Surface Characterisation of Titanium Alloy Implants

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INTRODUCTION

The excellent biocompatibility of titanium and some of its alloys, used for orthopædic and dental implants, is intimately connected with the properties of the surface in contact with the biological environment [1]. However, there is still a lack of scientific understanding as to how the chemical composition and topography of the titanium surface influences the performance of the implant in a biological environment. In this study the chemical composition and the topography of the surface of commercial pure (cp) Ti, Ti6Al7Nb (in wt.%), Ti6Al4V (in wt.%) and for comparison CoCrMo as well as their effect on the viability of the MC3T3E1 osteoblastic cell-line were investigated.

MATERIALS AND METHODS

Materials: All investigations were performed on discs, 15mm in diameter and 1 mm in thickness for cpTi and 5mm in thickness for all alloys. cpTi and Ti6Al7Nb samples were mechanically polished (p) to a mirror finish. The polished cpTi and Ti6Al7Nb samples were pretreated by double ultrasonic cleaning in hexane, acetone and ethanol 10 min for each, with intermediate rinsing in the subsequent solvent. Afterwards samples were rinsed in ultrapure water (18.2 MΩcm) and passivated in 30% HNO_3 for 1h. Finally, samples were ultrasonically rinsed in ultrapure water, dried with N_2, plasma cleaned in an O_2 plasma (0.42 mbar, 2 min.), stored in ultrapure water for 2h, dried with N_2 and packed in Al-foil. Polished samples were sterilized at 180°C for 3h. Ti6Al7Nb, Ti6Al4V and CoCrMo were either finely sandblasted (fsb) with glass beads or roughly sandblasted (rsb) with alumina and subsequently cleaned ultrasonically in a detergent. The sandblasted samples were sterilized by γ-irradiation.

Methods: X-ray photoelectron spectroscopy (XPS) data were obtained on a Specs Model SAGE 100 using unmonochromatized Mg K_α radiation at 300W (12kV, 25mA) with an electron detector pass energy of 50eV for survey spectra and 14eV for high-resolution spectra. The topography was investigated with a UBM System for optical surface rouhgness measurement using a red laser. Line profiles were obtained with a 1.75mm, 1400Points/mm line for polished, 5.6mm, 500Points/mm for finely sandblasted and 12mm, 150Points/mm for roughly sandblasted samples.

Cell culture testing: Cell culture tests were carried out with MC3T3E1 osteoblastic cell-line cultured in MEM alpha medium (Gibco) containing 5% fetal bovine serum, 10 mM β-glycerophosphate, 0.25 mM ascorbic acid, 0.2% gentamycin and 0.6% fungizone, at 37°C, 5% CO_2 and 95% relative humidity. For experiments, the cells were harvested by trypsinization, followed by seeding on polished and sandblasted specimens as well as on NaOH-etched glass controls. After 48 hours of incubation, cell viability was determined with a thiazolylblue tetrazolium-bromide (MTT) assay [2]. MTT-formazan, produced by intracellular succinate dehydrogenase, was extracted with ethanolic HEPES/NaCl. The solutions were transferred to MicroWell plates (Nunc) and the optical density of the solution was measured at 560 nm using a multiwell reader (Rainbow, SLT, Austria). A second series of test samples was fixed with 3% glutaraldehyde in PBS and prepared for scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Surface Roughness: UBM measurements (Table1) indicated that there were small differences between polished cpTi and polished Ti6Al7Nb surfaces. Sandblasted Ti6Al4V samples were smoother than corresponding Ti6Al7Nb samples and CoCrMo surface roughnesses

Alloy	Surface[1)]	R_a [µm] [2)]	R_q [µm] [2)]
cpTi	p	0.038 ± 0.005	0.050 ± 0.007
Ti6Al7Nb	p	0.015 ± 0.007	0.030 ± 0.014
Ti6Al7Nb	fsb	1.32 ± 0.18	1.93 ± 0.46
Ti6Al7Nb	rsb	4.05 ± 0.68	5.23 ± 0.36
Ti6Al4V	fsb	1.00 ± 0.08	1.31 ± 0.10
Ti6Al4V	rsb	3.78 ± 0.29	5.07 ± 0.49
CoCrMo	fsb	0.60 ± 0.04	0.79 ± 0.06
CoCrMo	rsb	2.88 ± 0.14	3.89 ± 0.27

Table 1: Roughness of cpTi and its alloys and CoCrMo surfaces. [1)] p = polished, fsb = finely sandblasted rsb = roughly sandblasted [2)] n = 3; mean values ± standard deviations

were smaller than that of Ti6Al4V surfaces. However,there was a statistically significant difference between the different type of surfaces.

Surface Composition: XPS analysis of untreated polished cpTi and Ti6Al7Nb surfaces indicated the presence of typical atmospheric contaminants, especially C and to some extent O (Table 2), as well as low-concentration contaminants such as Si, Pb, Na, Ca and Zn (<1.0 at.%) from the mechanical polishing. After pretreatment, XPS data indicated clean surfaces with reduced C values and

	cpTi[1)]	cpTi[2)]	Ti6Al7Nb[1)]	Ti6Al7Nb[2)]
Ti	18.5±1.6	26.7±0.9	19.5±0.4	22.2±0.9
Al	—	—	4.1±0.3	4.5±0.5
Nb	—	—	0.9±0.1	1.4±0.1
O	47.0±1.9	55.7±1.1	52.4±0.9	56.1±1.5
C	31.1±2.1	17.4±1.5	18.3±1.0	15.9±1.6
N	—	traces	—	traces

Table 2: XPS analysis (at.%) of polished cpTi and Ti6Al7Nb samples (n=5 for each surface; means ± standard deviations). [1)]untreated, [2)]pretreated

only traces of N from the nitric acid treatment. The cleaned surfaces showed an atomic concentration ratio of 0.66±0.08 for C/Ti and 2.09±0.04 for O/Ti compared to C/Ti = 1.71±0.25 and O/Ti = 2.55±0.14 for untreated cpTi surfaces. These results correlated with ToF-SIMS spectra (data not shown).

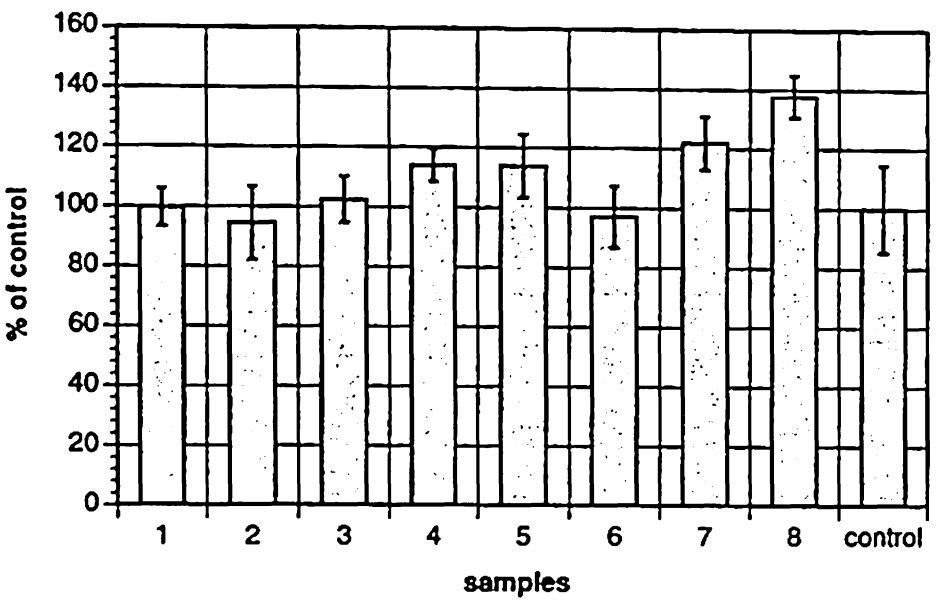
The oxide-layer thickness, calculated from the XPS intensity ratio Ti(metal)/Ti(oxide), was about 4 - 5nm for untreated polished cpTi and Ti6Al7Nb surfaces [3] and 5 - 6nm for the pretreated polished surfaces.

On finely and roughly sandblasted surfaces, Si, Na, Ca and Al from the sandblasting processes were found, as well as the contaminants C, O and N (Table 3). Nb was only detected on the roughly surface of Ti6Al7Nb. V in Ti6Al4V could not be detected (using unmonochromatized Mg K_α radiation).

	Ti6Al7Nb[1)]	Ti6Al7Nb[2)]	Ti6Al4V[1)]	Ti6Al4V[2)]
Ti	3.3±0.2	9.5±0.8	3.8±0.7	8.9±0.9
Al	4.5±0.3	18.4±1.2	3.8±0.4	15.3±2.9
Nb	—	0.6±0.1	—	—
V	—	—	—	—
O	52.6±1.0	52.2±0.6	49.7±1.5	49.4±2.6
C	13.8±1.7	16.8±1.3	19.7±2.1	23.2±5.9
Si	17.4±1.0	—	15.3±0.4	—
Na	6.0±0.4	2.5±0.5	5.9±0.4	2.8±0.6
Ca	2.4±0.3	—	1.7±0.2	traces
N	—	—	traces	traces

Table 3: XPS analysis (at.%) of sandblasted Ti6Al7Nb and Ti6Al4V samples (n=5 for each surface; mean values ± standard deviations). [1)] finely sandblasted, [1)] roughly sandblasted

Cell culture testing: On the Ti-alloy samples cell spreading varied with the different surface topographies. The cells on the roughly sandblasted surfaces were evenly spread and were often seen to form bridges between domains of the surface irregularities. On the finely sandblasted surfaces cell spreading appeared more regular and smoother. Figure 1 is a representative graph of one series out of three. It shows the activity of succinate-dehydrogenase on the different substrates. On the Ti6Al7Nb surfaces higher activity was observed with increasing roughness indicating a possible influence of surface topography on cell viability. However, no major influence of topography was observed on the different type of CoCrMo and Ti6Al4V surfaces.



1: CoCrMo, fsb
2: CoCrMo, rsb
3: cpTi, polished
4: Ti6Al4V, fsb
5: Ti6Al4V, rsb
6: Ti6Al7Nb, polished
7: Ti6Al7Nb, fsb
8: Ti6Al7Nb, rsb
control: glass etched (NaOH)

Figure 1: Activity of succinate-dehydrogenase (MTT) on CoCrMo, cpTi and Ti-alloys surfaces (n=4-6).

CONCLUSIONS

The preliminary results of the cell culture testing in this study indicate that topographical characteristics of roughly sandblasted Ti6Al7Nb surface enhance the viability of osteoblast-like cells. More detailed studies concerning osteoblast differentiation will be subject of further investigations.

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