, et al. Pedicle screw surface coatings improve fixation in nonfusion spinal constructs. *Spine*. 2009;34:335–43.
- Nebe JG, Luethen F, Lange R, Beck U. Interface interactions of osteoblasts with structured titanium and the correlation between physicochemical characteristics and cell biological parameters. *Macromol Biosci*. 2007;7:567–78.
- Schuh A, Uter W, Kachler W, Goske J, Zeiler G, Lill C. Comparative surface examinations on corundum blasted titanium implants and explants in total hip arthroplasty. *Arch Orthop Trauma Surg*. 2005;125:676–82.
- Masaki C, Schneider GB, Zaharias R, Seabold D, Stanford C. Effects of implant surface microtopography on osteoblast gene expression. *Clin Oral Implants Res*. 2005;16:650–6.
- Jennissen H, Zumbink T, Chatzinikolaïdou M, Steppuhn J. Biocoating of implants with mediator molecules: surface enhancement of metals by treatment with chromosulfuric acid. *Materialwiss Werkst*. 1999;30:838–45.
- Grubl A, Kolb A, Reinisch G, Fafilek G, Skrbensky G, Kotz R. Characterization, quantification, and isolation of aluminum oxide particles on grit blasted titanium aluminum alloy hip implants. *J Biomed Mater Res B Appl Biomater*. 2007;83:127–31.
- Kim H, Choi SH, Ryu JJ, Koh SY, Park JH, Lee IS. The biocompatibility of SLA-treated titanium implants. *Biomed Mater*. 2008;3:25011.
- Att W, Tsukimura N, Suzuki T, Ogawa T. Effect of supramicron roughness characteristics produced by 1- and 2-step acid etching on the osseointegration capability of titanium. *Int J Oral Maxillofac Implants*. 2007;22:719–28.
- Ganeles J, Zollner A, Jackowski J, ten Bruggenkate C, Beagle J, Guerra F. Immediate and early loading of Straumann implants with a chemically modified surface (SLActive) in the posterior mandible and maxilla: 1-year results from a prospective multicenter study. *Clin Oral Implants Res*. 2008;19:1119–28.
- Le Guehennec L, Goyenvalle E, Lopez-Heredia MA, Weiss P, Amouriq Y, Layrolle P. Histomorphometric analysis of the osseointegration of four different implant surfaces in the femoral epiphyses of rabbits. *Clin Oral Implants Res*. 2008;19:1103–10.
- Yang GL, He FM, Yang XF, Wang XX, Zhao SF. Bone responses to titanium implants surface-roughened by sandblasted and double etched treatments in a rabbit model. *Oral Surg Oral Med Oral Pathol Oral Radiol Endod*. 2008;106:516–24.
- Chatzinikolaïdou M, Zumbink T, Jennissen H. Stability of surface-enhanced ultrahydrophilic metals as a basis for bioactive rhBMP-2 surfaces. *Materialwiss Werkst*. 2003;34:1106–12.
- Moulder JF, Stickle WF, Sobol PE, Bomben KD. *Handbook of X-ray photoelectron spectroscopy*. Eden Prairie: Perkin Elmer Corporation; 1999.
- Oswald S, Nikolowski K, Ehrenberg H. Quasi in situ XPS investigations on intercalation mechanisms in Li-ion battery materials. *Anal Bioanal Chem*. 2009;393:1871–7.
- Elias C, Oshida Y, Lima J, Muller C. Relationship between surface properties (roughness, wettability and morphology) of titanium and dental implant removal torque. *J Mech Behav Biomed*. 2008;1:234–42.
- Farfan-Arribas E, Madix R. Different binding sites for methanol dehydrogenation and deoxygenation on stoichiometric and defective TiO₂(110) surfaces. *Surf Sci*. 2003;544:241–60.
- Lausmaa J, Kasemo B, Mattsson H, Odelius H. Multitechnique surface characterization of oxide-films on electropolished and anodically oxidized Titanium. *Appl Surf Sci*. 1990;45:189–200.

30. Augugliaro V, Kisch H, Loddo V, Lopez-Munoz M, Marquez-Alvarez C, Palmisano G, et al. Photocatalytic oxidation of aromatic alcohols to aldehydes in aqueous suspension of home-prepared titanium dioxide 1. Selectivity enhancement by aliphatic alcohols. *Appl Catal A Gen.* 2008;349:182–8.
31. Farfan-Arribas E, Biener J, Friend C, Madix R. Reactivity of methanol on TiO₂ nanoparticles supported on the Au(111) surface. *Surf Sci.* 2005;591:1–12.