Experimental determination and quantitative evaluation of the surface composition and topography of medical implant surfaces and their influence on osteoblastic cell-surface interactions

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Experimental Determination and Quantitative Evaluation of the Surface Composition and Topography of Medical Implant Surfaces and Their Influence on Osteoblastic Cell-Surface Interactions

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Acknowledgements
# Table of contents

Abstract ........................................................................................................................................ v

Zusammenfassung ................................................................................................................................... ix

1. General introduction ..................................................................................................................... 1
   1.1 Aim of the thesis ...................................................................................................................... 3
   1.2 Metallic implant materials ..................................................................................................... 4
      1.2.1 Titanium .......................................................................................................................... 4
      1.2.2 Co-Cr alloys ................................................................................................................... 12
      1.2.3 Stainless steel ............................................................................................................... 15
      1.2.4 Corrosion of metallic implants ...................................................................................... 18
   1.3 Hydroxyapatite (HA) ............................................................................................................. 19

2. Biocompatibility .................................................................................................................................. 25

3. Titanium as an implant material ...................................................................................................... 27
   3.1 Mechanical properties .......................................................................................................... 27
   3.2 Natural titanium oxide film .................................................................................................. 28
   3.3 Pourbaix-diagram for titanium-water .................................................................................. 30
   3.4 Solubility of TiO₂ .................................................................................................................. 31
   3.5 Adsorption of hydroxide on the TiO₂ surface and the interaction with biomolecules ........ 32
   3.6 Point of zero charge ............................................................................................................. 33
   3.7 Surface – tissue interaction .................................................................................................. 35

4. Materials .......................................................................................................................................... 41
   4.1 Materials used, chemical compositions and surface topographies .................................... 41
   4.2 Surface cleaning after treatments ......................................................................................... 45
   4.3 Sterilisation ........................................................................................................................... 46

5. Surface characterisation techniques .............................................................................................. 47
   5.1 X-ray-photoelectron-spectroscopy (XPS) ........................................................................... 47
5.1.1 Principles.................................................................48
5.1.2 Instrument..................................................................55
5.2 Time-of-flight secondary ion mass spectrometry (ToF-SIMS)........56
  5.2.1 Principles...............................................................57
  5.2.2 Instrument...............................................................63
5.3 Mechanical stylus..........................................................64
  5.3.1 Principles...............................................................64
  5.3.2 Instrument...............................................................66
5.4 Non-contact laser profilometry (LPM).................................69
  5.4.1 Principles...............................................................70
  5.4.2 Instrument...............................................................72
5.5 Interference microscopy (IM).............................................74
  5.5.1 Principles...............................................................74
  5.5.2 Instrument...............................................................77
5.6 Scanning electron microscopy (SEM), stereo-SEM....................79
  5.6.1 Principles...............................................................80
  5.6.2 Instrument...............................................................84
5.7 Atomic force microscopy (AFM).........................................87
5.8 Overview of surface characterisation and evaluation methods of
  roughness used in this thesis.............................................87

6. Evaluation of surface topography ........................................90
  6.1 Introduction.............................................................90
  6.2 Concept of wavelength-dependent roughness evaluation ..........95
    6.2.1 Overview..........................................................95
    6.2.2 Theoretical background.........................................98
  6.3 Concept of window-roughness........................................104
    6.3.1 FFT applied to synthetic roughness profiles: influence
          of wavelength and phase shift..................................106
    6.3.2 Cut-off filtering (COF) techniques............................112
    6.3.3 The inverse FFT, an application to window-roughness ....114
    6.3.4 Evaluation of three-dimensional areas........................116
  6.4 Surface treatment transfer function................................117
6.5 Application of the wavelength-dependent roughness evaluation to a real model surface ................................................................. 120

7. Results and discussion ................................................................................................................................. 124

7.1 Chemical characterisation of the implant surfaces ................................................................. 124

7.1.1 Chemical composition of polished cpTi, Ti6Al7Nb and Ti6Al4V surfaces after different cleaning regimens ........................................... 124

7.1.2 Chemical composition of polished CoCrMo surfaces after different cleaning treatment steps ................................................................. 138

7.1.3 Chemical composition of implant surfaces after blasting, blasting + etching, cpTi plasma spraying and HA plasma spraying .......... 140

7.2 Topographical characterisation of the implant surfaces ......................................................... 147

7.2.1 Comparison of mechanical stylus and non-contact laser profilometry (LMP) ................................................................. 149

7.2.2 Comparison of non-contact laser profilometry (LPM), interference microscopy (IM), stereo-SEM and atomic force microscopy (AFM) ......................................................................................... 153

7.2.3 Wavelength-dependent roughness evaluation of alumina particles blasted, etched and blasted + etched (SLA) cpTi surfaces ....... 164

7.2.4 Window-roughness evaluation of implant surfaces ......................................................... 175

7.2.5 SEM studies: angle dependent stereo-SEM and comparison of SEM and back-scattered electron (BSE) using stereo mode ..... 181

7.3 Biological characterisation of the implant surfaces using MC3T3E1 cell line and rat bone marrow cells ......................................................... 189

7.3.1 Materials and methods ......................................................................................................................... 189

7.3.2 Cell culture tests and SEM investigations ....................................................................................... 191

7.4 Correlation between window-roughness results and the biological data 201

8. Summary and outlook ................................................................................................................................. 207

9. References .................................................................................................................................................. 210

10. Appendix .................................................................................................................................................. 218
Abstract

The performance of bone-related implants is now realised to be strongly connected with the properties of the implant surface. Surface topography is one of the most important factors influencing the biological response to an implanted device. Chemical composition of the surface (oxide film, contaminants) is also considered to be an important factor in tissue response. However, there is still a lack of quantitative understanding as to how surface properties influence the performance of the implant in a biological environment. In this thesis, a method for the characterisation of surface topography is presented using wavelength-dependent roughness parameters obtained by Fast Fourier Transformation (FFT), cut-off filtering or average filtering techniques. In addition, the chemical composition and the topography of implant-relevant surfaces of commercially pure (cp) Ti, Ti6Al7Nb, Ti6Al4V, CoCrMo, and hydroxyapatite (HA) were investigated for their effects on the cell morphology, cell differentiation, cell number and cell size in a MC3T3E1 osteoblastic cell-line and primary rat bone marrow cells (RBM).

The chemical composition of the surfaces of cpTi, Ti6Al7Nb, Ti6Al4V, CoCrMo and hydroxyapatite (HA) were investigated by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). In the case of titanium, the native oxide layers of all three investigated materials consisted mainly of TiO$_2$ and the thickness was 4-6 nm. Suboxides such as Ti$_2$O$_3$ and TiO were present at the oxide/metal interface. In the case of Ti6Al7Nb and Ti6Al4V, the alloying elements were detected on the surface in oxidised form as Al$_2$O$_3$, Nb$_2$O$_5$ and VO$_x$. In the case of CoCrMo, the native oxide layer consisted mainly of Co$_2$O$_3$ and the thickness was 5-6 nm.

Finely and coarsely blasted surfaces were covered in the range of 16–18% of the surface with blasting particles such as glass beads and alumina particles, respectively. Also titanium plasma sprayed (TPS) surfaces were found to contain some Al, probably due to a previous alumina blasting process. In the case of HA, the detected atomic ratio of Ca/P of about 1.59 is close to the theoretical ratio of 1.67 of pure HA.

For bone-related implants, rough surfaces with roughness features in different scale ranges (mm to submicron range) are thought to lead to better performance in
many applications. Such surfaces were fabricated using particle blasting, etching, lithographic microfabrication and combinations of these techniques to produce controlled topographies across a range of about 100 μm to 100 nm. 2-D profiles and 3-D area scans were taken in exactly the same area for optimum comparability of the results of the different characterisation techniques. Non-contact laser profilometry (LPM) was found to be a useful method to characterise topographical features in the millimeter to micrometer range, whereas interference microscopy (IM) and stereo-SEM extended the accessible range into the sub-micrometer region. Stereo-SEM was particularly useful for quantifying topographies with complex, strongly corrugated ('sharp') and high-aspect-ratio properties with only minor risk of artefacts and 'distortions' of the true profiles. The techniques LPM, IM and stereo-SEM generally complemented each other in the study of rough surfaces across a wide range of dimensions. Due to tip-related envelope problems, AFM was not suitable for the type of surfaces investigated in this thesis, but clearly has merits for investigating low-roughness or smooth surfaces down to the nanometer range. It is in that respect highly complementary to stereo-SEM, which does not give satisfactory results for such smooth surfaces.

However, independent of the method used, the evaluation of topographical data in terms of standardised 'integral' amplitude roughness parameters such as Rₐ, Rₐ or R₂DIN were often of limited value for the description of real implant surfaces. For example, two surfaces that behave very differently in a given situation may have the same Rₐ value. In addition, on rough surfaces, fine roughness features in the low micron- or submicron-range that may be important for performance in a given application, are often hidden by the coarser contributions to roughness. This is often a major limitation in conventional topography evaluation, and therefore a general interest exists in describing surface profiles with wavelength-dependent functions rather than with integral topographical parameters.

Wavelength-dependent evaluation of the profiles was performed using Fast Fourier Transformation (FFT) and filtering techniques to determine roughness contributions in the different scale (dimension) ranges relevant to biomaterial surface performance. Wavelength-dependent roughness evaluation was demonstrated to be a valuable method for the quantitative description of surface topographies in various
characteristic roughness ranges from the mm to the nm range, opening up the possibility for correlation with data from in vitro and in vivo assays. Additionally the technique was demonstrated to be a useful quantitative indicator of the individual effects of consecutive surface treatment processes and to be useful in the development of surface treatment processes and in quality control.

Preliminary cell culture studies demonstrated that RBM cells appeared to be more sensitive than the MC3T3-E1 cell line to surface composition and topography as assessed by effects on cell number (DNA) and cell differentiation (ALP/DNA). The following correlations between surface topography and biochemical data obtained from primary RBM cell culture studies were found:

- In the range of 3 - 10 μm, a correlation was found between the roughness parameters $R_a$, $R_l$, $R_k$, $L_r$ and $S_m$ and cell differentiation (ALP/DNA). Cell differentiation increased with increasing $R_a$, $R_l$, $R_k$, $L_r$ and $S_m$ values.
- In the ranges of 10 - 50 μm and 50 - 500 μm, a correlation was only found between $S_m$ and the cell differentiation.
- No correlation at all was found between the roughness parameters and cell differentiation, when the values were calculated over the total wavelength range.

Thus it appears that topographical features in the size range of 3 - 10 μm are particularly relevant in influencing the differentiation (ALP/DNA) of RBM cells in vitro.

Furthermore, correlations between surface topography and bone contact were found, when the in vivo data of Buser et al. [5] and Wong et al. [6] were analysed by the wavelength-dependent method:

- For integral roughness parameters calculated over the total wavelength range and those calculated in the range of 50 - 500 μm, a correlation was found between the bone contact and the roughness parameters $R_a$, $S_m$, $R_l$, $R_k$, $S_k$ and $K$. Bone contact increased with increasing $R_a$, $S_m$, $R_l$ and $R_k$ values, and decreased with increasing $S_k$ and $K$ values.
• In the range of 3 – 10 μm, no correlation was found between the bone contact and the roughness values.

Thus it appears that topographical features in the size range of 50 – 500 μm are the prime factors influencing the formation of bone contact with implant in vivo.
Zusammenfassung


Die chemische Zusammensetzung von Reintitan (cp) Ti, Ti6Al7Nb, Ti6Al4V, CoCrMo und Hydroxyapatit (HA) wird mittels Röntgen-Photoelektronenspektroskopie (XPS) und Flugzeit-Sekundärionen-Massenspektrometrie (ToF-SIMS) untersucht. Die natürlich gebildete Oxidschicht auf den Titan Implantatwerkstoffen Reintitan (cp) Ti, Ti6Al7Nb und Ti6Al4V besteht vorwiegend aus TiO₂ und ist 4-6 nm dick. An der Grenzfläche Oxid/Metall sind zudem die Oxide Ti₂O₃ und TiO nachweisbar. Bei den Legierungen werden zusätzlich die Legierungselemente in oxidierter Form, als Al₂O₃, Nb₂O₅ bzw. VOₓ, in die Oxidschicht eingebaut. Die natürlich gebildete Oxidschicht auf CoCrMo besteht vorwiegend aus Co₂O₃ und ist 5-6 nm dick.

Die Untersuchung der fein (Glasperlen)- und grobgestrahlten (Korund-Partikel) Oberflächen zeigt, dass diese mit jeweils 16-18% Strahlmittel-Rückständen bedeckt sind. Auch auf plasmagespritzten (TPS) Titanschichten wird vereinzelt Korund
gefunden, welches dem vorangehenden Strahlprozess zugeordnet werden kann. Das Ca/P Verhältnis von 1.59 auf plasmagespritzten Hydroxyapatit (HA) – Schichten liegt nahe beim stöchiometrischen Wert für reines HA (1.67).


Die erhaltenen Resultate der topographischen Charakterisierung zeigen, dass die Standard Rauheitsparameter wie Rₐ, R₉ oder R₂DIN ungenügend sind, um die Topographien der Implantate vollständig zu charakterisieren. Es ist möglich, dass zwei sehr unterschiedliche Profile denselben Rₐ Wert zeigen. Weiter stellt man oft fest, dass kleine Partikel oder Strukturmerkmale gar nicht erfasst werden. Dies ist oft eine ernsthafte Einschränkung bei der Messung und Bewertung von Topographien. Deshalb besteht ein allgemeines Interesse, die Rauheitsparameter nicht als integrale Werte, sondern als Funktion der Wellenlänge darzustellen.

Die ersten Resultate der biologischen Untersuchungen zeigen, dass Primärzellen (RBM) bezüglich Zellproliferation (DNA) und Differenzierung (ALP/DNA) auf die chemische Zusammensetzung und auf die Topographie empfindlicher reagieren als Osteoblast Zellen der MC3T3-E1 Zelllinie. Die folgenden Korrelationen zwischen den Topographiedaten und den biologischen Ergebnissen der RBM Zellkultur Tests können dank der neuen Methode der wellenlängenabhängigen Rauheitsberechnungen aufgezeigt werden.

- Es existiert eine Korrelation zwischen den Rauheitsparametern $R_a$, $R_t$, $R_k$, $L_r$ und $S_m$ und der Differenzierungsneigung der Zellen (ALP/DNA) für den Bereich $3 - 10 \, \mu m$. Die Differenzierung der Zellen nimmt dabei mit steigenden Rauheitswerten $R_a$, $R_t$, $R_k$, $L_r$ und $S_m$ zu.
- In den Bereichen $10 - 50 \, \mu m$ und $50 - 500 \, \mu m$ kann eine Korrelation zwischen $S_m$ und der Differenzierung der Zellen beobachtet werden.
- Eine Korrelation zwischen der Differenzierung der Zellen und den Rauheitsparametem des ungefilterten Profils kann hingegen nicht gefunden werden.

Diese Resultate deuten darauf hin, dass hauptsächlich die Topographieanteile im Bereich $3 - 10 \, \mu m$ die in vitro Differenzierung der RBM Primärzellen beeinflussen.

Zusammenfassung

- Der Knochenkontakt und die Rauheitsparameter $R_a$, $R_t$, $S_m$, $R_k$, $S_k$ und $K$, berechnet für das ungefilterte Profil wie auch für den Bereich 50 – 500 μm, zeigen eine signifikante Abhängigkeit. Dabei steigt der Knochenkontakt mit steigenden $R_a$, $R_t$, $S_m$ und $R_k$ Werten und sinkt mit steigenden $S_k$ und $K$ Werten.

- Eine Korrelation zwischen dem Knochenkontakt und den Rauheitsparametern, berechnet für den Bereich 3 – 10 μm, kann hingegen nicht gefunden werden.

Diese Resultate deuten darauf hin, dass die Bildung von Knochengewebe in unmittelbarer Nähe der Implantatoberfläche hauptsächlich durch topographische Strukturmerkmale im Mikrometerbereich beeinflusst werden.
1. General introduction

Metals in various forms have been commonly used as implants since the 1920s. The first metal developed specifically for human use was “Sherman Vanadium Steel”, which was used to manufacture bone fracture plates and screws. Since then many different materials and designs have been employed, that have typically been developed through a trial and error approach. It is now realised that the interaction of implants such as artificial hip or knee joints, dental implants or bone-fracture plates with the biological environment is strongly connected with different properties of the implant surface (Figure 1) [1-3]. Surface topography is one of the most important factors influencing the biological response, e.g. cell adhesion, morphology, proliferation and differentiation [4]. In the case of titanium implants, increased surface roughness, achieved through processes such as particle blasting, plasma spraying of titanium and hydroxyapatite or chemical/electrochemical etching, is successfully used today to promote bone integration and long-term stability of the implant in the patient [5-10]. The chemical composition of the surface (oxide film, contaminants) is also considered to be an important factor as regards tissue response [11].

Fig.1: Biomaterial surface properties considered affecting the response of the biological environment in both in vitro and in vivo situations.
However, there is still a lack of scientific understanding as to how these surface properties quantitatively influence the performance of the implant in a biological environment:

- How does the chemical composition of the surface influence the biological response? What is the role of the surface contaminants?
- How important is the microstructure and topography of the surface at different scales of dimension? What is the optimum surface roughness? In what scale range?
- How can bone ingrowth be accelerated on the implant surface?

Therefore, the surface characterisation of biomaterials is particularly important if the biocompatibility of implants is to be understood, and if biomaterials are going to be designed, rather than arrived by purely empirical approaches [12].
1.1 Aim of the thesis

In my thesis, the chemical composition of different used implant surfaces (see Table VIII) will be characterised with X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion spectrometry (ToF-SIMS). In particular the study of the titanium- and CoCrMo-oxide layer on polished surfaces, composition of the finely and coarsely blasted surfaces as well as the characterisation of the air plasma sprayed titanium and hydroxyapatite surfaces. The topography of the used implant surfaces, in particular of finely and coarsely blasted, plasma sprayed or coarsely blasted + etched surfaces often show fine roughness features in the low micron- or submicron-range that may be important for performance in biological application, but are often hidden by the coarser contributions to roughness. This is often a major limitation in conventional topography evaluation. Therefore, my thesis aimed at developing a method to describe surface topographies with wavelength-dependent roughness parameters such as window roughness and transfer functions. A part from computational procedures and a combination of different experimental techniques were searched enabling the experimental measurement of topographies across the whole scale-size of interest, often extending from the nanometer to the millimeter range. Therefore, more than one topographical method will be used and compared: contact profilometry, non-contact laser profilometry (LPM), interference microscopy (IM), stereo-SEM as well as atomic force microscopy (AFM).

The ultimate goal of my thesis is the quantitative correlation of the in vitro biological performance data with surface topographical data in the various size ranges of biological relevance.

In this chapter, a short overview on metals used for implants as well as hydroxyapatite (HA) and their physical and chemical properties is given. In chapter 2, the definition of biocompatibility is discussed. In chapter 3, the importance of titanium as a biomaterial is pointed out. If not specified otherwise, the information given in the following chapters is taken from textbooks and review articles [13-22].
1.2 Metallic implant materials

1.2.1 Titanium

Occurrence

Titanium is widely distributed throughout the universe. It has been discovered in the stars, in interstellar dust, in meteorites, and on the surface of the earth. Its concentration within the earth’s crust (about 0.6%) makes it the fourth most abundant of the structural metals (after aluminum, iron, and magnesium). It is 20 times more prevalent than chromium, 30 times more than nickel, 60 times more than copper, 100 times more than tungsten, and 600 times more than molybdenum [13]. Concentrated sources of the metal are the minerals ilmenite (FeO·TiO₂), titanomagnetite (Fe₂O₃·TiO₂), rutile (tetragonal TiO₂), anatase (tetragonal TiO₂), and brookite (orthorombic TiO₂). At a temperature of 800°C, anatase and brookite transform into rutile [13]. Normally rutile and anatase are present. In the case of rutile, anatase as well as brookite, six O²⁻-ions are coordinated to one Ti⁴⁺-ion in the form of a slightly distorted octahedron (Figure 2). Each O²⁻-ion is coordinated to three Ti⁴⁺-ions [23]. Ti and O are bound 60% ionically and 40% covalently in TiO₂. Ilmenite and rutile are the most important titanium minerals.

![TiO₂ crystal structure of a) rutile and b) anatase.](image)

*Fig. 2: TiO₂ crystal structure of a) rutile and b) anatase.*
Discovery and fabrication

Titanium was first discovered in minerals now known as rutile by W. Gregor (England) and M.H. Klaproth (Germany) in 1794. The first commercial mill products were produced by the Titanium Metals Company of America (TMCA) around 1950. The most well known method of titanium production is the Kroll process, which involves the reduction of TiCl₄ by magnesium [13]. The first step in the process is the preparation of the tetrachloride itself, which is carried out by the chlorination of a mixture of carbon with rutile or ilmenite. The Kroll magnesium-reduction reaction takes place in a closed, heated reactor vessel under inert atmosphere. Liquid TiCl₄ is introduced to the liquid magnesium already present in the vessel, thereby initiating the reaction

\[ 2 \text{Mg} + \text{TiCl}_4 \rightarrow 2 \text{MgCl}_2 + \text{Ti} \] (1)

The reaction products are commercially pure sponge-titanium (in the form of a porous, grey, coke-like mass) and MgCl₂, most of which can be drained out of the reaction chamber as a liquid. The MgCl₂ is electrochemically recycled. The titanium sponge is consolidated by arc melting in a water-cooled copper crucible: this process involves several iterations of a procedure in which an arc is maintained between a consumable compacted-sponge-titanium electrode and a pool of molten sponge. The different qualities of commercially pure (cp) titanium (>99 wt%) are selected in different grades of purity, dependent on the impurity contents of hydrogen, oxygen, nitrogen, carbon and iron. Oxygen, carbon and nitrogen increase the strength, but decrease the ductility. Table I lists the different grades of quality of cp Ti together with the corresponding typical impurity contents (wt%) and their influences on the physical and chemical properties [14].
<table>
<thead>
<tr>
<th>Quality</th>
<th>Impurity Contents</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-purity Ti</td>
<td></td>
<td>High-purity Ti has one-half the oxygen content as commercially pure (ASTM Grade 1) titanium. High-purity Ti is produced from a special grade of sponge (&lt;0.1 wt% oxygen).</td>
</tr>
<tr>
<td>ASTM Grade 1</td>
<td>0.15 0.05 0.10 0.20</td>
<td>Grade 1 has the highest purity, lowest strength, and the best room temperature ductility and formability of the four ASTM unalloyed Ti grades.</td>
</tr>
<tr>
<td>ASTM Grade 2</td>
<td>0.25 0.03 0.10 0.30</td>
<td>ASTM Grade 2 Ti is the workhorse for industrial applications requiring good ductility and corrosion resistance. The guaranteed minimum yield strength of 275 MPa for Grade 2 is comparable to those of annealed austenitic stainless steels.</td>
</tr>
<tr>
<td>ASTM Grade 3</td>
<td>0.35 0.05 0.10 0.30</td>
<td>Like the other grades of Ti metals and alloys, Grade 3 bridges the design gap between aluminum and steel. Grade 3 has lower iron limits than Grade 4 Ti.</td>
</tr>
<tr>
<td>ASTM Grade 4</td>
<td>0.40 0.05 0.10 0.50</td>
<td>Grade 4 has the highest strength of the four ASTM grades of unalloyed Ti and outstanding corrosion fatigue resistance in salt water, but also moderate formability.</td>
</tr>
</tbody>
</table>

Tab. I: Different grades of quality of cp Ti together with the corresponding typical impurity contents (wt%) and their influences on the physical and chemical properties [14].

Commercially pure (cp) titanium and its alloys

Commercially pure titanium (cpTi) undergoes an allotropic phase-transformation from hexagonal-close-packed (hcp) structure, known as the α-phase to body-centred cubic (bcc) β-phase as its temperature is raised through 882.5°C. Figure 3 shows the hpc and bcc structures.
Elements dissolved in titanium that produce little change in the phase-transformation temperature (e.g. tin) or increase it (e.g. aluminum, oxygen, carbon or nitrogen) are known as α stabilisers. They are simple metals or interstitial elements – generally non-transition elements. As an example Figure 4 shows the Ti-Al phase diagram.

Fig. 4: Ti-Al phase diagram [13].
The transformation temperature increases with increasing weight percent of Al from 0 wt% up to a limit of 30 wt%. In this composition range the α-phase is stabilised. Alloying additions that decrease the phase-transformation temperature are referred to as β stabilisers. They generally belong to the family of transition metals (e.g. molybdenum, niobium or vanadium) and noble metals – i.e. metals that, like titanium, have unfilled or just-filled d-electron bands.

Figure 5 shows the classification scheme for binary titanium alloy phase diagrams. α and β are hcp and bcc solid-solution alloys, respectively. γ represents an intermetallic compound and l is the liquid phase.

Fig. 5: The classification scheme for binary titanium alloy phase diagrams. α and β are hcp and bcc solid-solution alloys, respectively, γ represents an inter-metallic compound and l is the liquid phase [13].
In the alloys, the single-phase-α and single-phase-β regions of the phase diagram are not in contact as they are in pure titanium; they are instead separated by a two-phase α+β region whose width increases with increasing solute concentration. Based on these considerations, technical alloys of titanium are classified as α, β and α+β. A list of some commercial alloys subdivided into these categories is presented in Table II.

<table>
<thead>
<tr>
<th>Composition (wt%)</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti5Al2.5Sn</td>
<td>α</td>
</tr>
<tr>
<td>Ti8Al1Mo1V</td>
<td>Near-α</td>
</tr>
<tr>
<td>Ti6Al2Sn4Zr2Mo</td>
<td>α+β</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>Near-β</td>
</tr>
<tr>
<td>Ti6Al6V2Sn</td>
<td>β</td>
</tr>
<tr>
<td>Ti3Al2.5V</td>
<td></td>
</tr>
<tr>
<td>Ti6Al7Nb</td>
<td></td>
</tr>
<tr>
<td>Ti6Al2Sn4Zr6Mo</td>
<td></td>
</tr>
<tr>
<td>Ti5Al2Sn2Zr4Cr4Mo</td>
<td></td>
</tr>
<tr>
<td>Ti10V2Fe3Al</td>
<td></td>
</tr>
<tr>
<td>Ti13V11Cr3Al</td>
<td></td>
</tr>
<tr>
<td>Ti15V3Cr3Al3Sn</td>
<td></td>
</tr>
<tr>
<td>Ti3Al8V6Cr4Mo4Zr</td>
<td></td>
</tr>
</tbody>
</table>

Tab. II: Classification of commercial multi-component alloys [13].

Figure 6 shows the composition of U.S. technical alloys mapped onto a pseudobinary β–isomorphous phase diagram. The heterogeneous Ti6Al4V and Ti6Al7Nb (wt%) alloys have an α–β structure, where Al is enriched in the α–phase, while V and Nb, respectively are enriched in the β–phase.
Fig. 6: Compositions of U.S. technical alloys mapped onto a pseudobinary $\beta$-isomorphous [13].

Applications

Titanium and its alloys have found widespread use in the aerospace industry, because of the high strength/weight ratio (for both frame and engine components), and in the chemical and medical industries, where advantages can be taken of their corrosion resistance. Table III summarises some physical properties of commercially pure titanium:

1. General introduction
<table>
<thead>
<tr>
<th>Ordinal Number</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Weight</td>
<td>47.90</td>
</tr>
<tr>
<td>Isotope</td>
<td>$^{46}\text{Ti}$ 7.95%</td>
</tr>
<tr>
<td></td>
<td>$^{47}\text{Ti}$ 7.75%</td>
</tr>
<tr>
<td></td>
<td>$^{48}\text{Ti}$ 73.45%</td>
</tr>
<tr>
<td></td>
<td>$^{49}\text{Ti}$ 5.51%</td>
</tr>
<tr>
<td></td>
<td>$^{50}\text{Ti}$ 5.34%</td>
</tr>
<tr>
<td>Specific Weight at 20°C</td>
<td>g/cm³ 4.507</td>
</tr>
<tr>
<td>Melting Point</td>
<td>°C 1667</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>°C 3260</td>
</tr>
<tr>
<td>Thermal Conductivity at 20°C</td>
<td>W/(m°C) 23.9</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion (20-500°C)</td>
<td>$10^5$ m/(m°C) 10.8</td>
</tr>
<tr>
<td>Specific Electr. Resistance at 0-100°C</td>
<td>Ωmm²/m 0.56</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>m/Ωmm² 1.25</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>N/mm² 295</td>
</tr>
<tr>
<td>Elastic Modulus at 20°C</td>
<td>N/mm² 105000</td>
</tr>
<tr>
<td>Hardness</td>
<td>HV 60 - 160</td>
</tr>
<tr>
<td>Dielectr. Const. (Rutile)</td>
<td>79</td>
</tr>
<tr>
<td>Isoelectr. Point</td>
<td>5.5 - 7</td>
</tr>
</tbody>
</table>

Tab. III: Physical properties of titanium [13-15].

About 30 commercial alloys were on the market in mill-product form by 1972 [13]. Ti6Al4V is the most widely used Ti alloy, accounting for 50% of all the titanium tonnage worldwide. The alloy is most commonly used in the annealed form. Ti6Al4V is also hardenable in sections up to 25 mm with yield strengths as high as 1140 MPa. The aerospace industry accounts for more than 80% of Ti6Al4V usage. The largest use of Ti6Al4V outside of the aerospace is for medical prostheses; this use accounts for about 3% of the market. The alloy also has a variety of weight-reducing applications in high-performance automotive and marine equipment. Wrought Ti6Al4V is a useful material for surgical implants because of its low modulus, good tensile and fatigue strength, and biological compatibility. It is used for bone screws...
and for partial and total hip, knee, elbow, jaw, finger, and shoulder replacement joints.

Ti6Al7Nb is a high-strength titanium alloy with excellent biocompatibility for surgical implants. The alloy was developed specifically for the manufacture of femoral components for hip prostheses [24]. Hot forging procedures and mechanical working practices are the same as for the standard interstitial Ti6Al4V. The $10^7$ cycle fatigue strength of Ti6Al7Nb in rotating bending is ±500 MPa, which is in the range of Ti6Al4V.

1.2.2 Co-Cr alloys

Microstructures

The Co-Cr alloys used for medical applications have a composition in the range of 70-75% Co and 25-30% Cr. Pure Co has a hexagonal-close-packed (hcp) structure at room temperature, like α-titanium (see Fig. 2a), and is face-centred cubic (fcc) at temperatures greater than 460°C [15, 16].

A number of alloying elements will affect the transformation temperature of Co. Additions of chromium, molybdenum and tungsten tend to increase the transformation temperature, whereas iron and nickel tend to lower it. The additions of molybdenum, tungsten, chromium, manganese and silicon may also harden the resulting alloys via solid-solution hardening. The addition of nickel will also toughen the alloys. As a result of varying types and concentrations of alloying elements, one- or two-phase alloys may exist. Figure 7 shows the phase diagram of Co-Cr [16, 17].

Low concentrations of carbon tend to produce hard, brittle carbides that may ultimately determine the ductility of the alloy. When the carbides are coherent in nature, brittle characteristics dominate; however, a considerable degree of ductility may be present if the carbides precipitate, as long as they are not continuous throughout the matrix.
The cast alloys contain several alloying elements (particularly molybdenum); however, they are essentially solid solutions of Cr in Co. The addition of Mo aids in the reduction of grain size, which normally results from the casting procedure. An additional strength increase also results. CoCrMo is face-centred cubic (fcc). Carbides may be present at either grain boundaries or within the grains themselves. The variations in strength observed with the various Co-Cr alloys are due in part to the overall grain size and in part to the amount and distribution of the existing carbides [16]. In the as-cast condition of PROTASUL® as well as in the heat-treated (below 1180°C) condition of PROTASUL-2®, the carbon-containing alloy has an austenitic crystalline structure with interdendritically arranged block carbides of the type $M_{23}C_6$ ($M = Cr + Mo + Co$). The wrought Co-Cr alloys have a slightly different composition compared to the cast alloys. Table IV shows the composition of the cast and wrought Co-Cr alloys.
<table>
<thead>
<tr>
<th>Element</th>
<th>Wrought Co-Cr alloys</th>
<th>Cast Co-Cr alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>W [wt%]</td>
<td>14-16</td>
<td>---</td>
</tr>
<tr>
<td>Cr [wt%]</td>
<td>19-21</td>
<td>27-30</td>
</tr>
<tr>
<td>Ni [wt%]</td>
<td>9-11</td>
<td>2.5 max</td>
</tr>
<tr>
<td>Mo [wt%]</td>
<td>---</td>
<td>5-7</td>
</tr>
<tr>
<td>Fe [wt%]</td>
<td>3.0 max</td>
<td>0.75 max</td>
</tr>
<tr>
<td>C [wt%]</td>
<td>0.05-0.15</td>
<td>0.35 max</td>
</tr>
<tr>
<td>Mn [wt%]</td>
<td>2.0 max</td>
<td>1.0 max</td>
</tr>
<tr>
<td>Si [wt%]</td>
<td>1.0 max</td>
<td>1.0 max</td>
</tr>
<tr>
<td>Co [wt%]</td>
<td>Balance (46-53)</td>
<td>Balance (57-65)</td>
</tr>
</tbody>
</table>

Tab. IV: Composition of wrought and cast Co-Cr alloys [15].

The wrought Co-Cr alloys have much greater ductility and are capable of being cold worked. Depending on the treatments, considerable differences in the resulting mechanical properties will result.

**Fabrication**

The major disadvantage of the cast Co-Cr alloy system is that these materials work harden rapidly, so that the normal fabrication procedure used with other metals cannot be employed. Instead the alloy is cast by a lost wax (or investment casting) method. Therefore a wax pattern of the desired component is made. Then the pattern is coated with a refractory material, first by a thin coating with a slurry (suspension of silica in ethyl silicate solution) followed by complete investing after drying. After that the wax is melted out in a furnace (100°C – 150°C). The mould is heated to a high temperature burning out any traces of wax or gas-forming materials. Molten alloy is poured with gravitational or centrifugal force. The mould temperature is about 800°C – 1000°C and the alloy is at 1350°C – 1400°C. Controlling the mould temperature will have an effect on the grain size of the final cast, coarse grains which will decrease the strength are formed at higher temperatures. However, high processing temperature will result in larger carbide precipitates with greater distances between
them resulting in a less brittle material. Again, there is a complementary relationship between strength and toughness.

**Applications**

The main attribute of these alloys is corrosion resistance in chloride environments, which is related to their bulk composition as well as to the surface oxide (normally Cr$_2$O$_3$). These alloys have been successfully used for a long time in the aerospace and biomedical industry. Biological acceptance was demonstrated for Stellite (Co-Cr alloys with star-like microstructures) and for Vitallium during the 1920s. Co-Cr alloys show perhaps the most useful overall balance of corrosion resistance, fatigue resistance and strength of all implant alloys. In the case of CoCrMo, molybdenum is added to produce finer grains, which results in higher strength values after casting or forging.

Currently available devices fabricated from Co-Cr alloys encompass virtually the entire range of orthopaedic implants and a large proportion of dental applications. Implants fabricated from Co-Cr alloys include bone plates and wires, screws, nails, joint replacement parts as well as, some cardiovascular prosthesis, heart valves and rings.

**1.2.3 Stainless steel**

**Microstructures**

Chromium (>11wt%) is a major component of corrosion-resistant stainless steel. Chromium is a reactive element but it and its alloys can be passivated to give an excellent corrosion resistance by forming a strongly adherent surface oxide (Cr$_2$O$_3$).
However, a disadvantage is that chromium tends to stabilise the ferritic phase (bcc, body-centred cubic). Therefore, the mechanical properties will be reduced.

The austenitic stainless steels, especially types 316 and 316L, are most widely used for implants. To improve the corrosion resistance of 316L stainless steel in chloride solution, the carbon content of 316 stainless steel is reduced from 0.08wt% to 0.03wt% maximum to restrict carbide formation. Ni is added to stabilise the austenitic phase (fcc) at room temperature and, in addition, to enhance corrosion resistance. The austenitic phase stability can be influenced by both the Ni and Cr content as shown in Figure 8 for 0.10wt% carbon stainless steel [25]. A small concentration of Mo is added to resist pitting corrosion. The corrosion resistance of austenitic stainless steels and Co-Cr alloys are similar [22, 26].

![Figure 8: The effect of Ni and Cr contents on the austenitic phase of stainless steels containing 0.10wt% C [25].](image)

Stainless steel 316 and 316L are not hardenable by heat treatment but can be hardened by cold-working. This group of stainless steel is nonmagnetic and possesses better corrosion resistance than any others. The chemical compositions of stainless steel 316 and 316L are listed in Table V.
<table>
<thead>
<tr>
<th>Element</th>
<th>Stainless Steel 316</th>
<th>Stainless Steel 316L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr [wt%]</td>
<td>17-20</td>
<td>17-20</td>
</tr>
<tr>
<td>Ni [wt%]</td>
<td>12-14</td>
<td>12-14</td>
</tr>
<tr>
<td>Mo [wt%]</td>
<td>2-4</td>
<td>2-4</td>
</tr>
<tr>
<td>Fe [wt%]</td>
<td>Balance</td>
<td>Balance</td>
</tr>
<tr>
<td>C [wt%]</td>
<td>0.08 max</td>
<td>0.03 max</td>
</tr>
<tr>
<td>Mn [wt%]</td>
<td>2.00 max</td>
<td>2.00 max</td>
</tr>
<tr>
<td>P [wt%]</td>
<td>0.03 max</td>
<td>0.03 max</td>
</tr>
<tr>
<td>S [wt%]</td>
<td>0.03 max</td>
<td>0.03 max</td>
</tr>
<tr>
<td>Si [wt%]</td>
<td>0.75 max</td>
<td>0.75 max</td>
</tr>
</tbody>
</table>

*Tab. V: Compositions of stainless steels 316 and 316L [16].*

**Fabrication**

Stainless steels are perhaps the easiest metal implant materials to fabricate; however, strict care is required for the manufacturing of quality implant specimens. It is also possible to cast these materials to the desired shape. The disadvantages of casting are the inferior corrosion and mechanical properties compared to hot-forged and cold-worked products. Electric arc furnaces are used for melting, and subsequent vacuum arc melting techniques are often used to remove excess impurities such as C, Si and Mn.

Fully annealed austenitic stainless steel exhibit a fairly high ultimate tensile strength. However, the yield strength is low and the ductility high. As a result, plastic deformation occurs quite easy with these materials. But these materials can be strengthened by cold-working. Therefore, the yield strength and the tensile strength will be increased without appreciable change of the elastic modulus.

**Application**

Stainless steel has been used as a standardised metal implant since the 1920s, when austenic 18Cr8Ni stainless steel alloys were successfully used as implants.
Stainless steel was basically chosen because of their corrosion resistance and relative tissue compatibility. Implants fabricated from stainless steel include metal fracture plates, nails, screws and joint replacement parts.

1.2.4 Corrosion of metal implants

Most metals such as Fe, Cr, Co, Ni, Ti, Ta, Mo and W used for manufacturing implants can be tolerated by the body in minute amounts, if they are present as dissolved species in ionic or neutral form. Sometimes these metallic elements, in naturally occurring forms, are essential for cell functions (Fe) or synthesis of vitamin B\textsubscript{12} (Co), but as a general rule they cannot be tolerated in large amounts in the body. The consequence of corrosion is loss of material, which will weaken the implant, and probably more important, the corrosion products escape into the tissue resulting in undesirable effects. Steinemann [22, 26] performed in vivo corrosion measure-ments on various metals and alloys using the polarisation resistance method (Figure 9). The noble metals Au and Ag have a resistance to corrosion that is about a factor of 100 lower than high-grade stainless steel and titanium. Au and Ag resist
oxidation in air but show much less corrosion resistance in sea water or biological fluids. Metals having lower corrosion resistance than Au and Ag, such as Al, Mo and Fe, show visible attack or oxidation in living tissue and abnormal or unhealthy cells are observed in their vicinity. In fact, the metals from Fe through Ag corrode so rapidly that the supply and migration of oxygen cannot keep up with the consumption of the oxidant so that the tissue contacting the foreign body is starved of oxygen. Metals released by the corrosion process, such as V, Co, Cu and Ni, are toxic to cells; sterile abscess and cell death are observed. Similar results are presented by Galante et al. [27]. The most toxic element is V. Although stainless steel, CoCr based alloy and titanium have similar levels of polarisation resistance, they induce different tissue reactions. Steinemann [22, 26] concluded that high corrosion resistance is apparently not sufficient to suppress the minor rejection reaction observed for the two classical alloys (stainless steel, CoCr based alloy) that contain the cell-toxic nickel and cobalt as essential components. Another example given by Steinemann is the Ti6Al4V alloy, a standard metallic implant material. He suggests that four percent of toxic V suffices to elicit a prominent foreign body reaction in vivo [22, 26] and recommends avoiding toxic components as alloying elements. However, stainless steel with Ni (12 - 17%) and Cr (17 - 20%) as well as Co-Cr alloys and Ti6Al4V are commonly used as implant materials and have performed successfully.

1.3 Hydroxyapatite (HA)

Chemical composition and microstructure

Calcium phosphates are minerals that occur naturally or can be synthetically produced in different modifications. Calcium phosphates are salts of the tribasic phosphoric acid H₃PO₄. Hydroxyapatite (HA) is a pentacalcium phosphate with the following structural unit: Ca₁₀(PO₄)₆(OH)₂. It is only stable at pH ≥ 4.2 at 37°C, whereas at pH ≤ 4.2, dicalcium phosphate or brushite (CaHPO₄·2H₂O) is stable. At
higher temperatures, other phases such as Ca₃(PO₄)₂ (β-tricalcium phosphate or TPC) and Ca₄P₂O₉ (tetracalcium phosphate) are present. The unhydrated high-temperature calcium phosphate phases interact with water or body fluids at 37°C to form HA:

$$4\text{Ca}_3(\text{PO}_4)_2(\text{solid}) + 2\text{H}_2\text{O} \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2(\text{surface}) + 2\text{Ca}^{2+} + 2\text{HPO}_4^{2-} \quad (2)$$

The mineral part of bone (60 – 70%) and teeth (> 98% of enamel) is made of a crystalline form of calcium phosphate similar to HA. Stoichiometric HA consists of 39.9wt% Ca, 18.5wt% P and 3.4wt% OH, the atomic ratio Ca/P is 1.67 and the calculated density is 3.219 g/cm³. However, the Ca/P ratio of biological apatite differs from the stoichiometric value of HA. Additionally, in biological apatite the Ca²⁺ cations are partly substituted by Na⁺, K⁺, Mg²⁺ and Sr²⁺, the PO₄³⁻ anions by CO₃²⁻, HPO₄²⁻ and P₂O₇⁴⁻ groups, and the OH⁻ groups by Cl⁻, F⁻, H₂O and CO₃²⁻. The chemical compositions of the inorganic components of enamel, dentine and bone, and of stoichiometric HA are shown in Table VI.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Enamel</th>
<th>Dentine</th>
<th>Bone</th>
<th>HA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca [wt%]</td>
<td>37.6</td>
<td>40.3</td>
<td>36.3</td>
<td>39.9</td>
</tr>
<tr>
<td>P [wt%]</td>
<td>18.3</td>
<td>18.6</td>
<td>17.1</td>
<td>18.5</td>
</tr>
<tr>
<td>CO₂ [wt%]</td>
<td>3.0</td>
<td>4.8</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>Na [wt%]</td>
<td>0.7</td>
<td>0.1</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>K [wt%]</td>
<td>0.05</td>
<td>0.07</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Mg [wt%]</td>
<td>0.2</td>
<td>1.1</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Sr [wt%]</td>
<td>0.03</td>
<td>0.04</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Cl [wt%]</td>
<td>0.4</td>
<td>0.27</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>F [wt%]</td>
<td>0.01</td>
<td>0.07</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Ca/P</td>
<td>1.59</td>
<td>1.67</td>
<td>1.65</td>
<td>1.67</td>
</tr>
</tbody>
</table>

*Tab. VI: Composition of the inorganic components of enamel, dentine, bone and HA [28].*

The crystal structure of HA is hexagonal with cell dimensions a = b = 9.42 Å and c = 6.88 Å. Six of the ten calcium ions in the unit cell are associated with the hydroxyls in these columns, resulting in strong interactions among them. *Figure 10*
shows a projection of the crystal lattice of HA on the (001) plane. However, HA can also occur in a monoclinic form if it is pure and free of vacancies.

![Projection of the constituting ions of the hexagonal Ca₁₀(PO₄)₆(OH)₂ structure on the (001) plane](image)

*Fig. 10: Projection of the constituting ions of the hexagonal Ca₁₀(PO₄)₆(OH)₂ structure on the (001) plane [18].*

The substitution of OH with F increases the chemical stability due to the closer coordination of F (symmetric shape) as compared to the hydroxyl (nonsymmetric, two atoms) by the nearest calcium. This is one of the reasons for the better caries resistance of teeth following fluoridation.

The chemistry of HA is more complex than that of other apatites, because HA prepared by precipitation in solution can have molar Ca/P ratios from 1.5 to 1.66, and sometimes even outside of this range. Additionally, precipitated calcium phosphates contain variable amounts of water and often hydrogen phosphate and carbonate contamination, which all disappear in a complex manner on heating.

HA has a very low solubility and is regarded as non-resorbable in a physiological environment. As shown in Figure 11, HA is the most stable phase of calcium phosphates in aqueous solutions at room temperature and at physiological
pH (pH = 7.4). Different and controversial values for the solubility product of HA can be found in the literature. They have been summarised in a review article by Chander et al. [29].

Fig. 11: Solubility isotherms of different calcium phosphates in the system CaO-P₂O₅-H₂O at 25°C [18].

Fabrication

Many different methods have been developed to make precipitates of hydroxyapatite from an aqueous solution of Ca(NO₃)₂ and NaH₂PO₄. One method uses precipitates that are filtered and dried to form a fine particle powder. After calcination for about 3 hours at 900°C to promote crystallisation, the powder is pressed into a final form and sintered at about 1050°C to 1500°C. The phases formed at high temperature depend not only on temperature but also on the partial pressure of water in the sintering atmosphere. This is because, in the presence of water, HA can be formed and is a stable phase up to 1360°C, as shown in the phase diagram for CaO and P₂O₅ with 500 mm Hg partial pressure (Figure 12). The temperature range of stability of HA increases with the partial pressure of water, as does the rate of phase transitions of
$Ca_3(PO_4)_2$ (also called $C_3P$) or $Ca_4P_2O_9$ (also called $C_4P$) to HA. Because of kinetic barriers that affect the rates of formation of the stable calcium phosphate phases, it is often difficult to predict the volume fraction of high-temperature phases that are formed during sintering and their relative stability when cooled to room temperature.

![Phase diagram of calcium phosphates in a water atmosphere.](image)

For applying thick calcium phosphate coatings, the method of plasma spraying is often used. Plasma spraying is a form of thermal spraying, in which the coating material is rapidly heated by a plasma flame and simultaneously launched at high velocity into a substrate surface. The different plasma spraying techniques can be distinguished by the surrounding atmosphere: i.e. air plasma spraying (APS), vacuum plasma spraying (VPS), controlled atmosphere plasma spraying (CAPS) and underwater plasma spraying (UPS).

1. General introduction
Application

Calcium phosphates are chosen as implant material for their biocompatibility and direct chemical bone bonding behaviour. Since the inorganic component of natural bone and teeth consists mainly of HA, the main calcium phosphate ceramic to be studied as implant material is HA [31]. The bulk material has been clinically applied for the augmentation of the jaw, in maxillofacial surgery and artificial middle ear implants [32]. In several studies it has been demonstrated, that HA can hasten the initial biological response to implant devices, improves bone adhesion to the implanted devices, and provides a good biological base for bone ingrowth [32-34]. However, a disadvantage of HA is its brittleness and poor strength, limiting its use for implants in experiencing loads. To eliminate this problem, it has been proposed to use thin coatings of HA on metallic substrates [35]. In this way the mechanical strength of the titanium implant and the biocompatibility of the calcium phosphate coating are combined [36-38].
2. **Biocompatibility**

The following definitions are based either on those suggested at the second consensus conference on definitions in biomaterials held under the auspices of the European Society of Biomaterials in Chester, UK, September 7-8th 1991, edited by D.F. Williams, J. Black and P.J. Doherty [21] or by Black [20].

**Biomaterials** are materials that are intended to interface with biological systems to evaluate, treat, augment or replace any tissue, organ or function of the body [21]. Suture threads, contact lenses, artificial hip joints, dental implants, and heart valves are some common examples of the application of biomaterials. When these materials evoke a biological response that is compatible with the intended functionality over the intended period of treatment, they have come to be termed biocompatible [20]. By contrast, a **biological material** is a material such as bone matrix or tooth enamel, produced by a biological system [21]. **Bioactive materials** are biomaterials that are designed to elicit or modulate biological activity [21]. **Osseointegration** is a description of clinical performance of devices and is not applicable to the description of biomaterial-bone interactions [21]. Originally, it was defined as direct bone deposition on the implant surface [39]. Osseointegration can be compared with direct or primary fracture healing, in which the fragment ends become united by bone, without intermediate fibrous tissue or fibrocartilage formation [10]. A fundamental difference, however, exists: osseointegration unites bone not to bone, but to an implant surface: a foreign material [21]. Thus the material plays a decisive role for the achievement of union (see section 3.7). **Bone bonding** is defined as the establishment, by physico-chemical processes, of continuity between implant and bone matrix [21]. **Biodegradation** is the breakdown of a material mediated by a biological system [21]. The term **biological performance** is now used as a descriptor of materials in order to replace the less specific idea of biocompatibility [20]. Biological performance is defined as the interaction between the materials and the living system [20]. The two aspects of this performance are: the host response as local and systemic response, other than the intended therapeutic response, of living systems to the material and the material response as the response of the material to living systems [20].
Biomaterials are used and developed to direct, supplement or replace organs or living tissues and, as such, they have to fulfill the mechanical and biological functions required. They also have to be sterilisable and be suited to processing. But, above all, these materials must be compatible with the living environment. The interaction of biomaterials with the living environment can be classified as either biotolerant, bioinert or bioactive [20, 40], conveying respectively the sense of negative (but tolerable) local host response, absence of local host response, and positive (desired) local host response.

Many classes of materials contribute to the field of biomaterials. For example, metallic elements (titanium, gold), alloys (stainless steel, titanium, cobalt-chromium alloys) and ceramics (porcelain, alumina, hydroxyapatite) can be used for structural purposes in orthopaedic, dental applications, or for cardiovascular devices; natural or synthetic polymers such as polysaccharides, collagen, polyurethane, silicones, polyacrylates, etc., can be used in suture materials (biodegradable or not), artificial organs, contact lenses, intraocular lenses, tissue regeneration, encapsulating membranes for drug delivery, adhesives for orthopaedic and dental applications, dialysis membranes, blood bags, and so forth.
3. Titanium as an implant material

3.1 Mechanical properties

Titanium and its alloys, Ti6Al7Nb and Ti6Al4V (wt %), are among the most commonly used implant materials [41 - 45], particular for dental, orthopaedic and osteosynthesis applications [5-7, 46]. These materials are known to have a combination of properties making them particularly suited for biomedical applications: passive surface promoting excellent corrosion resistance and low rates of metal ion release [22, 26, 27, 44, 47, 48], low specific weight, low modulus of elasticity, high tensile strength, poor heat conduction, and little or no tendency to cause adverse cell or tissue reactions.

Commercially pure titanium (cpTi), Ti6Al7Nb and Ti6Al4V, have been in use as implant materials for a shorter time compared to stainless steel or cast or wrought cobalt base alloys. cpTi is used for dental implants and as a substrate material for porous coatings such as plasma-sprayed titanium or hydroxyapatite. Pure metals are not strong enough for use as orthopaedic implants, and are not used for skeletal devices. To attain higher strength alloying elements are added. Such α+β as well as β alloys are used for surgical implants. Alloy design criteria are not based only on alloying elements contribution to strength but also on the biocompatibility of the resulting alloy. Alloying additions and thermomechanical processing dictate the microstructure of the implant material. The control of microstructure is a means to attain desirable properties. In case of Ti6Al4V, the alloying elements vanadium and aluminum have been found in surrounding tissues under conditions of high wear but no toxic effect has been connected to this debris, which also includes titanium [49]. Due to the perceived safety concern and possible toxic effect, different new alloys have been designed without vanadium [14] and in some case, without aluminum [14]. There are also safety concerns regarding other alloying elements such as molybdenum or niobium [14].

Some titanium alloys that are in use today or are being considered for use as implant materials are listed in Table VII together with their mechanical properties. In
addition, the mechanical properties of cast CoCrMo, stainless steel, HA, cortical bone, bone cement as well as of dentin are shown.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Elastic Modulus [GPa]</th>
<th>Ultimate Tensile Strength [MPa]</th>
<th>Yield Strength (0.2%) [MPa]</th>
<th>Elongation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPTi $\alpha$</td>
<td>105</td>
<td>240-617</td>
<td>165-520</td>
<td>18</td>
<td>[14]</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>88-116</td>
<td>990-1184</td>
<td>789-1013</td>
<td>13</td>
<td>[14]</td>
</tr>
<tr>
<td>Ti5Al2.5Fe</td>
<td>110</td>
<td>943-1050</td>
<td>818-892</td>
<td>16</td>
<td>[14]</td>
</tr>
<tr>
<td>Ti6Al7Nb</td>
<td>108</td>
<td>900-1100</td>
<td>910-970</td>
<td>10-12</td>
<td>[14]</td>
</tr>
<tr>
<td>Ti13Nb13Zr</td>
<td>$\alpha+\beta$</td>
<td>79</td>
<td>550-1035</td>
<td>8-15</td>
<td>[14]</td>
</tr>
<tr>
<td>Ti11.5Mo6Zr2Fe</td>
<td>74-85</td>
<td>1060-1100</td>
<td>1000-1060</td>
<td>18-22</td>
<td>[14]</td>
</tr>
<tr>
<td>Ti15Mo5Zr3Al</td>
<td>15-113</td>
<td>882-1312</td>
<td>870-1284</td>
<td>11-20</td>
<td>[14]</td>
</tr>
<tr>
<td>Ti15Mo3Nb</td>
<td>79</td>
<td>1035</td>
<td>993</td>
<td>15</td>
<td>[14]</td>
</tr>
<tr>
<td>CoCrMo</td>
<td>210</td>
<td>665</td>
<td>455</td>
<td>10</td>
<td>[20]</td>
</tr>
<tr>
<td>316L stainless steel cold-worked</td>
<td>200</td>
<td>965-1000</td>
<td>750-790</td>
<td>9-20</td>
<td>[15]</td>
</tr>
<tr>
<td>HA</td>
<td>80-120</td>
<td>40-200</td>
<td></td>
<td></td>
<td>[18]</td>
</tr>
<tr>
<td>Cortical Bone</td>
<td>18</td>
<td>140</td>
<td>130</td>
<td>1</td>
<td>[15]</td>
</tr>
<tr>
<td>Bone cement</td>
<td>3</td>
<td>55</td>
<td>27</td>
<td>2</td>
<td>[15]</td>
</tr>
<tr>
<td>Dentin</td>
<td>14</td>
<td>40</td>
<td>40</td>
<td>0</td>
<td>[15]</td>
</tr>
</tbody>
</table>

Tab. VII: Mechanical properties of some titanium implant materials as well as other materials of interest.

### 3.2. Natural titanium oxide film

The excellent corrosion resistance of titanium alloys results from the formation of a very stable, continuous, highly adherent, and protective natural oxide film on the surface [49]. Because titanium metal itself is highly reactive and has an extremely high affinity for oxygen, these beneficial surface oxide films form spontaneously and instantly when fresh metal surfaces are exposed to air and/or moisture [50]. In fact, a damaged oxide film can generally reheal itself instantaneously if at least traces (parts
per million) of oxygen or water (moisture) are present in the environment. The native oxide film has a thickness of 4 to 6 nm, or 25 times the interatomic distance. Its mode of growth is specific in that the oxygen ions migrate towards the metal and react with the titanium counter-ion at the base of the oxide (Figure 13) [22, 51]. This mechanism is unique for titanium and some other elements of valency IV, such as silicon and zirconium. Ordinarily, both the oxygen anion and the metal cation migrate when a metal undergoes oxidation, or corrosion. The specific mode of oxide growth on titanium has the positive effect that no metal ion will reach the surface and be released into the electrolyte.

![Diagram of oxide growth](image)

**Fig. 13:** Surface oxide on a metal. In case of titanium, the oxide grows by the transport of oxygen from the external surface towards the metal-oxide interface where the oxidation reaction proper takes place [22].

The nature, composition and thickness of the protective surface oxides that form on titanium alloys depend on environmental conditions. In most aqueous environments, the oxide is typically TiO₂, Ti₂O₃ or TiO (with the oxidation number +4, +3 and +2 respectively). High-temperature oxidation tends to promote the formation of the chemically resistant, crystalline form of TiO₂ known as rutile, whereas lower temperatures often generate the more amorphous form of TiO₂, anatase or a mixture of rutile and anatase. Although these naturally formed films are typically 4 to 6 nm

3. Titanium as an implant material
thick and are invisible to the eye, the TiO₂ oxide is generally chemically resistant and is attacked only by very few substances, including hot, concentrated HCl, H₂SO₄, NaOH, H₃PO₄ and HF. The TiO₂ film is an n-type semiconductor (band gap between Eᵮ = 3.0 and 3.2 eV at room temperature, dependent on the crystal structure [52 - 54]) and thus can conduct electronic charge to an extent, depending on the potential drop across the semiconductor film.

3.3. Pourbaix-diagram for titanium-water

The Pourbaix diagram [55] is a plot of regions of corrosion, passivity, and immunity as they depend on electrode potential and pH. The Pourbaix diagrams are derived from the Nernst equation and from the solubility of the degradation products and the equilibrium constants of the reaction. Corrosion is defined as equilibrium between metal and its ions at a concentration of more than 10⁻⁶ molar. Immunity is defined as equilibrium between metal and its ions at a concentration of less than 10⁻⁶ molar. In that case, the corrosion is energetically impossible. Passivity is defined as equilibrium between metal and its reaction products (oxides, hydroxides) at a concentration of 10⁻⁶ molar or less.

The Pourbaix diagram [55] for the titanium-water system (Figure 14) depicts the wide range over which the passive TiO₂ film is predicted to be stable, based on thermodynamic (free energy) considerations. Oxide stability over the full pH scale is indicated over a wide range of highly oxidising to mildly reducing potentials, whereas oxide film breakdown and the resultant corrosion of titanium occur under reducing acidic conditions. Under strongly reducing (cathodic) conditions, titanium hydride formation is predicted. Titanium alloys are highly resistant to practically all salt solutions over the pH range of 3 to 11 and to temperatures well in excess of 100°C.
3.4. Solubility of TiO₂

The solubility of TiO₂ in water is very low. The constant value of 3 µM between pH 3 and pH 12 suggests that an electrochemical species dominates in solution (Figure 15). The core of this dissolved neutral species is Ti(OH)₄ (aq), where a titanium ion with its four positive charges is surrounded by four negatively charged hydroxyl groups. At physiological pH values (between pH 6.9 to pH 7.3), the first charged species are the cation Ti(OH)₃⁺ and the anion Ti(OH)₅⁻, both with a concentration of not more than 0.1 nM, which is three orders of magnitude lower than the concentration of the hydrogen ion, which is always present in solution.
3.5. Adsorption of hydroxide on the TiO₂ surface and the interaction with biomolecules

The biocompatibility and biofunctionality of implant materials are strongly connected with the interaction of biomolecules such as proteins. Most metal oxides are hydroxylated at room temperature and when water or its vapour has access to the surface [23, 56, 57]. However, proton transfer to neighbouring oxide ions should result in better neutralisation. According to Pauling’s electrostatic valence rule, the “ideal charges” in this case would be $-2/3$ for singly coordinated anions and $-4/3$ for doubly coordinated anions. The $-1$ charge of hydroxide ions comes nearer to these values than the charges 0 and $-2$ of H₂O molecules and O²⁻ ions, respectively. This model has general validity [23, 56]. It is applicable not only to (001) of anatase (Figure 16), but to other crystal faces, too, as well as to other oxides. In fact, a water molecule adsorbed on a bare metal site loses a proton, which jumps to the neighbouring surface oxide ion, leaving a hydroxyl (OH) on the metal ion. These reactions lead to two types of hydroxyl groups (Figure 16). In the case of titanium dioxide, one is bound to one Ti⁴⁺-ion site (terminal OH), and the other to two Ti⁴⁺-ion...
sites (bridging OH), and these would be expected to exhibit quite different types of chemical behaviour. The bridging groups should be strongly polarised by the two cations and therefore be acidic in character, whereas the terminal OH group is expected to be predominantly basic and exchangeable with other anions. This surface has an amphoteric nature: it has the ability to bind with both acids and bases.

The acid groups react, for example, with amines (such as ammonia and methylamine), and basic OH groups exchange with phosphates. Amino acids are also amphoteric and thus can act both as donors and acceptors: the amino (-NH₂) group is basic, while the carboxyl group (-COOH) is acidic.

3.6 Point of zero charge

The point of zero charge (PZC) is the pH at which the concentrations of the potential-determining ions on an oxide are equal. At this pH the total charge on the oxide may not be zero. The isoelectric point (IEP) is the pH at which the charge on the solid
arising from all sources is zero, i.e. adsorption of positively charged species equals that of negatively charged ones. PZC equals IEP for a pure oxide when no specific adsorption of counter ions on the oxide is involved.

For oxides with a hydrated surface, the surface chemistry in water is dominated by the chemical reactions

\[ \text{MOH}^+_{\text{surface}} \rightleftharpoons \text{MOH}_{\text{surface}} + \text{H}^+_{\text{solution}} \]  
\[ \text{MOH}_{\text{surface}} \rightleftharpoons \text{MO}^-_{\text{surface}} + \text{H}^+_{\text{solution}} \]

where M represents a metal ion at the surface, such as Al\(^{3+}\), Cr\(^{3+}\), Si\(^{4+}\), Ti\(^{4+}\) or Zr\(^{4+}\). PZC is defined in terms of the pKs of reactions (3) and (4):

\[ \text{PZC} = \frac{pK_1 + pK_2}{2} \]

For TiO\(_2\) in the two structure variants of rutile and anatase, PZC lies between pH 5 and pH 6.7 [49, 56-58]. Gold et al. [59] found the point of zero charge of the titanium dioxide surface to be in the range of pH 5 - 7. Therefore in physiological solutions, at a pH of 7.4, titanium has a weakly negatively charged surface, which gently interacts with the adsorbed proteins. In Figure 17 the TiO\(_2\)-surface charge is indicated as a function of pH in pure water systems (after Gold et al. [59]).

Other oxides such as Al\(_2\)O\(_3\), Cr\(_2\)O\(_3\) and ZrO\(_2\), have a PZC of about pH 9 [57], pH 8.4 [60, 61] and pH 2 [57], respectively. Interestingly, the PZC of pure HA is about pH 7 [58].

In the case of Ti6Al7Nb and Ti6Al4V, the PZC is certainly modified by the presence of Al, Nb (PZC of Nb\(_2\)O\(_5\) is about pH 4.5) or V (PZC of V\(_2\)O\(_5\) is between pH 1 and 2.5) [61].

3. Titanium as an implant material
3.7 Surface – tissue interaction

The interaction of the implant, such as hip or knee joints, dental implants or bone-fracture plates, with the biological environment, the formation of the foreign material/tissue interface and the long-term success or failure of the integration in the body is now realised to be strongly connected with the chemical, physical and topographical surface properties of the implant device [41, 42, 62] — in the case of titanium, with the oxide layer. On the molecular level, the chemical, physical and topographical properties of the implant surface, e.g. structure, defects, roughness,
contamination layer, surface energy and surface charges [63, 64], are highly significant in determining the type and degree of surface/biomolecule interactions [65]. It is well understood that osteoblast proliferation and differentiation are sensitive to the chemical composition and topography of an implant surface [66]. Similar observations have been noted by Lincks et al. [67] using MG63 cells on different roughened cpTi and Ti6Al4V discs.

The following sections are focussed on the interaction between either the topographical properties, the chemical properties or the physical properties and the biological environment.

**Interaction between surface topography and biological environment**

Surface topography is probably the most important single surface factor influencing the biological response. The effects of surface topography on cell adhesion vary with the type of cell. Osteoblast-like cells demonstrate significantly higher levels of cell attachment on rough surfaces than they do on smooth surfaces [68]. In contrast, more human gingival fibroblast attach to electropolished surfaces than to etched or blasted surfaces [69]. Furthermore, the geometric dimensions of microstructured surface features [70-74] and the roughness of random surfaces [75-79] are known to influence cell adhesion, morphology, orientation and motility as well as proliferation, differentiation and production of local factors in cell culture (in vitro) investigations. Studies examining the behaviour of osteoblastic cells on commercially pure titanium (cpTi) have demonstrated that proliferation decreases with increasing surface roughness, whereas differentiation increases [76-79]. Moreover, when the cells are cultured on surfaces with an average roughness $R_a \geq 2 \, \mu m$, their response to 1,25-dihydroxyvitamin D$_3$ [$1,25-(OH)_2D_3$] is enhanced, as is their production of transforming growth factor beta-1 (TGF-β1) and prostaglandin E$_2$ (PGE$_2$) [78]. Ong et al. [80] have shown that response to bone morphogenetic protein-2 (BMP-2) is also increased on rougher topographies. There appears, however, to be an upper limit to the stimulatory effect of surface roughness on osteoblastic differentiation. If surface
roughness (height and space) exceeds the dimensions of the cell, the cell will perceive the surface as smooth [81]. In some clinical contexts, this may not be a critical factor, since bone may form throughout the interstices of the rough surface creating a mechanical interlock. However, when the clinical goal is to promote bone formation along as much of an implant surface as possible, the qualities of the material, which enhance this process, are of importance.

In vivo, a major influence of surface topography on the evolution and the properties of the implant-tissue interface such as the degree of foreign body response and the percentage of newly formed bone close to the implant surface have been observed [8]. In the case of titanium implants, increased surface roughness, achieved through processes such as particle blasting, plasma spraying, or chemical/electrochemical etching has been found to promote bone integration and long-term stability of implants [5-10, 39, 46, 82]. Surface roughness has been reported to determine the shear strength of the implant-bone interface-important for the long-term fixation [5, 7, 9, 82]. The work of Buser et al. [5] and Cochran et al. [83] suggest that, at least for dental implants, surfaces with an average roughness $R_a$ of 3 to 4 $\mu$m provide excellent substrates for this purpose. Wennerberg [8] found a $R_a$ of about 1.5 $\mu$m with an average spacing of 11.1 $\mu$m and an area ratio of 1.5 as an optimum to give the firmest bone fixation among the surface structures. Two reasons for the different results could be that different implants with different manufactured topographies were investigated and that the methods used to characterise the topographies were also different (mechanical stylus versus confocal laser scanning microscopy (CLSM)).

Porous implants allow tissue ingrowth. In orthopedic implants with pores larger than about 150 $\mu$m, bony ingrowth into the pores occurs and this is useful to anchor the implant. This minimum pore size is on the order of the diameter of osteons in normal Haversian bone. It was found experimentally that small pores (less than 75 $\mu$m in size) did not permit the ingrowth of bone tissue [16].

3. Titanium as an implant material
Interaction between surface chemistry and biological environment

The chemical constituents and pH of the biological environment influence the interactions at the surface [42, 84] (Figure 18). Reactions between a biomolecule and the material surface may lead to a permanent or temporary bond formation, that can be either weak, such as van der Waals or hydrogen bonding, or strong such as ionic or covalent bonds [42]. It is also well known that the adsorption of specific cell-binding proteins depends both on the surface energy and on the sign and density of the surface charges [63, 64]. In contrast, interactions may be so strong that, for example, proteins are reversibly or irreversibly denatured by formation of multiple bonds with the surface, potentially accompanied by breaking of internal bonds within the protein [85].

3. Titanium as an implant material
Both the composition of the alloy and the manufacturing processes (thermal, mechanical and chemical treatments) influence the composition and the structure of the oxide film and therefore play an important role in biocompatibility properties. The surfaces of the implant alloys Ti6Al7Nb and Ti6Al4V are shown by x-ray photoelectron spectroscopy (XPS) and scanning Auger microscopy (SAM) to have a laterally inhomogeneous natural oxide film with a local composition that reflects the underlying duplex α-β microstructure of the alloys [86]. Lateral force measurements (LFM) in an electrolyte, taken as a function of pH, indicate slight differences in the pH-dependence of frictional force on the two oxide phases of the Ti6Al7Nb alloy: at pH 6.9 nearly no difference of friction force was observed between the two phases, while at pH 3.8 and pH 7.9 slightly higher friction forces were detected on the α-phase. It has been proposed that these differences reflect different pH-dependent surface ranges [87].

Osteoblast-like cells can discriminate between bulk materials like cpTi and Ti6Al4V, even though the surfaces of both are primarily titanium oxides [67]. These studies and others have shown that osteoblasts are sensitive to the ion composition of a material surface as well as to the crystallinity of the material [88, 89].

The surface contamination is believed to be important in modifying biological responses to the surface [42, 90]. Fresh titanium oxide surface is very reactive towards both inorganic and organic contaminants. XPS evaluations of prepared cpTi and Ti alloys surfaces revealed the presence of O, C and N containing contaminants [42, 90-92]. In an investigation of non-osseointegrated dental implants [91], contaminants such as Fe, Zn, Sn or Pb have been found on the implant surface and are believed to have contributed to the observed lack of osseointegration. Lausmaa et al. [50] reported that on cpTi and Ti6Al4V the oxide was basically TiO2 with usual ubiquitous contaminants present (O, C, N). Additional inorganic contaminants including Na, Cl, Si, Ca, P, and S were occasionally observed on an individual specimen basis. Keller et al. [92] also found O, C and N contaminants. However, inorganic contaminants such as Na, Ca and Cl were not found in contrast to Lausmaa et al. [50] or Arys et al. [91]. On the other hand, the effects of elements such as C, H, N and O on the biological response are not well known. Also it has not
been clearly established how surface treatment processes specifically influence the type and degree of surface contamination on titanium.

Interaction between physical surface properties and biological environment

Surface charge on biomaterial surfaces (metals, oxides and polymers) has been shown to influence surface properties that are relevant to the biocompatibility of the materials [41, 59, 93]. This is particularly true for anchorage-dependent cells such as osteoblasts, where surface charge affects the attachment, morphology, migration and phenotypic expression of cells *in vitro* [94]. The attachment and spreading of osteoblast cells is reported to be extraordinarily strong on very positively charged surfaces, with very intimate contact between the ventral cell membrane and the biomaterial surface. On negatively charged surfaces on the other hand, osteoblast cells tend to show a stand-off morphology with very localised attachment points [95]. It is very likely that this is an indirect effect of the biomaterial surface charges on cell behaviour, the surface charges influencing the protein species present in the culture medium and the conformation of the adsorbed proteins through electrostatic interaction. The type and conformation of the adsorbed proteins, in turn, triggers osteoblast behaviour such as adhesion, migration, spreading, proliferation and differentiation of the cells [95].
4. Materials

4.1 Materials used, chemical compositions and surface topographies

The investigation of surface chemistry and topography of commercially pure titanium (cpTi), Ti6Al4V, Ti6Al7Nb, hydroxyapatite (HA) as well as CoCrMo surfaces were performed in the form of discs, 15 mm in diameter and 1 mm in thickness for cpTi and 5 mm in thickness for all alloys. A stamping procedure was used to produce the Ti discs out of a grade 2 cpTi sheet in an annealed condition (ASTM F67). The Ti6Al4V discs as well as Ti6Al7Nb discs were turned from a 15 mm diameter wrought rod. CoCrMo discs were turned from a 15 mm diameter cast rod. CpTi bulk material was supplied by Institut Straumann AG, CH-4437 Waldenburg, Switzerland, Ti6Al4V, Ti6Al7Nb, HA and CoCrMo by Sulzer Orthopedics Ltd., CH-8404 Winterthur, Switzerland.

Mechanically polished samples were prepared by using SiC grinding paper (ultimate grit size 600-15 μm particle diameter), subsequently polished to a mirror finish with 10 μm diamond paste in oil and finally with a 0.06 μm SiO₂ suspension. The fine surface finish was obtained by blasting the surface with glass beads 150 - 230 μm in diameter. The rough surface was attained by blasting the surface with 200 - 500 μm diameter alumina particles. The room temperature blasting process was carried out with a boron carbide nozzle placed 60 to 100 mm from the sample, and a pressure of 5 to 6 bar was used. The TPS surface was produced by alumina blasting (average particle size: 250 μm) followed by plasma spray coating with titanium hydride powder using a process of Institut Straumann AG. The blasted + etched surface was obtained by alumina blasting (average particle size: 250 μm) and a subsequently HCl/H₂SO₄ acid etching (hot solution, a few minutes). The hydroxyapatite (HA) surface was produced by alumina blasting (particle size: 200 - 500 μm) of cpTi followed by APS (air plasma spraying) coating according to ASTM F1185 to produce a 150 μm thick HA layer. The structured + etched surface was first structured by electrochemical micromachining in 3 M H₂SO₄ – methanol electrolyte [96] followed by acid etching with a hot solution of HCl/H₂SO₄ for a few minutes.

Table VIII lists all investigated implant materials together with their type of
surfaces as well as their surface treatments.

<table>
<thead>
<tr>
<th>Material</th>
<th>Type of Surface</th>
<th>Surface Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>cpTi grade 2 annealed sheet (ASTM F67)</td>
<td>- polished</td>
<td>- polished to a mirror finish</td>
</tr>
<tr>
<td></td>
<td>- finely-blasted</td>
<td>- blasted with glass beads (particle size: 150-230 μm)</td>
</tr>
<tr>
<td></td>
<td>- coarsely-blasted</td>
<td>- blasted with alumina beads (particle size: 200-500 μm)</td>
</tr>
<tr>
<td></td>
<td>- titanium plasma sprayed (TPS)</td>
<td>- blasted with alumina beads (average particle size: 250 μm)</td>
</tr>
<tr>
<td></td>
<td>- hydroxyapatite (HA) sprayed</td>
<td>- acid etched with a solution of HCl/H₂SO₄ at 125-130°C for 5min.</td>
</tr>
<tr>
<td></td>
<td>- etched</td>
<td>- blasted with alumina beads (average particle size: 250 μm) and acid etched</td>
</tr>
<tr>
<td></td>
<td>- blasted + etched (SLA)</td>
<td>- first structured by electrochemical micromachining in 3 M H₂SO₄ – methanol</td>
</tr>
<tr>
<td></td>
<td>- structured + etched</td>
<td>- etched with a hot solution of HCl/H₂SO₄ for a few minutes.</td>
</tr>
</tbody>
</table>

| wrought Ti6Al7Nb rod (PROTASUL®-100) | - polished                       | - polished to a mirror finish                                                    |
| ISO 5832-11                           | - finely-blasted                 | - blasted with glass beads (particle size: 150 - 230 μm)                         |
|                                       | - coarsely-blasted               | - blasted with alumina beads (particle size: 200 – 500 μm)                      |

| wrought Ti6Al4V rod (PROTASUL®-64WF) | - polished                       | - polished to a mirror finish                                                    |
| ISO 5832-3                            | - finely-blasted                 | - blasted with glass beads (particle size: 150 - 230 μm)                         |
|                                       | - coarsely-blasted               | - blasted with alumina beads (particle size: 200 – 500 μm)                      |

| cast CoCrMo rod (PROTASUL®-20)        | - polished                       | - polished to a mirror finish                                                    |
| ISO 5832-12                           | - finely-blasted                 | - blasted with glass beads (particle size: 150 - 230 μm)                         |
|                                       | - coarsely-blasted               | - blasted with alumina beads (particle size: 200 – 500 μm)                      |

Tab. VIII: All investigated implant materials together with type of surfaces and surface treatment.

All polishing and etching surface treatments as well as the TPS and SLA processes were carried out by Institut Straumann AG. Sulzer Orthopedics Ltd. did all blasted
surface treatments including HA coating. The electrochemical micromachined structuring [96] was carried out by C. Madore, Dept. des Matériaux, EPFL Lausanne, Lausanne, Switzerland. The subsequent etching process was carried out by Institut Straumann AG.

The chemical composition of the bulk materials was analysed by the industrial companies who supplied the materials (Table IX).

<table>
<thead>
<tr>
<th>Element</th>
<th>cpTi</th>
<th>Ti6Al4V</th>
<th>Ti6Al7Nb</th>
<th>CoCrMo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti [wt%]</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>--</td>
</tr>
<tr>
<td>Al [wt%]</td>
<td>0.0055</td>
<td>5.91</td>
<td>5.85</td>
<td>--</td>
</tr>
<tr>
<td>V [wt%]</td>
<td>&lt; 0.03</td>
<td>4.13</td>
<td>0.01</td>
<td>--</td>
</tr>
<tr>
<td>Nb [wt%]</td>
<td>--</td>
<td>--</td>
<td>6.95</td>
<td>--</td>
</tr>
<tr>
<td>O [wt%]</td>
<td>0.14</td>
<td>0.12</td>
<td>0.17</td>
<td>--</td>
</tr>
<tr>
<td>C [wt%]</td>
<td>0.002</td>
<td>0.015</td>
<td>0.001</td>
<td>0.052</td>
</tr>
<tr>
<td>N [wt%]</td>
<td>0.01</td>
<td>0.007</td>
<td>0.01</td>
<td>0.17</td>
</tr>
<tr>
<td>H [wt%]</td>
<td>0.0013</td>
<td>--</td>
<td>0.003</td>
<td>--</td>
</tr>
<tr>
<td>Cu [wt%]</td>
<td>0.0015</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ni [wt%]</td>
<td>0.008</td>
<td>--</td>
<td>--</td>
<td>0.01</td>
</tr>
<tr>
<td>Mn [wt%]</td>
<td>0.006</td>
<td>--</td>
<td>--</td>
<td>0.65</td>
</tr>
<tr>
<td>Fe [wt%]</td>
<td>0.0245</td>
<td>0.18</td>
<td>0.20</td>
<td>0.24</td>
</tr>
<tr>
<td>Zr [wt%]</td>
<td>&lt; 0.005</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Co [wt%]</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>balance</td>
</tr>
<tr>
<td>Cr [wt%]</td>
<td>&lt; 0.005</td>
<td>--</td>
<td>--</td>
<td>27.70</td>
</tr>
<tr>
<td>Mo [wt%]</td>
<td>&lt; 0.005</td>
<td>--</td>
<td>--</td>
<td>5.74</td>
</tr>
<tr>
<td>W [wt%]</td>
<td>&lt; 0.01</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Sn [wt%]</td>
<td>0.0105</td>
<td>--</td>
<td>--</td>
<td>--</td>
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<tr>
<td>Ta [wt%]</td>
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<td>--</td>
<td>0.05</td>
<td>--</td>
</tr>
<tr>
<td>S [wt%]</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.0008</td>
</tr>
<tr>
<td>Si [wt%]</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Tab. IX: Chemical analysis of the bulk material of cpTi, Ti6Al4V, Ti6Al7Nb and CoCrMo.
Figure 19 shows the metallography images of cpTi, Ti6Al7Nb, Ti6Al4V and CoCrMo. CpTi has a coarse-grained \( \alpha \)-microstructure (hcp). Both Ti6Al7Nb and Ti6Al4V show a duplex \( \alpha \)-\( \beta \) microstructure (see section 1.1.1). Al stabilises the low-temperature \( \alpha \)-phase (hcp), while Nb (or V) stabilises the high-temperature \( \beta \)-phase (bcc). The \( \alpha \)-phase contains a higher concentration of Al, whereas Nb (or V) is enriched in the \( \beta \)-
phase. The grains in the images correspond to the $\alpha$-phase, whereas between them there is a mixture of $\alpha$-$\beta$ phases. The $\alpha$-grains are larger for the Ti6Al7Nb than for the Ti6Al4V alloy. CoCrMo has an austenitic crystalline structure. Because of the small carbon concentration in the alloy, no carbides are present in the structure.

### 4.2 Surface cleaning after treatments

Low-concentration contaminants such as Pb, Na, Ca and Zn (<1.5 at.-%), mainly due to the mechanical polishing, were detected by X-ray photoelectron spectroscopy (XPS) on untreated, polished cpTi, TiAlNb and TiAlV surfaces (see section 7.1). Furthermore, polydimethylsiloxane (PDMS), a frequently detected surface contaminant, as well as common atmospheric hydrocarbon contamination were detected by X-ray-photoelectron-spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) (see section 7.1).

PDMS may be removed by hexane. To detach the hexane from the titanium oxide surface, the samples were cleaned in acetone and ethanol. To remove ethanol, the surface was rinsed in ultrapure water (18.2 M$\Omega$cm). Contaminants such as Pb, Na, Ca and Zn may be removed by passivation in 30% HNO$_3$ for 1h. Common atmospheric hydrocarbon contamination may be removed with an oxygen plasma (Harrick PDC-32G). Therefore the following cleaning procedure for titanium was developed in collaboration with C. Sittig [97]:

1. Ultrasonic cleaning twice in hexane, acetone and ethanol (10 min for each at room temperature), with intermediate rinsing in the subsequent solvent
2. Ultrasonic rinsing in ultrapure water (18.2 M$\Omega$cm) at room temperature
3. Passivation in 30 vol% HNO$_3$ for 1h
4. Ultrasonic rinsing in ultrapure water
5. Drying with N$_2$
6. Plasma cleaning in an O₂ plasma (0.42 mbar, 2 min.) and storing in ultrapure water for 2h
7. Drying with N₂ and packing in Al-foil.

The finely and coarsely blasted samples of each material were subsequently cleaned ultrasonically in a detergent by Sulzer Orthopedics Ldt. SLA and TPS were only oxygen plasma cleaned to remove the common atmospheric hydrocarbon contamination.

4.3 Sterilisation

Polished, SLA, TPS and structured + etched samples were cleaned and packed in Al-foil and sterilised within the autoclave at 180°C for 3h. Finely and coarsely blasted samples of each material as well as HA samples were cleaned and packed in Al-foil and sterilised by γ-irradiation with 30 kGy. The γ-sterilisation was carried out by Sulzer Orthopedics Ldt.
5. Surface characterisation techniques

The important question in biocompatibility issues is how the device or material and its chemically and topographically modified surfaces influence the response of proteins, cells, tissue, and organism. The key interactions between the material and the host occur at the surface. Therefore, we need to understand the surface structure of biomaterials. A complete characterisation of the surface requires the use of many techniques to compile all the information needed [98]. Unfortunately, we cannot yet specify in detail which surface parameters are critical for understanding biological responses to surfaces.

The chemical compositions of the different surfaces were investigated with X-ray-photoelectron-spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Surface topographies were investigated with mechanical stylus, non-contact laser profilometry (LPM), interference microscopy (IM), scanning electron microscopy (SEM), stereo-SEM, and atomic force microscopy (AFM). In section 5.9, an overview of the resolution, advantages, limitations and applications of each method is given.

5.1 X-ray-photoelectron-spectroscopy (XPS)

XPS is an abbreviation for X-ray Photoelectron Spectroscopy. Another acronym is Electron Spectroscopy for Chemical Analysis (ESCA). In this technique photoelectrons to be analysed are caused to be emitted by absorption of X-rays. The kinetic energy of the analysed electrons depends on the energy of the source but is usually less than 1500 eV. The mean free path of electrons in this kinetic energy range is in the nm range for solid materials. XPS is therefore characterised as a surface-sensitive technique. The measurement is performed under ultra-high (UHV) vacuum. If not specified otherwise, the information given in the following sections is taken from textbooks and review articles [99-101].

5. Characterisation techniques
5.1.1 Principles

The principle of the XPS technique is the emission of photoelectrons from atoms by absorption of photons. A beam of X-rays is produced by electron bombardment of an anode material (Al, Mg, Si). This causes the ejection of core-level electrons if the energy of the incident electrons is larger than the ionisation threshold. Relaxation of the ionised atom can occur by filling the core vacancy with an electron from an outer shell. The relaxation is then dissipated in either of two ways. It produces either a characteristic X-ray photon or a second electron, called Auger electron. An energy diagram is shown in Figure 20. There are two different notations that are normally used in photoelectron spectroscopy and in Auger electron spectroscopy. In the case of photoelectron emission, the electron orbitals are written in the form nlj, for example 1s½, 2s½, 2p½, 2p¾, etc. The quantum numbers nlj represent the principal (n), the angular momentum (l), and the total angular momentum (j), respectively. The notations s, p, d, and f are used for l = 0, 1, 2, 3, respectively. The total quantum number is j = l + s, where s = ± ½ is the spin quantum number. In case of the Auger electron emission, three electron levels are involved in an Auger transition, each of which is designed by its principal quantum number n. The capital letters K, L, M, N, etc. are used for states with n = 1, 2, 3, 4, etc. respectively. Different subshells are distinguished using the suffices 1, 2, 3, 4, etc. which correspond to the spectroscopic levels s½, p½, p½, d½, d½, etc. Should a vacancy in the 1s½ level be filled by a 2s½ electron and a 2p½ electron be ejected as shown in Figure 20, the corresponding Auger transition would be designed as K1L1L2, or KL1L2.
The binding energy of a particular electron is dependent on the unclear charge. In the case of X-ray photoelectron emission, the binding energy, $E_B$, of an electron level can be determined by measuring the kinetic energy, $E_{\text{kin}}$, of the photoelectron. The energy diagram in Figure 20 gives the relationship:

$$E_{\text{kin}} = hv - \phi - E_B \quad (6a)$$

and

$$E_B = hv - \phi - E_{\text{kin}} \quad (6b)$$

where $hv$ is the energy of the characteristic X-ray, $h = \text{Planck's constant}, 41.3\times10^{-16}$ eVs, $v$ is the frequency, and $\phi$ is the spectrometer work function. In principle, the work function should be the work function of the analysed sample, but the photoelectron passes an electric field created by the difference between the work functions of the spectrometer and the sample so that $\phi$ becomes constant.

The kinetic energy of an Auger electron emitted after a VXY transition can be calculated from:

$$E_{\text{kin}} = E_V - E_X - E_Y - F_{XY,a} + R_a \quad (7)$$

where $E_V$, $E_X$ and $E_Y$ are the binding energies of the electron states involved and $F_{XY,a}$ is the interaction energy between the X and Y holes in the final state $a$. $R_a$ is the relaxation energy caused by screening the core level vacancies.
X-ray sources used are generally either Al Kα (hv = 1486.6 eV) or Mg Kα (hv = 1253.6 eV). The advantage of Mg Kα is that the line-width of Mg Kα is smaller than the line width of Al Kα (0.7 eV and 0.85 eV, respectively). The resolution of the recorded spectra becomes therefore higher if Mg Kα radiation is used. Modern instruments are often equipped with monochromators, the radiation most commonly used being Al Kα. The main advantage of the monochromator is that the energy resolution of the recorded spectra is increased, which facilitates the interpretation. Furthermore, a monochromator eliminates satellite signals such as Kα3, Kα4 and Kβ X-ray lines and also lowers the background due to elimination of Bremsstrahlung. Figure 21 shows a survey spectrum of a polished and cleaned cpTi surface obtained using non-monochromatic Mg Kα radiation. The binding energy range, 0 eV to 1100 eV, covers all measurable XPS signals from cpTi. Due to the Bremsstrahlung and secondary electron production, the background is high. The signals Ti 2p, Ti 3s and Ti 3p and O 1s are detected from the native oxide film of titanium. Ti 3s and Ti 3p are weaker than Ti 2p, since the ionisation probabilities are lower. The O(KVV)- and Ti(LMM)-peak are Auger signals from oxygen and titanium in the oxide, respectively. In the spectrum, a C 1s signal and its C(KLL)-peak also appear. The electrons are emitted from a C-contamination layer present on the surface. Figure 21 also shows satellites from the Kα3,4 radiation.

Fig. 21: XPS survey spectrum of using non-monochromatic Mg Kα radiation.

5. Characterisation techniques
Chemical shift

Figure 22 shows the high-resolution XPS spectrum of the Ti 2p signal. The peak at the highest binding energy is due to the 2 electrons of the 2p$_{1/2}$ state, the higher signal due to the 4 electrons of the 2p$_{3/2}$ state. The two peaks represent Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ of TiO$_2$. Furthermore, the 2p$_{3/2}$ signal of metallic Ti is detected. The binding energies of the oxide and metal states of Ti 2p$_{3/2}$ are 459.1 eV and 454.1 eV, respectively. The difference between the binding energies of the oxide and metal states is called the chemical shift; in this case, the shift between Ti(O) and Ti(IV) is 5.0 eV. The full width at half-maximum (FWHM) of the oxide and the metal peaks is 1.53 eV and 1.50 eV, respectively, which is significantly smaller than the chemical shift. Thus, the determination of the individual chemical states is possible. This is one major advantage of the XPS-method.

Fig. 22: The high-resolution XPS spectrum of Ti 2p shows the chemical shift between the TiO$_2$ 2p$_{3/2}$ and Ti (met) 2p$_{3/2}$ signal. The chemical shift allows to the determination of the individual chemical states.
Shake-up satellites

During the photoelectron emission a multi-electron transition process can take place by transferring electrons from the valence band to unoccupied states in the conduction band. The photoelectron emitted from the 2p level loses energy corresponding to the measured energy-difference between the satellite and the main peak. The survey spectrum (Figure 21) shows a shake-up satellite on the high binding energy (low kinetic energy) side of the O 1s and Ti 2p signal.

Curve fitting

In many cases the information provided by XPS is contained in a spectrum that consists of a number of overlapping peaks, often of different peak shapes and intensities. The spectra often cannot be unambiguously analysed and there is no standard way to proceed with the analysis. In our case, we mainly consider the core region. In the core region the spectra frequently consist of overlapping peaks due to different chemical environments (chemical shift). The peak positions can sometimes be determined in a qualitative manner by derivative spectra. Once approximate peak positions have been found the data can be fitted by curve fitting methods. In the SAGE 100 software, Gaussian and Lorentzian functions are used. However, before fitting the background was subtracted either linearly or by Shirley.

XPS quantification

In a homogenous surface, the peak intensity $I_A$ detected for element A can be expressed as follows:

$$I_A = N_A \cdot \sigma_A^s (hv) \cdot L_A (\gamma) \cdot \lambda_A (E_{k\alpha}) \cdot B$$  \hspace{1cm} (8)
where $I_A$ : XPS measured intensity of atom A [cps-eV]
$N_A$ : atomic density of atom A [atoms/volume]
$\sigma^0_A(h\nu)$: cross section for atom A, electron $e^-$ and photon energy $h\nu$
$L_A(\gamma)$ : angular asymmetry factor
$\gamma$ : angle between the X-ray beam and the $e^-$ beam to the spectrometer [$^\circ$]
$\lambda_M(E_{kin})$ : mean free path of $e^-$ at $E_{kin}$ in the matrix M [Å]
$E_{kin}$ : kinetic energy [eV]
$B$ : instrumental constant including:
- the transmission function $T = f(E_A)$
- detector efficiency
- flux of the X-ray characteristic line
- etc.

The atomic concentration of $X_A$ can be easily calculated from equation 8:

$$X_A = \frac{I_A/I_A^m}{\sum_{i=A,B} I_i/I_i^m} \quad (9)$$

where $I_A^m$ is the intensity from pure A and may be considered to be a sensitivity factor. The sum is over all of the constituents of the solid.

**Calculation of the oxide thickness and depth information**

If the thickness, $d$, of the oxide-layer is thin enough compared to the mean free path length, $\lambda$, ($d < 3\lambda\cdot\sin\alpha$, where $\alpha$ is the angle between the surface plane and the detector), signals originating from the bulk material can be detected. For example, the high-resolution XPS spectrum of Ti 2p (Figure 22) shows the TiO$_2$ 2p$_{1/2}$ and TiO$_2$
2p_{3/2} of the oxide-layer as well as Ti (met) 2p_{3/2} and Ti (met) 2p_{3/2} signal of the bulk material. The electron mean free paths in Ti and TiO_2 have been calculated [97] according to Briggs and Seah [99]. The values are between 1.5 – 2.0 nm, which correspond to values found in the literature [102, 103]. In this case, the oxide-layer thickness, d, can be calculated according to equation 10 from the intensity ratio of the metal to the oxide signal Ti(metal)/Ti(oxide). The assumption is that the surface is flat and the two-layer system is laterally homogeneous.

\[
d = \lambda_{\text{TiO}_2} \cdot \sin \alpha \cdot \ln \left( \frac{I_{\text{TiO}_2}}{I_{\text{Ti}}} \cdot \frac{N_{\text{Ti}} \cdot \lambda_{\text{Ti}}}{N_{\text{TiO}_2} \cdot \lambda_{\text{TiO}_2}} + 1 \right)
\]

where

- \( d \) : oxide-layer thickness [Å]
- \( \lambda_{\text{TiO}_2} \) : mean free path of e\(^{-}\) at \( E_{\text{kin}} \) in TiO_2 [Å]
- \( \alpha \) : angle between the surface plane and the spectrometer [°]
- \( I_{\text{Ti}}, I_{\text{TiO}_2} \) : measured intensity of Ti and TiO_2, respectively [cps-eV]
- \( N_{\text{Ti}}, N_{\text{TiO}_2} \) : atomic density of pure Ti and TiO_2, respectively [atoms/volume]
- \( \lambda_{\text{Ti}}, \lambda_{\text{TiO}_2} \) : mean free path of e\(^{-}\) at \( E_{\text{kin}} \) in pure Ti and TiO_2, respectively [Å]

The contribution of the intensity of a homogeneous, infinitely thick layer is decreasing with increasing of the depth \( z \):

\[
l(z) = I_0 \cdot \left[ 1 - e^{-\frac{z}{\lambda \cdot \sin \alpha}} \right]
\]

where

- \( l(z) \) : Intensity from the depth \( z \leq z \)
- \( I_0 \) : Intensity of the total signal
- \( \alpha \) : angle between the surface plane and the spectrometer [°]
Therefore, 95% of the measured signal originates from a layer between \( z = 0 \) up to \( z = 3\cdot \lambda \cdot \sin \alpha \). This depth is called sampling depth.

### 5.1.2 Instrument

XPS data were obtained on a Specs Model SAGE 100, developed by Specs D-12103 Berlin, Germany, using non-monochromatized Mg \( K_{\alpha} \) radiation at 300 W (12 kV, 25 mA) and Al \( K_{\alpha} \) radiation at 390 W (13 kV, 30 mA). Measurements were carried out using a take-off angle of 90° with respect to the sample surface. The analysed area was typically 9x9 mm², which is suitable for survey analysis. Survey scans over a binding energy range of 0 to 1100 eV were taken for each sample with a constant electron detector pass energy of 50 eV. For quantitative determination of binding energy and atomic concentration, high-resolution spectra with a pass energy of 14 eV were measured. *Table X* shows the typical acquisition conditions for XPS instrument SAGE 100:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value for Survey Spectra</th>
<th>Value for High Resolution Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured Area</td>
<td>9x9 mm²</td>
<td>9x9 mm²</td>
</tr>
<tr>
<td>Emission Angle (between the sample surface plane and the detector)</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td>X-ray source</td>
<td>Mg (300 W, 12 kV)</td>
<td>Mg (300 W, 12 kV)</td>
</tr>
<tr>
<td></td>
<td>Al (390 W, 13 kV)</td>
<td>Al (390 W, 13 kV)</td>
</tr>
<tr>
<td>Pass Energy Step Measure Period</td>
<td>50 eV</td>
<td>14 eV</td>
</tr>
<tr>
<td></td>
<td>1 eV</td>
<td>0.1 eV</td>
</tr>
<tr>
<td></td>
<td>0.1 s</td>
<td>0.1 s</td>
</tr>
<tr>
<td>Vacuum during Measurements</td>
<td>2.5x10⁻⁶ mbar</td>
<td>2.5x10⁻⁶ mbar</td>
</tr>
</tbody>
</table>

*Tab. X:* Typical acquisition conditions for Specs SAGE 100.
Background subtraction, peak integration and fitting were carried out using the SpecsLab software. For C 1s, O 1s and Ti 2p, the Shirley approximation was used for the background subtraction; for all other elements the background was subtracted linearly. To convert peak areas to surface concentration, sensitivity factors published by Evans et al. [104] were used.

5.2 Time-of-flight secondary ion mass spectrometry (ToF-SIMS)

Secondary ion mass spectrometry (SIMS) is the mass spectrometry of atomic or molecular particles, which are emitted when a surface, usually a solid although it may be a liquid, is bombarded by energetic primary particles, usually ions. This process is known as sputtering. The secondary ions, which are detected, may be emitted from the surface in the ionised state or they may be initially emitted as uncharged species to be post-ionised before analysis.

In the case of dynamic SIMS, a high flux of primary ions is directed at the material surface. The surface is eroded very rapidly and it is possible to monitor changes of elemental composition with depth and thus a depth profile may be generated.

The importance of SIMS in surface analysis only emerged when it became possible in the early 1970’s to reduce the primary bombarding beam density to a very low level and yet retains high sensitivity in a modification of the technique, static SIMS, demonstrated by Benninghoven [105]. In this mode, secondary ions are emitted from areas not previously damaged and the surface monolayer lifetime is well in excess of the time required for analysis. The importance of static SIMS for surface analysis arises from the fact that a surface mass spectrum is generated and thus in principle the power associated with analytical organic mass spectrometry for chemical structure characterisation is available to surface analysis.
By raster scanning the beam across an area of surface and collecting the secondary ions at each point a chemical image can be generated. This variant of the technique is known as imaging SIMS.

Static Time-of-flight secondary ion mass spectrometry (ToF-SIMS) allows monolayer analysis with high sensitivity, a wide mass range, high mass resolution, and high lateral resolution. Besides information on elements and isotopes, the technique yields direct information on the molecular level. The method can be applied to practically all types of materials and sample forms, including insulators in particular. The static ToF-SIMS technique and the instrument used are described in the following sections. More information may be found in [106-109].

5.2.1 Principles

When a low–energy ion (keV range) interacts with a solid, if it is not reflected, it penetrates into the solid to a depth corresponding to its implantation range, at the same time losing its kinetic energy. The stopping power or energy loss per unit length in the solid (dE/dx) is dominated by elastic collisions between the ion and atomic nuclei of the target. As a result, energetic, recoiling target atoms are produced and they, in turn, initiate other collisions, producing new recoil atoms so that collision cascades are developed in a region around the primary ion impact. The collision cascades can transfer energy and momentum back to the surface and when transferred recoil energy exceeds the surface binding energy, neutral particles, as well as positive and negative secondary ions, are emitted from the surface. In the production of secondary ions from organic molecules, proton transfer and cation addition both play dominant roles. A characteristic feature of an organic molecule $M$ is the appearance of the quasi-molecular ions $(M+H)^+$, $(M+$cation$)^+$, and $(M-H)^-$. Large molecular ions of organic or molecular materials are believed to be produced only at some distance from the point of primary ion impact, where the deposited energy from the collision cascades is limited. Figure 23 summarises the principle of static SIMS.
In the SIMS technique, only the positively and negatively charged fraction of the secondary particle flux is detected. When secondary ion emission is used for surface analysis it is desirable that the information obtained should relate to the uppermost monolayer of the solid with as little modification as possible. Thus the total number of primary ions that hit the surface area to be analysed must be low enough (static limit is $10^{13}$ primary impacts per cm$^2$) to ensure that the probability of a particular surface region receiving more than one primary ion is negligibly small (see also section ‘Primary Particle Beams for Static SIMS’).

![Schematic representation of the static SIMS principle.](image)

There are three main motivations to develop time-of-flight mass analysers for static SIMS purposes. Firstly, ToF mass analysers allow a virtually unlimited mass range just by extending the flight time interval. This is particularly advantageous for studies of polymers, surface contaminations as well as in the biological and medical field. Secondly, they allow all secondary ions injected into the instrument to be detected rather than only those a mass scanning analyser would be tuned to (parallel detection). In the case of multiple mass line analysis, such as in polymers or surface contaminations, this characteristic may increase sensitivity dramatically. Parallel detection, in particular, allows static SIMS imaging of multiple molecular patterns. Thirdly, in contrast to quadrupole and magnetic sector analysers, ToF transmission
can be kept essentially constant even up to high mass resolution, which is also advantageous from a sensitivity point of view in multiple species situations.

**Mass resolution**

The principal arrangement of a linear time-of-flight mass spectrometer is shown in Figure 24. The main difference to conventional SIMS is that the primary ion source is pulsed (\(\Delta t_p\)). Time-of-flight analysers used in SIMS use static or quasi-static electric fields for the secondary beam. This means that all secondary ions are accelerated by passage through a fixed accelerating voltage \(U_{ac}\) to the same kinetic energy, so that the time they need to complete their flight path varies as the square root of mass. Secondary ions are registered by their arrival time at the detector. For a linear drift tube and singly charged ions, the time difference is given by equation 12:

\[
 t - t_0 = \frac{L \sqrt{m}}{\sqrt{2U_{ac}}} \tag{12}
\]

where
- \(t\) : arrival time of secondary ions
- \(t_0\) : start time of secondary ions
- \(L\) : total flight path
- \(m\) : mass of secondary ions
- \(U_{ac}\) : accelerating voltage

**Fig. 24:** Principle of a linear time-of-flight mass spectrometer.
The mass resolution $\Delta m/m$ (typically $< 1$ ppm) in a linear time-of-flight mass spectrometer is determined by the flight-time differences of isobaric ions. It is limited by the primary pulse duration $\Delta t_p$, the time resolution $\Delta t_D$ of the detection system, the initial energy $\Delta E$ of the emitted secondary ions, and the total flight time $T$ ($T = t - t_0$). Mass resolution is then given by equation 13:

$$
\frac{\Delta m}{m} = \frac{\Delta E}{E} + \frac{2(\Delta t_p + \Delta t_D)}{T}
$$

where

- $\Delta m/m$ : mass resolution
- $\Delta E$ : initial energy
- $\Delta t_p$ : primary pulse duration
- $\Delta t_D$ : time resolution
- $T$ : total flight time ($T = t - t_0$)

**Primary particle beams for static SIMS**

In static SIMS it is essential to have high surface sensitivity with a minimal surface damage. To a first approximation surface damage is dependent solely on the sputter rate, although particle bombardment may generate additional surface chemical modification, which can also be regarded as damage. Considering sputtering alone, a crucial parameter is the lifetime $t_m$ of the surface monolayer:

$$
t_m = 10^{15}/S \cdot i_p
$$

where the density of atoms in the surface is taken as $10^{15}$ cm$^{-2}$, $S$ is the number of secondary particles removed per primary particle impact or sputter rate, which usually lies between 0.1 and 10, and $i_p$ is the number of primary particles incident at the surface in cm$^{-2}$s$^{-1}$. Thus when $i_p$ is 1nA ($10^{10}$ particles cm$^{-2}$s$^{-1}$) and the sputter rate...
S = 1, then \( t_m = 10^5 \) s, and therefore good conditions for static SIMS are achieved. Table XI shows the primary particle conditions for different SIMS modes.

<table>
<thead>
<tr>
<th>Analysis mode</th>
<th>Source</th>
<th>Primary Beam Parameters</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static SIMS</td>
<td>( \text{Ar}^+, \text{Xe}^+, \text{Cs}^+ )</td>
<td>(&lt; 10 , \text{nA cm}^{-2} )</td>
<td>Spectra</td>
</tr>
<tr>
<td>Dynamic SIMS</td>
<td>( \text{Ar}^+, \text{O}_2^+, \text{Cs}^+ )</td>
<td>( &gt; 10 , \text{µA cm}^{-2} )</td>
<td>Depth profiles</td>
</tr>
<tr>
<td>Imaging SIMS</td>
<td>( \text{Ga}^+, \text{In}^+ )</td>
<td>( \sim 10 , \text{nA cm}^{-2} )</td>
<td>Images or Maps</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 2-3 , \text{mm} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \geq 10 , \text{µm} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 100 , \text{nm} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( &gt; 10^3 , \text{s} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( &gt; 10^3 , \text{s} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \leq 10^3 , \text{s} )</td>
<td></td>
</tr>
</tbody>
</table>

**Table XI: Primary particle conditions for different SIMS modes.**

Particle bombardment disrupts surface chemistry, it roughens metal surfaces, it can reduce oxide surfaces and there is good evidence that it can cause extensive chemical fragmentation of organic materials. Therefore, it has been found that in general the limiting static fluence is \( 10^{13} \) primary impacts per cm\(^2\) [110].

**Modern spectrometer and performance data**

*Figure 25 shows schematically the construction of a modern, energy-focusing time-of-flight secondary ion mass spectrometer. The instrument consists of three main components: the primary ion source, the accelerating and flight path system, and the detector. The primary ion source produces mass-separated pulses of primary ions with a frequency of several kHz; this is achieved by pulsed 90° bending and subsequent compression of a continuous ion beam, which is generated, for example, by an electron-impact ion source. This pulsed beam can then be focused by means of an ion-optic lens system to a diameter of less than 5 \( \mu \text{m} \) if required. If a liquid-metal ion source is used instead, the pulsed ion beam can be reduced to a diameter of less than 0.1 \( \mu \text{m} \).

The beam path contains several ion-optic elements: a beam extractor, an ion lens which focuses the ion beam onto the detector, and a reflectron with a retarding electric field, which has an energy-focusing function on the secondary ions and thus*
largely eliminates the adverse effect of their initial energy spread on the mass resolution. The detection system consists of a detector (combining a photoconverter electrode, channel plate, scintillator, and photomultiplier) and a counter allowing for high time resolution.

The performance of a time-of-flight secondary ion mass spectrometer is determined by the characteristics of the primary ion source, the flight path, and the detection system. The quality of the primary ion source is determined by the mass separation, the duration of the primary ion pulse, and the focusing of the beam. The transmission efficiency and the energy focusing determine that of the secondary ion optical system and of the overall flight path. Lastly, the quality of the detection system depends on its response probability, time resolution, dead time, and maximum data-handling rate.

Fig. 25: Construction of a modern high-resolution time-of-flight secondary ion mass spectrometer. The system includes two primary ion sources giving different beam diameters, a pulsed, mass-separating electron impact ion source (1) and a pulsed, fine-focusing liquid metal ion source (2), as well as the target (3), a reflectron for energy focusing of the mass-separated secondary ions (4), a detector (5), and a laser for post-ionisation of emitted neutral particles (6) [107].
Quantification with an internal standard

Matrix effects based on the extreme sensitivity of sputtered ion yields to variations in the matrix composition of the sample present a serious obstacle to quantitative analysis [106, 107]. Secondary ion emission will only be proportional to the area covered by a particular surface constituent if it is present in the same bonding state throughout. However, calibration is possible by introducing a suitable standard of known composition [106, 107]. By directly comparing the intensities of corresponding ion peaks of the analysed surface and the standard, whose composition and concentration on the surface is known, a semi-quantitative analysis can be carried out.

5.2.2 Instrument

Time-of-flight-secondary-ion mass spectra were recovered using a Physical Electronics 7200 ToF-SIMS system, Eden Prairie, Minnesota, USA, equipped with a 8 keV Cs⁺-gun which produces 1 ns FWHM primary ion pulses, a reflectron type mass analyser with a band pass energy of 70 eV and a minimal resolution of 0.15625 ns. This configuration allowed for a routine mass resolution $\Delta m/m > 4500$ at mass 48. The measurement area was 100x100 μm² or 200x200 μm². During the data acquisition process, ion doses were kept in the range of $1.0 \times 10^{12}$ ions/cm², well below the static SIMS limit. The mass range was calibrated using well-defined hydrocarbon peaks (CH₃⁺, C₂H₅⁺ and C₃H₅⁺ in positive and CH⁺, OH⁻ and C₂H⁺ in negative mode). Table XII shows the typical acquisition conditions for the Physical Electronics 7200 ToF-SIMS system.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion Gun</td>
<td>Cs+, pulsed</td>
</tr>
<tr>
<td>Beam Voltage</td>
<td>8.0 kV</td>
</tr>
<tr>
<td>Beam Size</td>
<td>50.00 μm</td>
</tr>
<tr>
<td>Focus</td>
<td>70.1%</td>
</tr>
<tr>
<td>Extractor State</td>
<td>pulsed</td>
</tr>
<tr>
<td>Ion Polarity</td>
<td>pos &amp; neg.</td>
</tr>
<tr>
<td>Deceleration</td>
<td>478 V</td>
</tr>
<tr>
<td>Focus</td>
<td>570 V</td>
</tr>
<tr>
<td>Post Accelerator Voltage</td>
<td>10.00 kV</td>
</tr>
<tr>
<td>Multiplier</td>
<td>1900 V</td>
</tr>
<tr>
<td>Pulse Length</td>
<td>10.000 ms</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>5000 Hz</td>
</tr>
<tr>
<td>Mass Range</td>
<td>0-1000 amu</td>
</tr>
<tr>
<td>Raster Size</td>
<td>100 x100 mm² and 200x200 mm²</td>
</tr>
<tr>
<td>Spatial Resolution</td>
<td>64x64 and 128x128</td>
</tr>
<tr>
<td>Time per Step</td>
<td>0.625 ns</td>
</tr>
<tr>
<td>Ion Dose</td>
<td>10¹¹ - 10¹² ions/cm²</td>
</tr>
<tr>
<td>Vacuum during Measurements</td>
<td>5x10⁻⁹ mbar</td>
</tr>
</tbody>
</table>

Tab. XII: Typical acquisition conditions for Physical Electronics 7200 ToF-SIMS system.

5.3 Mechanical stylus

The contact stylus approach is currently the most widely used method in industry for surface roughness measurements. This technique is well known and well described in several textbooks and review papers [111-114].

5.3.1 Principles

The principle for contact stylus instruments is that a stylus is traversed across the surface (in the x-direction) at a constant velocity. The tip is generally a pyramidal or
### Tab. XII: Typical acquisition conditions for Physical Electronics 7200 ToF-SIMS system.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion Gun</td>
<td>Cs+, pulsed</td>
</tr>
<tr>
<td>Beam Voltage</td>
<td>8.0 kV</td>
</tr>
<tr>
<td>Beam Size</td>
<td>50.00 μm</td>
</tr>
<tr>
<td>Focus</td>
<td>70.1%</td>
</tr>
<tr>
<td>Extractor State</td>
<td>pulsed</td>
</tr>
<tr>
<td>Ion Polarity</td>
<td>pos &amp; neg.</td>
</tr>
<tr>
<td>Deceleration</td>
<td>478 V</td>
</tr>
<tr>
<td>Focus</td>
<td>570 V</td>
</tr>
<tr>
<td>Post Accelerator Voltage</td>
<td>10.00 kV</td>
</tr>
<tr>
<td>Multiplier</td>
<td>1900 V</td>
</tr>
<tr>
<td>Pulse Length</td>
<td>10.000 ms</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>5000 Hz</td>
</tr>
<tr>
<td>Mass Range</td>
<td>0-1000 amu</td>
</tr>
<tr>
<td>Raster Size</td>
<td>100 x100 mm² and 200x200 mm²</td>
</tr>
<tr>
<td>Spatial Resolution</td>
<td>64x64 and 128x128</td>
</tr>
<tr>
<td>Time per Step</td>
<td>0.625 ns</td>
</tr>
<tr>
<td>Ion Dose</td>
<td>$10^{11}$ - $10^{12}$ ions/cm²</td>
</tr>
<tr>
<td>Vacuum during Measurements</td>
<td>5x10⁻⁹ mbar</td>
</tr>
</tbody>
</table>

#### 5.3 Mechanical stylus

The contact stylus approach is currently the most widely used method in industry for surface roughness measurements. This technique is well known and well described in several textbooks and review papers [111-114].

#### 5.3.1 Principles

The principle for contact stylus instruments is that a stylus is traversed across the surface (in the x-direction) at a constant velocity. The tip is generally a pyramidal or
conical diamond with a flat or rounded tip. A load is applied to the stylus, which assures that the stylus tip never loses contact with the surface. A pick-up is physically connected to the tip. The pick-up is either a linear variable differential transformer (LVDT) or an optical transducer. The vertical movements (in the z-direction) of the pick-up are converted to an electrical signal, which is amplified before being converted into digital information or displayed as a profile line, with the height amplified relative to the distance along the surface. In order to realise 3-D measurements, a third dimension, y, is needed in the measurement. Generally, a number of closely spaced parallel profile traces are taken. They are referenced to a common origin to give the third dimension. The third dimension, y, is perpendicular to the X-Z plane. When the system starts to scan each trace, the origins must be kept in the same Y-Z plane.

The advantages of this method include the large measuring range, long experience with the method and available standards for 2-D measurements. However, the stylus is not a mathematical point but an artefact of finite dimensions. Furthermore, it is constrained to move in an vertical plane, or nearly so, relative to the moving pick-up. Furthermore the stylus will fail to follow peaks and valleys faithfully and hence will produce a distorted record of the surface.

The so called 'effective profile' recorded by the stylus instrument will be the locus of some point on the stylus. If the contacting portion of the stylus is assumed to be spherical in section the effective profile will correspond to the contacting envelope (also called envelope system) [115] where the radius of the rolling circle is that of the

---

**Fig. 26:** Envelope system where the radius of the rolling circle is that of the spherical portion of the stylus tip [115].
spherical portion of the stylus tip (Figure 26). The radius of curvature of a peak may be exaggerated, while a valley may be represented as a cusp. This effect may be generalised to a three-dimensional 'effective surface'. Another problem is the deformation of the surface by the tip [116].

Therefore for a complete surface topography description, methods other than the stylus method are necessary. Figure 27 compares the mechanical stylus, the laser beam and electron beam methods.

![Comparison of the mechanical stylus, the laser beam and the electron beam.](image)

**Fig. 27:** Comparison of the mechanical stylus, the laser beam and the electron beam.

### 5.3.2 Instrument

2-D profiles and 3-D surface topographies were determined with a mechanical stylus on a UBM profiling device, developed by UBM Messtechnik GmbH, D-76275 Ettlingen, Germany. The diamond tip has a pyramidal shape with a radius of 5 μm. 2-D profiles of finely and coarsely blasted Ti6Al7Nb surfaces were measured according to DIN 4768 [117] over a distance of 12.5 mm with a resolution of 150 points/mm. Area measurements were done over 0.5 mm x 0.5 mm square and the resolution in X- and Y-direction were 2 μm and 4 μm, respectively. Table XIII shows the data acquisition
conditions for polished, finely and coarsely blasted surfaces of cpTi, Ti6Al7Nb, Ti6Al4V and CoCrMo as well as TPS.

<table>
<thead>
<tr>
<th>Type of surface</th>
<th>Alloy</th>
<th>Scan Length [mm]</th>
<th>Area [mm²]</th>
<th>Cut-off λc [mm]</th>
<th>Lateral Resolution [points/mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>polished</td>
<td>cpTi, Ti6Al7Nb, Ti6Al4V, CoCrMo</td>
<td>---</td>
<td>0.5 x 0.5</td>
<td>0.29</td>
<td>500 x 250</td>
</tr>
<tr>
<td>finely blasted</td>
<td>CpTi, Ti6Al7Nb, Ti6Al4V, CoCrMo</td>
<td>12.5</td>
<td>0.5 x 0.5</td>
<td>2.5</td>
<td>150</td>
</tr>
<tr>
<td>coarsely blasted</td>
<td>CpTi, Ti6Al7Nb, Ti6Al4V, CoCrMo</td>
<td>12.5</td>
<td>0.5 x 0.5</td>
<td>0.58</td>
<td>150</td>
</tr>
<tr>
<td>TPS</td>
<td></td>
<td>---</td>
<td>0.5 x 0.5</td>
<td>0.58</td>
<td>500 x 250</td>
</tr>
</tbody>
</table>

Tab XIII: Topographic data acquisition conditions for polished, finely and coarsely blasted surfaces of cpTi, Ti6Al7Nb, Ti6Al4V and CoCrMo as well as TPS and cut-off wavelength, λc.

Roughness evaluation

Measured profiles and areas consist of many different wavelengths, some resulting from the waviness and some from the roughness of the surface. The waviness is a part of the manufactured surface texture. Before roughness calculation has been carried out, the waviness should be separated by a phase-correct filtering in accordance with standards such as DIN 4777 [118]. The cut-off wavelength, λc, is used to separate the roughness and waviness of a profile or an area. The Gaussian weighting function s(x) of the phase-corrected profile filter is defined in equation 15 (see Figure 28):

\[ s(x) = \frac{1}{\alpha \cdot \lambda_c} \exp \left[ -\pi \left( \frac{x}{\alpha \cdot \lambda_c} \right)^2 \right] \]  

(15)
where

$x$ : x-coordinate of the weighting function

$\lambda_c$ : cut-off wavelength of the phase-corrected profile filter

$\alpha$ : amplitude of the sinusoidal signal of the wavelength $\lambda$

$$\alpha = \sqrt{\frac{\ln 2}{\pi}} = 0.4697$$

The transmission characteristic for the waviness profile (mean line) results from the Fourier transformation of the phase-corrected weighting function:

$$\frac{a_1}{a_0} = \exp\left[-\pi \left(\frac{\alpha \cdot \lambda_c}{\lambda}\right)^2\right]$$

(16)

$a_0$ : amplitude of the sinusoidal profile before filtering

$a_1$ : amplitude of the sinusoidal profile of the waviness profile

$\lambda_c$ : cut-off wavelength of the phase-corrected profile filter

$\lambda$ : wavelength of the sinusoidal profile

The transmission of the roughness profile is complementary to that of the transmission of the waviness profile (mean line), because the roughness profile is the difference between the actual profile and the mean line.

$$\frac{a_2}{a_0} = 1 - \exp\left[-\pi \left(\frac{\alpha \cdot \lambda_c}{\lambda}\right)^2\right]$$

(17)

$a_2$ : amplitude of the sinusoidal profile of the roughness profile

5. Characterisation techniques
The roughness parameters of the 2-D profiles and 3-D surface topographies obtained by the mechanical stylus were calculated with the software provided with the laser profilometer (UBM version 1.5). A Gauss filter and an attenuation factor of 50% at the cut-off wavelength, $\lambda_c$, were chosen [118]. In all cases, the cut-off was set at 2.5 mm (Table XIII).

In the following sections, the two optical methods, non-contact laser profilometry (LPM) and interference microscopy (IM) as well as stereo-SEM for profile calculations and atomic force microscopy (AFM) are discussed.

5.4 Non-contact laser profilometer (LPM)

Many of the optical non-contact focus detection methods use a laser beam for illumination. The reason for this is that the laser is a very bright light source and can be focused to a very small diffraction limited spot. In the case of the non-contact Laser Profilometry (LPM) a laser light beam is used as an optical stylus, which is moved over the surface either by stage scanning (the specimen is moved) or by beam scanning (the laser beam is moved relative to the surface). For detection, an autofocus system is used. More information about optical instruments is given in several textbooks [111-114].
5.4.1 Principle

The sensor of the LPM uses the autofocus principle [119, 120]: the spot diameter of a laser light reflected on the probe surface is minimised by moving a collimator lens. The Z-coordinate of the surface point is inferred from the collimator lens position. Figure 29 shows the schematic diagram of the microfocus sensor used in our instrument.

![Schematic diagram of the microfocus sensor](image)

*Fig. 29: The schematic diagram of the microfocus sensor.*

The light produced by the laser diode (1) passes through the prism with beam splitter (2) and is deflected by the beam splitter (3). The light reaches the probe surface through the collimator lens (4) and the objective (5). The position of the collimator lens is controlled by the magnet-coil system (6: permanent magnet, 7: coil). The light reflected from the probe surface follows the way back to the beam splitter (2) and is led to the photodiodes (8).

The illuminated point on the probe surface is in focus when the output of the photodiodes (8) is minimal. Thus, the photodiode signal represents the input signal of the regulator, which controls the current in the coil (7). The position of the collimator
lens in monitored with the light detector (9). The read-out of the light detector is proportional to the Z-coordinate of the illuminated point on the sample surface.

2-D profile measurements as well as 3-D area measurements are realised by moving the sample with the translation stages. For 3-D measurements, a number of closely spaced parallel profile traces are taken. When the system starts to scan each trace, the origins must be kept in the same Y-Z plane as described in section 5.3.1. The advantages of the LPM include: the method is non-destructive, there is no problem with wear on the stylus tip, and the method can detect small structures (>3 μm), which could be inaccessible to mechanical stylus instrument depending on the radius of the stylus tip. The measurement speed is high for scanning 2-D profiles and the scan range can be up to several millimeters.

However there are also some disadvantages. The measurement speed is very slow for scanning 3-D areas compared to the mechanical stylus, because of the higher point density. The instrument is sensitive to surface inclination. The more the surface is inclined, the more difficult the focusing becomes. For a surface with ideal reflection the critical angle is <20° (see Figure 30). The reflectivity of samples is a crucial factor in influencing measurement values. Focusing can become impossible if the surface to be measured reflects less than 1.2% of the radiated laser light. The measurement results are influenced by the microgeometry of the sample. Distorted results may be obtained from measuring a spatially small tip, or a pore, or a sharp step feature.

\[ \text{Fig. 30: Loss of reflected light due to surface inclination [120].} \]
5.4.2 Instrument

2-D profiles and 3-D surface topographies were determined with the non-contact laser profilometer (LPM) developed by UBM Messtechnik GmbH, D-76275 Ettlingen, Germany, using a Microfocus sensor (vertical resolution 10 nm) [119,120]. It operates with an optical head incorporating 780 nm wavelength semiconductor laser, yielding a measurement spot size of ~ 1µm. It is recommended that the sensor is positioned close to its zero position to minimise drift caused by excessive static coil current. The characteristics of the Microfocus (see Figure 29) are summarised here:

- Operation distance: 2 mm
- Measurement range: 1000 µm or 100 µm (adjustable)
- Vertical resolution: 100 nm or 10 nm (depending upon the selected measurement range)
- Lateral resolution: 1 µm (given by the spot diameter)
- Surface inclination < 20°

In this case, LPM is limited to lateral topographical features of ≥ 1 µm size. The vertical resolution of the system is 50 nm. Table XIV lists the typical experimental conditions for LPM measurements:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement Range</td>
<td>± 50 µm or ± 500 µm with a vertical resolution of 10 nm and 100 nm, respectively</td>
</tr>
<tr>
<td>Laser Power</td>
<td>1.00 for smooth surfaces and 1.16 for rough surfaces</td>
</tr>
<tr>
<td>Control Type</td>
<td>accurate</td>
</tr>
<tr>
<td>Damping Level</td>
<td>1</td>
</tr>
<tr>
<td>Reflection Threshold</td>
<td>1.2%</td>
</tr>
<tr>
<td>Action if Surface is lost</td>
<td>hold</td>
</tr>
<tr>
<td>Type of Measurement</td>
<td>stepwise</td>
</tr>
<tr>
<td>Delay Time</td>
<td>10 µs</td>
</tr>
</tbody>
</table>

Tab. XIV: Typical experimental conditions for LPM measurements.
2-D profiles of each type of surface were measured according to DIN 4768 [117]. Additionally, each type of surface was also measured with 1000 measurements points/mm over either a length of 2.048 mm or 4.096 mm. These profiles were used for the wavelength-dependent roughness evaluation \((R=f(\lambda))\) (see Section 6.2 and 7.2.4). Area measurements were done over 0.3 mm x 0.3 mm square and resolution in X- and Y-direction of 1 \(\mu m\) and 2 \(\mu m\), respectively. Other measurements were done over 0.5 mm x 0.5 mm square and a resolution in X and Y-direction of 2 \(\mu m\). Table XV shows the data acquisition conditions for all measurements together with the chosen cut-off wavelength, \(\lambda_c\).

<table>
<thead>
<tr>
<th>Type of Surface</th>
<th>Alloy</th>
<th>Scan Length [mm]</th>
<th>Area [mm²]</th>
<th>Lateral Resolution [points/mm]</th>
<th>Cut-off (\lambda_c) [mm]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>polished</td>
<td>cpTi, Ti6Al7Nb, Ti6Al4V, CoCrMo</td>
<td>1.75 2.048</td>
<td>0.5 x 0.5</td>
<td>1400 1000 500 x 500</td>
<td>0.25 0.29</td>
<td>DIN 4768 ((R=f(\lambda)))</td>
</tr>
<tr>
<td>finely blasted</td>
<td>cpTi, Ti6Al7Nb, Ti6Al4V, CoCrMo</td>
<td>5.6 2.048</td>
<td>0.5 x 0.5</td>
<td>500 1000 500 x 500</td>
<td>0.80 0.29</td>
<td>DIN 4768 ((R=f(\lambda)))</td>
</tr>
<tr>
<td>coarsely blasted</td>
<td>cpTi, Ti6Al7Nb, Ti6Al4V, CoCrMo</td>
<td>12.5 4.096</td>
<td>0.3 x 0.3</td>
<td>150 1000 1000 x 500 500 x 500</td>
<td>2.50 0.58 0.58</td>
<td>DIN 4768 ((R=f(\lambda)))</td>
</tr>
<tr>
<td>TPS</td>
<td>cpTi,</td>
<td>12.5 4.096</td>
<td>0.5 x 0.5</td>
<td>150 1000 500 x 500</td>
<td>2.50 0.58</td>
<td>DIN 4768 ((R=f(\lambda)))</td>
</tr>
<tr>
<td>SLA</td>
<td>cpTi,</td>
<td>12.5 4.096</td>
<td>0.3 x 0.3</td>
<td>150 1000 1000 x 500</td>
<td>2.50 0.58</td>
<td>DIN 4768 ((R=f(\lambda)))</td>
</tr>
<tr>
<td>HA</td>
<td>12.5 4.096</td>
<td>150 1000</td>
<td>2.50 0.58</td>
<td>DIN 4768 ((R=f(\lambda)))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>structured + etched</td>
<td>cpTi,</td>
<td>0.3 x 0.3</td>
<td>1000 x 500</td>
<td>0.58</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

Tab XV: Topographic data acquisition conditions for polished, finely and coarsely blasted surfaces of cpTi, Ti6Al7Nb, Ti6Al4V and CoCrMo as well as HA and the chosen cut-off wavelength, \(\lambda_c\).

* Only coarsely blasted cpTi were measured.
** Measurement conditions chosen for determining wavelength-dependent roughness parameters.

5. Characterisation techniques
Roughness evaluation

The roughness parameters of the 2-D profiles and 3-D surface topographies obtained by the LPM were calculated within the software provided with the laser profilometer (UBM version 1.5). A Gauss filter and an attenuation factor of 50% at the cut-off wavelength, $\lambda_c$, were chosen [118] (see also section 5.3.2). Table XV lists the chosen cut-off wavelength, $\lambda_c$. The wavelength-dependent roughness evaluations using FFT (Fast Fourier Transformation) were performed with the software program 'Maple' (Version Maple V Release 5). Therefore, the profiles obtained by the LPM were filtered according to DIN 4768 [115] and exported as an ASCII file and read in by 'Maple'. The profile calculations using the "window roughness" concept were also performed within 'Maple' and again imported in the UBM software, where the window roughness parameters in the different predefined scale ranges were calculated.

5.5 Interference microscopy (IM)

Optical interferometry has been used to measure surface topography and many interferometric instruments based on two or multibeam interferometers have been proposed. Overviews on interference microscopes are given in several textbooks [111-114].

5.5.1 Principles

The principle of interferometry is that two light waves can interfere with each other when they interact. If the crest of one wave coincides with the trough of the other, the interference is destructive and the waves cancel out. On the other hand, if two crests
or two troughs coincide, the waves reinforce each other. Therefore, an optical fringe with parallel and dark bands would be produced. A typical interferometer, the Michelson interferometer, is shown in Figure 31.

In the Michelson interferometer an optical wavefront from a source, S, is split into two beams with coherence and nearly equal amplitudes by a beam splitter B. These two beams are reflected back at a smooth flat reference surface and a sample surface, and return to B where they are recombined and emerge at O. This is only true on condition that the reference surface and the sample surface are normal to each other. Texture on the specimen’s surface changes the distance travelled by the second beam. When the beams recombine, some parts of the second beam will be in phase with the first, while others will be out of phase. The spatial relation between the two beams contains detailed information about the topography of the surface. In fact, if an ideally flat surface is measured with an interferometer, the fringes in the obtained interferograms would be straight-lined and equally spaced from each other. If a rougher surface is measured, the fringes will depart from being straight and equally spaced. The undulations of each fringe reveal the peaks and valleys of the profile of the measured surface (see Figure 31). Therefore, the aim of interferometric instruments for 3-D surface topography measurements is to interpret the fringes and transform them to produce the 3-D surface topography.

5. Characterisation techniques
All currently commercially available interferometry instruments for 3-D surface topography measurement are actually a combination of an interferometer, a microscope and a computer. A large number of interferometers, such as the Michelson, Fizeau, Mirau, Linnik, and Nomarski interferometers, can be used to construct 3-D interferometric instruments. According to profiling mechanisms, these interferometers can be classified into two major categories:

a) Michelson, Fizeau, Mirau, and Linnik methods: these measure surface topography height directly.

b) Nomarski method: it measures the slope of the surface.

Phase shifting interferometry and scanning differential interferometry are now commonly used 3-D surface topography measurement and commercial instruments of these types are available. In my thesis, a phase shifting interferometric instrument, the WYKO NT 2000, was used. Therefore, a description of a phase shifting interferometric instrument is given below.

**Phase shifting interferometric instruments**

Surface height is determined not by looking at the interference fringes and by measuring how they depart from being straight and equally spaced, but by finding the phases of the interference pattern produced by the two reflected wavefronts from the reference surface and the sample surface at all co-ordinate pairs (X,Y). Once the phase, $\phi (X,Y)$, is obtained across the interference field, the corresponding height distribution $h (X,Y)$ is determined by equation 18:

$$h(X,Y) = \frac{\lambda}{4\pi} \phi(X,Y)$$

where $\lambda$ is the wavelength of the incident light.

5. Characterisation techniques
In order to realise phase shifting, and to detect the phase of the interference patterns, a driving device is used for moving the reference surface or the sample. The interferometer is located at the bottom of the instrument, and the reference surface (or the sample) is attached to a piezoelectric transducer (PZT). The phase shift is realised by exerting a voltage to the PZT, which then produces a force to drive the reference surface (or the sample) through a displacement. The formed fringes are detected by a CCD (charge-coupled-device) array. There are always the same numbers of CCD array elements in the profile or in the area. However, the profile length or the measured area can vary, depending on the magnification of the microscope objective used.

The advantages of the interference microscopy include: the method is non-destructive, there is no problem with wear on the stylus tip, and it has the ability to detect small structures (>1.0 μm) (which may be filtered out with a mechanical stylus tip depending on the radius of the tip) the measurement speed is high for scanning 3-D areas, and the vertical and lateral resolutions are better (1 nm and 3 μm) compared to LPM.

However there are also two main disadvantages. The reflectivity of samples is a crucial factor in influencing measurement values and the measured areas are limited by the magnification of the objective. For high-resolution images taken over a large area, images of adjacent areas have to be added together.

5.5.2 Instrument

2-D profiles and 3-D surface topographies were determined by optical interference microscopy using a WYKO NT 2000 white-light interference microscope (Vecco Instruments Inc., Tucson AZ 85706, USA) based on phase shifting and vertical scanning interferometry [121]. The WYKO NT2000 system is equipped with a Michelson interferometer and with objectives with magnifications of 5x, 10x and 50x. The nominal lateral and vertical resolution are 1.5 to 0.3 μm and <1 nm (VSM) and

5. Characterisation techniques
< 0.1 nm (BSM) respectively [121]. Figure 32 shows a systematic diagram of the WYKO NT 2000 interference microscope.

The white-light scanning interferometer measures surface heights by changing the path length of the sample arm of the interferometer to determine the location of the sample for which the white-light fringe with the best contrast is obtained [122]. The surface is in proper focus when the white-light fringe is obtained, which is important in measuring surface microstructures for which obtaining correct focus is critical [123]. Area measurements were done over 617.4 μm x 460.7 μm, 124.0 μm x 92.5 μm, and 59.9 μm x 44.7 μm with the objective with magnifications of 10x, 49.8x and 103.1x, respectively. Table XVI shows the data acquisition conditions for all measurements:

5. Characterisation techniques
<table>
<thead>
<tr>
<th>Type of Surface</th>
<th>Alloy</th>
<th>Mode</th>
<th>Magnification</th>
<th>Area [μm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>finely blasted Ti6Al7Nb,</td>
<td>VSI</td>
<td>10 x</td>
<td>617.4 x 460.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>49.8x</td>
<td>124 x 92.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>103.1x</td>
<td>59.9 x 44.7</td>
<td></td>
</tr>
<tr>
<td>coarsely blasted cpTi,</td>
<td>VSI</td>
<td>10 x</td>
<td>617.4 x 460.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>49.8x</td>
<td>124 x 92.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>103.1x</td>
<td>59.9 x 44.7</td>
<td></td>
</tr>
<tr>
<td>SLA cpTi,</td>
<td>VSI</td>
<td>10 x</td>
<td>617.4 x 460.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>49.8x</td>
<td>124 x 92.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>103.1x</td>
<td>59.9 x 44.7</td>
<td></td>
</tr>
<tr>
<td>structured + etched cpTi,</td>
<td>VSI</td>
<td>10 x</td>
<td>617.4 x 460.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>49.8x</td>
<td>124 x 92.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>103.1x</td>
<td>59.9 x 44.7</td>
<td></td>
</tr>
</tbody>
</table>

*Tab. XVI: Data acquisition conditions for all measurements.*

Roughness evaluation

2-D and 3-D roughness calculations were carried out within the WYKO Vision 32 software (Version 2.000) provided with the WYKO NT 2000. To compare the profiles obtained from both the LPM and IM measurements, the same profiles as obtained with the LPM were selected within the IM data set and read in by the UBM software. Then, the roughness parameters were calculated according to the same procedure described for the LPM data. For the wavelength-dependent evaluation and the subsequent profile calculations in the different wavelength ranges, the IM profiles were treated according to the same procedures as the LPM data.

5.6 Scanning electron microscopy (SEM), stereo-SEM

Scanning electron microscopy (SEM) is widely used and well documented in the literature [124-126].

5. Characterisation techniques
5.6.1 Principles

Scanning electron microscopy (SEM)

The principle of SEM is the focusing and rastering of a relatively high-energy primary electron beam (typically 5 to 35 kV) on a sample. Secondary electrons (SE), back-scattered electrons (BSE) and X-rays are emitted from the surface and are collected by suitable detectors for evaluation. SE signals have a very low energy in the range of 8 eV, which corresponds to an attenuation length of 5 to 10 nm. The minimum lateral resolution of a SE image will be in the same range. BSE have energies of the order of the primary electron energy. Therefore, an attenuation length of 100 to 1000 nm will be expected, depending on the sample and the energy of the primary electron beam. The primary electron beam also results in the emission of X-rays. These element-characteristic X-rays are used to identify elements with the technique called energy-dispersive X-ray (EDX) analysis. Figure 33 shows schematically the pear-shaped interaction volume generated by the high-energy primary electron beam.

![Diagram of SEM interaction volume](image)

*Fig. 33: A high-energy primary electron beam penetrates into a sample will create a pear-shaped interaction volume.*

5. Characterisation techniques

80
The most important topographic contrast mode using SE is a consequence of the dependence of the SE yield on the local tilt of the sample surface, the enhanced emission at edges and small particles and the shadowing contrast, which is superimposed on the surface tilt contrast [124]. SE can therefore be useful for visualisation of rough surfaces with high slope angles, but it is practically useless for smooth, mirror-like surfaces. However, charging problems can occur on sharp surface features and non-conductive particles. The topographic contrast can also be generated by the back-scattered electrons (BSE). The application of BSE imaging eliminates charging problems [127]. Additionally BSE imaging is well known for its ability to generate material contrast based on atomic number differences within the sample. Bright regions are associated with heavy elements in the analysed area. A multiple detector system using two semi-annular semiconductor detectors A and B has been used to generate either material or topographic contrast. The detectors A and B indicate opposite surface tilt and shadow contrast. In the case of the A+B signal, the material contrast is increased and the topographic contrast is decreased. In the case of the A-B signal, the material contrast is decreased and the topographic contrast increased.

SEM has some advantages, such as the large depth of focus, the high lateral resolution down to the nm range, the feasibility to study structures with high aspect ratio, and direct production of images of the surfaces. SEM images easily give a three dimensional impression of the surface. However, quantitative information about the topography could not be obtained from a single micrograph. Therefore, viable non-destructive techniques for extracting surface microtopography from SEM images were developed and can be grouped into the following: a) the stereo technique based on photogrammetry using a SEM stereo pair obtained by tilting the sample [128-132]; b) the stereo technique using a SEM stereo pair obtained by tilting the electron beam [133, 134] and c) the multiple detector technique [133, 135].

5. Characterisation techniques
Stereo-SEM

The main problem in stereo vision is to precisely locate corresponding points in left and right images [136, 137]. Photogrammetry [129, 130] needs sharp image details to calculate the height difference $h$ between two images points A and B from the parallax $P$, which is the difference between the distance $x_i$ of two points A and B in the left image and the corresponding distance $x_r$ in the right image (Figure 34).

![Figure 34: Calculation of the height difference $h$ between two images points A and B from the parallax $P$.](image)

In the initial position, the camera must be mounted normally above the sample and the tilt axis must be parallel to the vertical borders of the images. When the sample is tilted between the left and right exposures about an axis normal to the electron beam the height $h$ can be easily calculated using the general equation 19 [124, 129-133].

$$h = \frac{P}{M \cdot 2 \sin(\omega/2)}$$  \hspace{1cm} (19)

5. Characterisation techniques
where \( h \) is a height difference normal to the plane of an image which might have been taken in the central position with the half-way tilt position between the left and right image, \( P \) is the parallax, \( M \) the magnification and \( \omega \) the total tilt angle. *Equation 19* is valid only for parallel projection (high magnification \( \geq 1000x \)).

Other methods have been developed to solve the correspondence problem and to extract topography data: a) the application of digital image processing in photogrammetry: the stereo evaluation of the two images can be automatically performed to a large degree by means of digital image correlation [138]; b) a binary linear programming approach, which is a powerful tool to tackle constrained optimisation problems, especially in cases that involve matching between one data set and another [137]; c) In the case of *in situ* measurement of surface height based on tilting the electron beam to obtain the two images, cross-correlation is used to determine the parallax between the image pair which is then used to dynamically correct height of the tilt axis by changing the lens focus. As a result, the lens focus tracks the sample topography [135, 139]; d) the application of a multi-stage approach to the dense estimation of disparity from stereo SEM using different fitting algorithm and Laplace filter [140].

The major advantage of the stereo-SEM method is the calculation of 2-D profiles and their roughness parameter with a high lateral resolution in the range of 20 to 50 nm. However, the vertical resolution (0.5 to 0.1 \( \mu \)m) is a function of the tilt angle and the magnification (see *equation 19* and Figure 36). The resolution characteristics of the stereo-SEM are the reverse of those of the IM. The disadvantage of the method is, that because of the parallax calculation, only 2-D profiles can be calculated.
5.6.2 Instruments

A JEOL 840A SEM was used throughout this thesis. On the finely and coarsely blasted surfaces as well as on the TPS surface, areas with different elemental composition were detected with the BSE mode and specifically analysed using EDX (Tracor Northen TN 5400). A Philips XL30 SEM and a Hitachi S-4100 field-emission SEM were used for stereo-SEM investigations. SE and BSE imaging were recorded on blasted, etched, blasted + etched, structured + etched, TPS and HA surfaces. The HA surface was coated with gold in a sputter coater. Cell morphology analyses were carried out with a Hitachi S-2500C SEM. The samples were fixed with 3% glutaraldehyde in phosphate buffered saline and dried in a critical point dryer (Bal-Tec CPD 030) and coated with platinum in a sputter coater.

Roughness evaluation

The reconstruction of the stereo-SEM images and the computation of the height profile were performed using the analySIS® software (Version 2.11) of Soft Imaging System GmbH, D-48153 Münster, Germany. The reconstruction is based on the work of Desai [132]. A cross-correlation has been used to determine the parallax P between the left and right image. The cross-correlation works on the basis of the similarity of the corresponding areas in the left and right images, in the same way as a human observer detects a point on an image using the pattern of its surroundings [141]. Because the direction of the tilt axis is parallel to the image, the tilt can only yield horizontal shifts between the position of a point on the first and the second image expressed by the parallax P (see Figure 34). Therefore, the height h of any point A results from its X-shift $X_{sh}$ and the X-scale $X_{sc}$ of the image as shown in Figure 35:
\[ h = \frac{X_{sh} \cdot X_{sc}}{2 \sin(\omega/2)} \]  

where \( \omega \) : total tilt angle

and

\[ X_{sh} = \frac{P}{\cos(\omega/2)} \]  

Fig. 35: Principle of height calculation from the stereo-SEM method.

Stereo-SEM images have been obtained by tilting the object by \(-3^\circ\) or \(-4.8^\circ\) (left image) and \(+3^\circ\) or \(+4.8^\circ\) (right image) out of the initial position. Figure 36 shows the dependence of the vertical resolution on the tilt angle and the magnification,
expressed through the X-scale of the image. In that case, the stereo-SEM images were obtained with the Philips 30 XL using the high-definition mode.

![Graph showing dependence of vertical resolution on total tilt angle and magnification.](image)

**Fig. 36:** Dependence of the vertical resolution on the tilt angle and the magnification, expressed through the X-scale of the image.

*Table XVII* shows the settings typically used for the computation of the height profile using the analySIS® software.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stereo Angle [°]</td>
<td>6 or 9.6</td>
</tr>
<tr>
<td>Step Width X</td>
<td>1</td>
</tr>
<tr>
<td>Step Width Y</td>
<td>1</td>
</tr>
<tr>
<td>Max. X-Shift</td>
<td>10</td>
</tr>
<tr>
<td>Max. Y-Shift</td>
<td>6</td>
</tr>
<tr>
<td>Pattern Width</td>
<td>15</td>
</tr>
<tr>
<td>Pattern Height</td>
<td>15</td>
</tr>
<tr>
<td>Simple correlation</td>
<td>Yes</td>
</tr>
<tr>
<td>Sub-pixel interpolation</td>
<td>50%</td>
</tr>
</tbody>
</table>

*Tab. XVII:* Settings for the computation of the height profile.

Hence the more structure the images contain, the more accurate the measured heights will be. The computed profiles were exported and read in by the UBM.

5. Characterisation techniques
software. Then, the roughness parameters were calculated according to the same procedure described for the LPM data. The wavelength-dependent roughness evaluation and the "window roughness" calculations were based on the procedures already described for the LPM profiles.

5.7 Atomic force microscopy (AFM)

In addition to the other techniques, atomic force microscopy (AFM) was used to compare AFM with LPM, IM and stereo-SEM on rough surfaces. The principle of this technique is based on a distance dependent force between the surface and a very sharp tip, typically < 100nm radius. By scanning the tip over a surface, the surface topography or the lateral force distribution can be obtained. The force can be calculated from the deflection of a static cantilever, and typically is in the order of 1 nN.

An AFM instrument Nanoscope E (Digital Instruments, Santa Barbara, CA 93117, USA) was used to measure the topographies of coarsely blasted, structured + etched and SLA surfaces.

5.8 Overview of surface characterisation and evaluation methods of roughness used in this thesis

Table XVIII summarises the different surface characterisation methods, their advantages and limitations and Table XIX lists the different evaluation methods used to calculate the roughness parameters in this thesis. To separate the roughness and the waviness of the profiles, a Gauss filter and an attenuation factor of 50% at the cut-off wavelength, \( \lambda_o \), were chosen for all profiles.
<table>
<thead>
<tr>
<th>Method (Environment)</th>
<th>Advantages</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>XPS (UHV Vacuum)</td>
<td>- Surface selective &lt;br&gt;- Chemical oxidation state &lt;br&gt;- Easy quantification &lt;br&gt;- Information depth (\leq 10) nm &lt;br&gt;- Depth profiling with variable angle &lt;br&gt;- Imaging possible</td>
<td>- Possible sample damage &lt;br&gt;- Sample charging, particularly for monochromatised X-ray source</td>
</tr>
<tr>
<td>ToF-SIMS (UHV Vacuum)</td>
<td>- Excellent mass resolution (ppm range) &lt;br&gt;- Info on molecular structure and composition &lt;br&gt;- Information depth: &lt;br&gt;- 1- 3 monolayer &lt;br&gt;- Depth profiling possible &lt;br&gt;- Imaging</td>
<td>- Quantification difficult &lt;br&gt;- Peak interpretation often complicated and time-consuming</td>
</tr>
<tr>
<td>Mechanical Stylus (Air)</td>
<td>- Well-known &lt;br&gt;- Standardised (e.g. Din Norm) &lt;br&gt;- 2-D profiles with scan range of mm or cm feasible</td>
<td>- Limited lateral resolution &lt;br&gt;- Artefacts (deformation of surface) &lt;br&gt;- 3-D images less common</td>
</tr>
<tr>
<td>Non-Contact Laser Profilometer (Air)</td>
<td>- Non-contact, non-destructive &lt;br&gt;- Fast (for 2-D profiles, min.) &lt;br&gt;- Resolution: vertical appr. 50 nm lateral appr. 1 (\mu)m &lt;br&gt;- 2-D profiles with scan range of mm or cm feasible</td>
<td>- Artefacts (reflections at locally shiny areas, optical effects at sharp edges) &lt;br&gt;- Time-consuming for 3-D images (h)</td>
</tr>
<tr>
<td>Interference Microscope (Air)</td>
<td>- Non-contact, non-destructive &lt;br&gt;- Fast (for 3-D images, min.) &lt;br&gt;- Resolution: vertical appr. 1 nm lateral appr. 0.5 (\mu)m</td>
<td>- Only small area measured at high lateral resolution &lt;br&gt;- For larger areas, adjacent images with high resolution have to be combined</td>
</tr>
<tr>
<td>SEM (high Vacuum)</td>
<td>- High resolution: vertical 1 nm lateral 10 nm &lt;br&gt;- High depth of focus &lt;br&gt;- Morphological information &lt;br&gt;- Local analytical analysis (EDX)</td>
<td>- No quantitative topography information</td>
</tr>
</tbody>
</table>

5. Characterisation techniques
<table>
<thead>
<tr>
<th>Method (Environment)</th>
<th>Advantages</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stereo-SEM (Vacuum)</td>
<td>- High depth of focus</td>
<td>- Not widely used</td>
</tr>
<tr>
<td></td>
<td>- High dynamic x,y,z-range (mm to nm)</td>
<td>- Unsuitable for smooth surfaces</td>
</tr>
<tr>
<td></td>
<td>- Resolution: vertical: 0.5 to 0.1 μm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>lateral: 20 to 50 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- 2-D quantitative topographical information</td>
<td></td>
</tr>
<tr>
<td>STM/AFM (liquid, air,</td>
<td>- Highest resolution in both lateral and vertical directions (atomic to nm)</td>
<td>- Limited z-range (rough surfaces)</td>
</tr>
<tr>
<td>vaccum)</td>
<td></td>
<td>- Artefacts (convolution of profile by tip shape)</td>
</tr>
</tbody>
</table>

Tab. XVIII: Advantages and limitations of the used surface characterisation techniques.

<table>
<thead>
<tr>
<th>Method</th>
<th>Evaluation Method</th>
<th>Cut-off used [mm]</th>
<th>Software used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical</td>
<td>Norm DIN 4768 [117]</td>
<td>According DIN 4768</td>
<td>UBM Version 1.5</td>
</tr>
<tr>
<td>stylus</td>
<td></td>
<td>or 0.29&lt;sup&gt;1&lt;/sup&gt;, 0.58&lt;sup&gt;2&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FFT technique</td>
<td>0.29&lt;sup&gt;1&lt;/sup&gt;, 0.58&lt;sup&gt;2&lt;/sup&gt;</td>
<td>Maple V Release 5</td>
</tr>
<tr>
<td></td>
<td>COF filtering</td>
<td>0.29&lt;sup&gt;1&lt;/sup&gt;, 0.58&lt;sup&gt;2&lt;/sup&gt;</td>
<td>+ UBM Version 1.5</td>
</tr>
<tr>
<td></td>
<td>AFT filtering</td>
<td></td>
<td>UBM Version 1.5</td>
</tr>
<tr>
<td>IM</td>
<td>IM software applied</td>
<td>Unknown</td>
<td>WYKO Vision 32</td>
</tr>
<tr>
<td></td>
<td>LPM software applied</td>
<td>0.29&lt;sup&gt;1&lt;/sup&gt;, 0.58&lt;sup&gt;2&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FFT technique</td>
<td>0.29&lt;sup&gt;1&lt;/sup&gt;, 0.58&lt;sup&gt;2&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Stereo-SEM</td>
<td>LPM software applied</td>
<td>0.29&lt;sup&gt;1&lt;/sup&gt;, 0.58&lt;sup&gt;2&lt;/sup&gt;</td>
<td>UBM Version 1.5</td>
</tr>
<tr>
<td></td>
<td>FFT technique</td>
<td>0.29&lt;sup&gt;1&lt;/sup&gt;, 0.58&lt;sup&gt;2&lt;/sup&gt;</td>
<td>Maple V Release 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>+ UBM Version 1.5</td>
</tr>
</tbody>
</table>

Table XIX: Different evaluation methods used to calculate the roughness parameters in this thesis.
<sup>1</sup> for polished and finely blasted surfaces
<sup>2</sup> for coarsely blasted surfaces, TPS, SLA, HA, etched and structured + etched surfaces

5. Characterisation techniques
6. Evaluation of surface topography

6.1 Introduction

For a quantitative evaluation of the height variation (amplitude) of a rough surface structure, the lateral scan length (or lateral scan area in the 3-D case) must be clearly stated. This length, called the cut-off wavelength $\lambda_c$ (see section 5.3.2), is related to the low frequency limit of the measurement. The high-frequency end of the measurement is determined by the possible resolution of the measurement system. It might either be determined by the radius and shape of the contacting stylus tip (called envelope system) [101], the optical resolution of a microscope, or the distance between the sampling points if this is larger than the attainable resolution. The roughness parameters are defined for 2-D line profiles in the International Standards ISO as well as in different national standards (e.g. ASTM, DIN) based on the ISO standards, e.g. DIN 4678 [103] and DIN 4777 [104]. However, most of them are based on contact stylus profilometry. Progress with new instruments such as optical profilometer, interference microscope, confocal microscope or atomic force microscope have made 3-D measurements with much extended spatial frequency compared to the contact stylus profilometry. Unfortunately, there is still a lack of standards for 3-D surface roughness measurements. Therefore in my thesis, most of the roughness calculations are based on 2-D profile measurements.

Roughness parameters are often divided into three groups based on the characteristics of the surface that they quantify [8, 111-114, 142].

1. **Amplitude parameters**: these are solely height descriptive, for examples: $R_a$, $S_a$, $R_q$, $S_q$, $R_{z\text{DIN}}$, $R_{\text{max}}$ or $R_t$;

2. **Spacing parameters**: these describe the spacing between the topographical irregularities, for example: $S_m$;

3. **Hybrid parameters**: these include information about height as well as space, for example: $S_k$, $K$ (see Figure 37) or $L_r$.

*Table XX summarises all standardised 2-D and 3-D roughness parameters used in my thesis.*
<table>
<thead>
<tr>
<th>Roughness parameter</th>
<th>Definition</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Amplitude:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ra</td>
<td>$R_a = \frac{1}{m \cdot n} \sum_{i=1}^{m} \sum_{j=1}^{n}</td>
<td>z(x_i)</td>
</tr>
<tr>
<td>Rq</td>
<td>$R_q = \frac{1}{m} \sqrt{\sum_{i=1}^{m} z^2(x_i)}$</td>
<td>The root mean square of the values of all points of the surface;</td>
</tr>
<tr>
<td>RzDIN</td>
<td>$R_{z\text{DIN}} = \frac{1}{5} \sum_{i=1}^{5} z(x_i)$</td>
<td>The arithmetic average of the maximum peak to valley height of the roughness values $z(x_i)$ to $z(x_5)$ of five consecutive sampling sections over the filtered profile.</td>
</tr>
<tr>
<td>R_{max}</td>
<td></td>
<td>The maximum individual roughness depth encountered as determining $R_{z\text{DIN}}$.</td>
</tr>
<tr>
<td>R_l</td>
<td></td>
<td>The maximum peak-to-valley height of the entire measurement trace.</td>
</tr>
<tr>
<td><strong>Spacing:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S_m</td>
<td>$S_m = \frac{1}{m} \sum_{i=1}^{m} S_i$</td>
<td>Arithmetic average spacing between the falling flanks of peaks on the mean line.</td>
</tr>
<tr>
<td><strong>Hybrid:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S_k</td>
<td>$S_k = \frac{1}{m} \sum_{i=1}^{m} \frac{z^3(x_i)}{R_q^3}$</td>
<td>Amplitude distribution skew</td>
</tr>
<tr>
<td>K</td>
<td>$K = \frac{1}{m} \sum_{i=1}^{m} \frac{z^4(x_i)}{R_q^4}$</td>
<td>Curtosis is the comparison of the profile with a Gaussian amplitude and characterises the density as 'smooth' or 'peaky'.</td>
</tr>
<tr>
<td>L_r</td>
<td>$L_r = \frac{L_0}{L_m}$</td>
<td>The relation of the stretched length of the profile $L_0$ to the scanned length $L_m$.</td>
</tr>
</tbody>
</table>

**Table XX:** Definition and description of the roughness parameters.
Figure 37 illustrates the roughness parameters used in this thesis. The skew shows the degree of symmetry of the profile while the curtosis shows the degree of pointedness or bluntness of the waveform.

Another method to describe the surface is the material ratio curve, also called bearing curve or Abbott-Firestone curve (see Figure 38). An equivalent straight line is calculated for the centre section of the material ratio curve, which includes 40% of all the measured profile points. The straight line is given by the minimum mean square deviation in the direction of the profile ordinates. The height of the distribution is then split into three parts: \( R_{pk} \), \( R_k \) and \( R_{ok} \). \( R_{pk} \) estimates the reduced height of the peaks,
R_k measures the basic core of the surface and R_{vk} estimates the reduced depth of the valleys. M_{r1} and M_{r2} define the range of the material core profile for R_k. R_{pk}^* is the difference of the complete peak height and the reduced peak height of the bearing curve. R_{vk}^* is the difference of the complete valley depth and the reduced valley depth of the bearing curve.

Fig. 38: Material ratio curve, also called bearing curve or Abbott-Firestone curve.

There are three major difficulties related to the experimental measurement and evaluation of surface topographies:

1. The experimental measurement of topographies across the whole scale-size of interest, often extending from the nanometer to the millimeter range, is generally impaired a) by distortion of the true surface profiles [111-114] (e.g. envelope system [111, 115], b) limited lateral and/or vertical resolution and accessibility of surface features) and c) by artefacts. Artefacts include deformation of the surface in contact-type measurements [116] and optical artefacts in laser non-contact type measurements because of microgeometry, inclination and reflectivity of the surface [114, 120]. The conclusion is that often a combination of different experimental techniques with different advantages/limitations is mandatory in order to get the best possible data [114].

6. Evaluation of surface topography

93
2. 2-D surface profiles $Z(x_j)$, although easier to determine, often do not adequately reflect the surface properties of technological interest. For example, in the study of formability and lubrication, the presence of pit-like cavities that favour the presence of lubricant-filled pockets that enhance lubrication are of interest, but their existence cannot be determined from 2-D profiles [143]. Three dimensional (3-D) surface data $Z(x_j,y_j)$ may therefore be a more practical approach to describing topography-related surface functionality [8, 113, 114].

3. The evaluation of topographical data in terms of standardised 'integral' amplitude roughness parameters such as $R_a$, $R_q$ or $R_{2DIN}$ is often of limited value for the description of real surfaces [111-114]. For example, two technical surfaces behaving very differently in a given situation may have the same $R_a$ and $R_q$ values (see Figure 39). In addition, fine roughness features on random surfaces in the low micron- or submicron-range that may be important for performance in a given application, are often hidden by the coarser contributions to roughness. This is often a major limitation in conventional topography evaluation, and therefore a general interest exists in describing surface profiles with wavelength-dependent functions [111, 113, 144-145], rather than with integral topographical parameters.

![Graph](image-url)  
*Fig. 39: Two different profiles with the same $R_a$ and $R_q$ values.*
In order to be able to compare surface roughness values obtained with different instruments it must be ensured that the two measurements cover the same spatial frequency domain. This is an extremely important issue that is overlooked by far too many users of roughness measurement equipment [142].

Therefore, a method has been developed to extract wavelength-dependent surface topography information from 2-D profiles $Z(x)$ and 3-D surfaces $Z(x,y)$ data (see section 6.2). Two applications of the wavelength-dependent roughness evaluation are the “window roughness” concept (see section 6.3) and the surface treatment transfer function (see section 6.4). The window-roughness concept allows the calculation of roughness values within different wavelength ranges, which are of particular relevance to applications such as formability, adhesion, tribology (wear and lubrication), optics and biocompatibility. Furthermore, topographical data within the same range either obtained from different surfaces using the same instrument or from the same surface using different instruments, can be compared. The surface treatment transfer function allows the separation of the effects of each consecutive surface treatment step used in the fabrication of a surface.

6.2 Concept of wavelength-dependent roughness evaluation

6.2.1 Overview

Before our concept of wavelength-dependent roughness evaluation is discussed, an overview of possible methods to characterise surface profiles and areas will be summarised. These methods are different to the standardised integral roughness parameters discussed above.

Roughness parameters are scale-dependent; the values will depend on the measurement scale and the sampling interval. Figure 40 illustrates these facts. The topography of a finely blasted Ti6Al4V surface was determined using the LPM. In the first case, $R_a$ was determined at increasing scan length while the resolution was held
constant at 2 μm. For each scan length, seven profiles were measured. In the second case, the same profile was measured over the same scan length with different resolutions.

![Graph showing scale-dependence of roughness parameters](image)

**Fig. 40:** Scale-dependence of the roughness parameters; the values will depend on a) the measurement scale \((n = 7, \text{ mean values } \pm \text{ standard deviation})\) and b) the sampling interval (resolution).

Sayles and Thomas [111, 144] demonstrated that the variance of the height distribution or \(R_q\) of a profile is linearly related to the measured distance along the surface. Furthermore, it is well known that many types of surfaces used in engineering practice have a random structure. Such surface topographies can completely be defined by two characteristics: one related to the roughness height

6. Evaluation of surface topography
distribution or amplitude of the waveform and the other related to the spacing or wavelength [145, 146]. The power spectra or the autocorrelation function are functions, that provide information related to wavelengths of the surface, whether periodic or random [111, 113, 144-147]; both are based on the Fourier transform. In recent years, a lot of effort has gone into investigating alternatives to the Fourier transform. The new transforms introduced fall into two main categories: 1. faster and simpler ways of producing comparable results; 2. transforms giving more information. In the first class there are the Walsh [148, 149], Hartley [150, 151], Hadamard [150-152], and Haar [153] transforms. They are all orthogonal transforms. In the second case there are the Wigner [154-156], ambiguity [154, 156, 157], wavelet [158] and Gabor [159, 160] transforms, which are space-frequency transforms. Whitehouse [113] discusses the algorithms, advantages and disadvantages of these transformations. The discrete one-dimensional Hartley transform offers advantages over the FFT for numerical spectral analysis and therefore it has great potential in communications, but there has been difficulty in carrying the advantage over to more than one dimension. Mulvaney [161] came to the general conclusion that the Fourier transform is best for surface characterisation. Although the orthogonal binary transforms such as Walsh, Haar, etc were faster, they did not give spectral estimates that converged rapidly as a function of record length. The phase-invariant ones, such as Fourier, were slower to evaluate yet converged quickly. Also the Fourier transform has the advantage that it is very well known and understood and is standard in many existing instruments. Displacing it would pose many educational and usage problems.

The wavelength-dependence can also be shown using cut-off filtering in the form of an infinitely sharp cut-off or one stage or two stage RC or Gaussian filters [113, 146], which are used in surface metrology for separating the waviness from the roughness of the surface, or using average filters. RC filter is a digital implementation of the analog RC filter, which is build into most surface roughness measurements instruments. A complete overview on different kinds of filters has been given by Whitehouse [113].

Fractal analysis is another method used to characterise surface topographies. The essential difference to the approach discussed in this paper is the fact that while
fractal analysis is a *scale-independent* evaluation technique, in this thesis, it is precisely the *scale-dependence* (the scale being a spatial frequency or wavelength dimension) that is of prime interest. For surfaces of fractal nature [162], a single *scale-independent* parameter — the fractal dimension — can be defined. Since our main interest is the extraction of wavelength-dependent topographical data from experimental profiles and the correlation of roughness data from different wavelength ranges with physico-chemical or biological surface properties, the single *scale-independent* description using fractal analysis is not our preferred approach. Since the introduction of the concept of fractal dimensionality, by Mandelbrot [162, 163], a large number of analytical strategies have been developed to allow the measurement of fractal dimensions [164-168].

### 6.2.2 Theoretical background

The basic aim of this section is to outline and compare procedures for the evaluation of wavelength-dependent surface topography data. The introduction of an additional dimension (the scale, being a spatial frequency or wavelength dimension) requires a certain amount of computational effort, but it enables a particular surface topography to be described in more detail and wavelength-dependent surface changes taking place following a specific surface treatment such as etching, blasting, coating, etc., to be quantified.

Three different computational methods, the *Fast Fourier Transformation (FFT)* [169], *Cut-Off Filtering (COF)* [113, 118] and the *Average Filtering Technique (AFT)* [113], are outlined and discussed in the following subsections.
Fourier transformation procedure

Following a procedure discussed in detail by Beck and Gutsch [170], the profile $Z(x)$ can be written as a Fourier series expansion of periodic sine and cosine functions

$$Z(x/L) = \frac{A_0}{2} + \sum_{n=1}^{N/2} \left[ A_n \cdot \sin \left( f_n \cdot \frac{x}{L} \right) + B_n \cdot \cos \left( f_n \cdot \frac{x}{L} \right) \right]$$

(21)

where $N$ is the number of points within the profile and $L$ is the profile length normalised to unity and therefore dimensionless. Alternatively by introducing phase shifts $\varphi_n$ for each wave considered:

$$Z(x/L) = \frac{A_0}{2} + \sum_{n=1}^{N/2} \left[ C_n \cdot \sin \left( f_n \cdot \frac{x}{L} + \varphi_n \right) \right]$$

(22)

where

$$C_n = \sqrt{A_n^2 + B_n^2} \quad \text{and} \quad \frac{A_n}{B_n} = \tan(\varphi_n)$$

in equation 22 are the amplitude and phase shift of each periodic sine function, respectively. The coefficients $C_n$ correspond to the amplitude contribution of the $n^{th}$ periodic wave to the surface profile and represent the normalised wavelength-dependent contributions to the profile. The spatial frequencies $f_n$ are linked to the wavelengths $\lambda_n$ through equation 23:

$$\frac{1}{f_n} = \frac{\lambda_n}{2\pi} \quad \text{or dimensionless:} \quad \frac{L}{f_n} = \frac{\lambda_n^*}{2\pi}$$

(23)

with $\lambda_n^*$ as the normalised wavelength. The transformations are mathematically strictly correct only for line profiles of infinite extension and of infinitesimal step size. In real situations (finite profile length and resolution), limits to the choice of $\lambda_n$, as well as edge boundary conditions, have to be observed:

6. Evaluation of surface topography
1. According to the Nyquist theorem [99], the smallest $\lambda_n$ (highest spatial frequency) that can be defined corresponds to twice the lateral distance between experimental points ('step size'). It is however safer to use 4 points for the smallest wavelength of interest.

2. The largest meaningful wavelength $\lambda_n$ (lowest spatial frequency) is approximately 0.2 times the scan length L of the profile. Despite the fact that larger $\lambda_n$ can be theoretically be detected, their amplitudes are statistically very uncertain.

**Relation between coefficients $C_n$ and roughness parameter $R_q$**

The root mean square roughness value, $R_q$, is defined for a 2-D surface profile $Z(x)$ according to equation 24, where L denotes the length of the profile in x direction. The waviness $\bar{Z}(x)$ has to be subtracted; alternatively $Z(x)$ in the equations 4 to 6 has to be replaced by $Z(x) - \bar{Z}(x)$:

$$R_q^2 = \lim_{L \to \infty} \frac{1}{L} \int_0^L (Z(x))^2 \cdot dx$$

Expressing $Z(x)$ as a Fourier series expansion according to equation 22 results in:

$$R_q^2 = \lim_{L \to \infty} \frac{1}{L} \int_0^L \left( \frac{A_0}{2} + \sum_{n=1}^{N/2} \left[ C_n \cdot \sin \left( f_n \cdot \frac{x}{L} + \phi_n \right) \right] \right)^2 \cdot dx$$

If L approaches infinity, equation 24 and 25 can be converted to:

$$R_q^2 = \lim_{L \to \infty} \left\{ \frac{1}{L} \int_0^L (Z(x))^2 \cdot dx \right\} = \frac{A_0^2}{2} + \frac{1}{2} \sum_{n=1}^{N/2} C_n^2 = \frac{A_0^2}{2} + \frac{1}{2} \sum_{n=1}^{N/2} (A_n^2 + B_n^2)$$

6. Evaluation of surface topography
Equation 26 proves that the mean square roughness parameter $R_q^2$ is proportional to the integral of the terms $C_n^2 = A_n^2 + B_n^2$. The series of $C_n = \sqrt{A_n^2 + B_n^2}$ terms is called the power spectrum. In other words, $R_q^2$, also called the variance of the height distribution, is proportional to the area under the power spectrum [144, 171, 172]. $R_q^2$ is a function of the wavelength and therefore a function of the resolution [144, 173]. This relationship is true for both 2-D line profiles $Z(x)$ as well as 3-D surface topography images $Z(x, y)$. Figure 41 illustrates the relation. In Figure 41a, a synthesised profile based on four sine waves with different wavelengths, phase shifts and amplitudes (Table XXI) is shown. The whole profile length was 5.0 mm.
Fig. 41: a) A synthetic profile based on 4 sine waves with different wavelengths, phase shifts and amplitudes. b) The corresponding square of the FFT power spectrum $C_n^2 = A_n^2 + B_n^2$ versus the logarithm of the profile wavelength. c) $R_q^2$ as a function of the profile wavelength $\lambda$. According to equation 26, $R_q^2$ of the profile corresponds to the sum of the individual roughness contributions $R_{iq}^2$ from the different resolution steps.
In Figure 41b, the square of the FFT power spectrum \(C_n^2 = A_n^2 + B_n^2\) of the profile is plotted versus the logarithm of the profile wavelength, i.e., the inverse of the spatial frequency. Figure 41c illustrates the roughness \(R_q^2\) as a function of the profile wavelength, \(\lambda\). The higher cut-off wavelength, \(\lambda_{th}\), steadily decreases from 0.2 times the profile length to three times the step size of adjacent data points, while the lower resolution length, \(\lambda_i\), is fixed at three times the resolution limit. \(R_q^2\) was calculated using equation 26 for \(n = N/2\) to \(n = 1\). The result demonstrates the dependence of the roughness \(R_q^2\) on the profile wavelength, \(\lambda\), and the relationship to the square of the power spectrum \(C_n^2\). The plot of \(R_q^2\) versus profile wavelengths falls in four steps, whose positions correspond to the wavelengths of the four sine wave of the synthetic profile.

The coefficients \(C_n^2\) are proportional to the weighting factors characterising the changes in roughness values \(R_q^2\) as a function of the changes in resolution. The relationship between \(R_q^2\) and the Fourier coefficients (equation 26) allows the roughness of a profile to be understood as the sum of individual roughness contributions \(R_{qi}^2\) from the different resolution steps (Figure 41c).

The important advantage of the FFT formalism is the fact that individual contributions to \(R_q\) from any wavelength (or spatial frequency) range \((\lambda_{th} to \lambda_i)\) of interest can be accurately and easily calculated.

<table>
<thead>
<tr>
<th>Fig.</th>
<th>Synthetic Profile</th>
<th>Amplitude [μm]</th>
<th>Wavelength (\lambda) [μm]</th>
<th>Phase Shift (\phi) [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>41a</td>
<td>I</td>
<td>1 0.75 2 1</td>
<td>16 64 128 512</td>
<td>90 0 0 90</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1 1 1 1</td>
<td>8 16 32 64</td>
<td>90 90 90 90</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>1 1 1 1</td>
<td>8 32 128 512</td>
<td>90 90 90 90</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>1 1 1 1</td>
<td>16 64 128 512</td>
<td>90 90 90 90</td>
</tr>
<tr>
<td>43a</td>
<td>I</td>
<td>1 1 1 1</td>
<td>8 16 32 64</td>
<td>90 90 90 90</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1 1 1 1</td>
<td>16 32 64 256</td>
<td>90 90 90 90</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>1 1 1 1</td>
<td>8 32 128 512</td>
<td>90 90 90 90</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>1 1 1 1</td>
<td>16 64 128 512</td>
<td>90 90 90 90</td>
</tr>
<tr>
<td>44a</td>
<td>I</td>
<td>1 1 1 1</td>
<td>16 32 64 256</td>
<td>90 90 90 90</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1 1 1 1</td>
<td>16 32 64 256</td>
<td>90 0 0 90</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>1 1 1 1</td>
<td>16 32 64 256</td>
<td>90 0 90 0</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>1 1 1 1</td>
<td>16 32 64 256</td>
<td>0 45 45 90</td>
</tr>
</tbody>
</table>

Tab. XXI: List of all synthetic profiles, each based on four sine waves.

6. Evaluation of surface topography
6.3 Concept of the window-roughness

It is possible to define a "differential roughness" as the limiting value of the change of roughness as the resolution step approaches zero, i.e. the first derivative of the roughness of the analysed profile versus the resolution. In every practical case, however, one has a limited number of data points. In such a case, the roughness defined as $R_q^2$ corresponds to the sum of the squared FFT coefficients in the corresponding range:

$$R_q^2(n,m) = \frac{A_{nm}^2}{2} + \frac{1}{2} \sum_{i=n}^{m} C_i^2$$

or approximately

$$R_q^2(n,m) = \frac{1}{2} \sum_{i=n}^{m} C_i^2$$

(27)

since the term $\frac{A_{nm}^2}{2}$ is generally negligible.

Equation 27 will be defined as window-roughness, where $n$ and $m$ are the range of the Fourier coefficients, corresponding to the range of wavelengths and defining a certain "window". The lowest meaningful value $n$ is the resolution length, the highest value is the cut-off length for the waviness.

Using the philosophy of a Fourier-transformed, resolution-dependent roughness curve as outlined above, the roughness is no longer a single value but a function of the resolution and of the waviness. In the window-roughness concept, the roughness $R_q^2$ is proportional to the integral (equation 26) with a lower limit $\lambda_i$ (resolution) and an upper limit $\lambda_h$ (waviness) of the Fourier coefficients. In the discrete notation (equation 27) it is the sum of the squares of the FFT coefficients between a lower limit $n$ and an upper limit $m$.

This concept allows roughness coefficients to be defined for different windows in the wavelength domain of interest and to separate contributions to the roughness parameters arising from different resolution ranges. Individual $R_q$ values can be calculated for defined regions of interest by calculating the corresponding integrals or sums of the Fourier coefficients. This can also be done graphically (Figure 42) in the plot of $R_q$ versus the logarithm of the profile wavelength, choosing the two limit wavelengths ($\lambda_i$ and $\lambda_h$) and reading off the contribution of this region to $R_q$. 

6. Evaluation of surface topography
This formalism is closely related to the distinction of roughness, waviness and shape of surfaces. The high-pass (low spatial frequency) cut-off that is chosen sets the limit separating roughness and waviness. Using fixed cut-off values (such as defined in DIN 4768 [103] and DIN 4777 [118]), a part of the information contained in experimental surface profiles, which may be relevant in practice, is completely lost (see section 6.3.2.).
6.3.1 FFT applied to synthetic roughness profiles: influence of wavelength and phase shift

The first and second illustrative examples are based on profiles synthesised through the superposition of periodic sine-wave functions with different wavelengths or phases but with equal amplitudes. The FFT of such profiles simply corresponds to the amplitudes for the given sine-waves, with $R_q$ being equal to the sum of the power spectrum. This means that with a constant number of amplitudes present in the spectrum, the wavelengths and phase shifts of the different sine waves (correlated to the Fourier coefficients) do not influence the standardised $R_q$ value.

To illustrate the influence of the wavelength, four profiles were synthesised, each of them using four sine waves with different wavelengths but with equal amplitude (1 µm) and phase shift (90°) (see Table XXI). The profile length was 4.096 mm and the resolution 1 µm. The synthetic profiles have different aspects, but the standardised $R_q$ values are the same for all of them ($R_q = 1.414$ µm, see Table XXII). Each of the four profiles has been transformed by the FFT technique and $R_q$ calculated as a function of the wavelength. Figure 43a shows the four profiles together with the corresponding FFT amplitude- and phase- plot, which are also different. Simulating a low-pass filter, the lower wavelength was steadily increased from three times the step size of adjacent data points (3 µm, $n = 3$) to 0.2 times the profile length (0.820 mm, $n = 820$), while the upper resolution length (waviness) was fixed (0.820 mm, $m = 820$). After each filtering step, $R_q$ was calculated using equation 26. Figure 43b shows the variation of $R_q$. The curves $R_q = f(\lambda)$ are clearly different reflecting the different wavelengths in the profiles. The plots start from the lowest wavelength at the standardised $R_q$ value and fall in four steps at positions corresponding to the wavelengths of the sine-wave periodicity of the synthetic profiles. In the same figure the dependence on $R_q$ is indicated using the average and the low pass filtering technique (discussed in section 6.3.2.).
Fig. 43a: The profiles I to IV were each synthesised using four sine waves with different wavelengths but equal amplitudes and phase shifts. On the right hand side the corresponding FFT amplitude- and phase-shift plots are shown.
Fig. 43b: The comparison of the dependence of the roughness $R_q$ on the profile wavelength for the four profiles I to IV using the FFT, COF and average filtering technique are shown.
Table XXII: List of all synthetic profiles, based on four sine waves, with their standardised roughness value $R_q$ and their graphical results after calculation of $R_q$ versus $\lambda$ using equation 27.

<table>
<thead>
<tr>
<th>Fig.</th>
<th>Synthetic Profile</th>
<th>Standardised $R_q$ Value [(\mu m)]</th>
<th>FFT Amplitude and Phase Plot</th>
<th>$R_q$ vs. $\lambda$ Curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>41a</td>
<td>I</td>
<td>1.811</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>43a</td>
<td>I, II, III, IV</td>
<td>1.414</td>
<td>I to IV are different</td>
<td>I to IV are different</td>
</tr>
<tr>
<td>44a</td>
<td>I, II, III, IV</td>
<td>1.414</td>
<td>for I to IV only phase plots are different</td>
<td>I to IV are equal</td>
</tr>
</tbody>
</table>

In the second example four profiles were synthesised with a length of 4.096 mm and a resolution of 1 \(\mu m\), each of them using four sine waves with constant wavelength of 16, 32, 64 and 256 \(\mu m\) respectively and equal amplitude of 1 \(\mu m\), changing only the phases of the single waves (Table XXI). The synthesised profiles are again different (Figure 44a), but have the same standardised $R_q$ values ($R_q = 1.414$ \(\mu m\), Table XXII). Since $R_q$ is only a function of the square of the amplitudes but does not depend on the phases, all these profiles have the same dependence on $R_q$ versus wavelength (Figure 44b). Such profiles can only be distinguished from each other by plotting their Fourier coefficients with the corresponding phases (Figure 44b). In this case the plot of $R_q$ versus profile wavelengths is not sufficient to distinguish the four profiles from each other.

In Figure 41a not only wavelengths and phases are different, but also amplitudes. The standardised $R_q$ value ($R_q = 1.811$ \(\mu m\)) is consequently different (Table XXII).

In most cases, the plot of $R_q$ versus wavelength $\lambda$ is well suited to the adequate characterisation of a profile. However, such a plot may in certain practical cases be too complicated or time-consuming for a simple comparison of specific, topographical characteristics of a surface. In such cases, standardised roughness values may therefore be preferred.

6. Evaluation of surface topography
Based on the Fourier transformation technique it is possible to demonstrate mathematically the correlation between the Fourier coefficients and the roughness R_q. Roughness values other than R_q can also be expressed as a function of wavelength. The mathematical procedure, however, is more complex and not further discussed here.

**Fig. 44a:** The profiles I to IV were each synthesised using four sinus waves with constant wavelength of 16, 32, 64 and 256 µm respectively and equal amplitude of 1 µm, changing only the phases of the single wave.
Fig. 44b: The comparison of the dependence of the roughness $R_q$ on the profile wavelength for the four profiles I to IV using the FFT technique. On the right hand side are the corresponding FFT amplitude- and phase-shift plots.

6. Evaluation of surface topography
6.3.2 Cut-off filtering (COF) techniques

Cut-off filtering (COF) is a standardised procedure [113, 118] applied before roughness parameters are calculated from experimental profiles. Low-frequency cut-off filters are used to cut off the range considered to be waviness, generally corresponding to 1/7 of the measured length of the profile. Valuable information may be lost by this standard technique, however.

An alternative to FFT, albeit a mathematically less accurate procedure, band-pass filtering may be applied to various spatial frequency/wavelength ranges of particular interest. To calculate wavelength-dependent roughness values similar to the FFT procedure discussed in section 6.2, the effect of a varying low- or high-end cut-off is applied and the corresponding roughness values determined from the individual manipulated profiles.

Another more pragmatic way to handle the problem is to use filtering techniques such as those used for the cut-off filtering (gliding gauss- or average-filter), but with an intention other than just eliminating waviness. The procedure uses a continuously changing filter width starting from three times the data step size and ending at the cut-off for the waviness correction (1/7 of the profile length) or at any other predefined cut-off length shorter than half of the profile length. The result is a set of filtered profiles suitable for roughness calculations with cut-offs ranging from the predefined cut-off length to three times the measuring step size, and a second set of filtered profiles with waviness information and cut-offs ranging from three times the measuring step size to the predefined cut-off length. At the higher limit the roughness profile is a straight (zero) line because the whole profile is interpreted as waviness. The lower the cut-off length, the larger the part of the profile that is considered to be roughness and the smaller the part considered to be waviness. From such profiles it is possible to calculate roughness parameters, not as a single value, but as a function of the resolution or of the waviness.

In the case of the roughness profile, the curve $R(\lambda)$ starts at zero with a positive slope and a sigmoidal shape up to the $R_a$ or $R_q$ values, characteristic for the integral roughness values including the standard cut-off.
In the case of the *waviness profile*, the curve \( W(\lambda) \) starts at \( R_a \) or \( R_q \) with a negative slope and a sigmoidal shape and ends at a value of zero for the standard waviness cut-off. \( R(\lambda) \) and \( W(\lambda) \) are simply related via equation 28

\[
R(\lambda) + W(\lambda) = \text{const.} = R_a \text{ or } R_q \tag{28}
\]

*Figure 43b* shows the application of the average filtering technique (AFT) to the four synthetic profiles in *Figure 43a*. The filter width was continuously varied from three times the resolution limit (3 \( \mu \)m, i.e. the data step size between adjacent points) to the cut-off length (0.82 mm = 0.2 times the scan length). In the case of the cut-off roughness, the resulting curves decreases with increasing average filter length. Compared with the curves obtained using the FFT procedure (*Figure 43b*), the \( R_q \) values are, however, lower for the same wavelength and show no abrupt steps, since the AFT technique does not correspond to a set of orthonormal functions like the sine and cosines curves of the Fourier transformations. \( R_q \) becomes zero at the highest profile wavelength. Although mathematically not strictly correct, the AFT technique is less cumbersome and time-consuming than the FFT technique. Additional examples with the low-pass cut-off filtering technique (COF) are shown in *Figure 43b*. The low pass cut-off was raised from 3 \( \mu \)m to the upper limit of 0.82 mm. The result depends on the choice of the filter form (average, Gauss, rectangular, etc.). With COF techniques, it is also essential to cut off at the lower and higher limit with a filtering dimension corresponding to half the filter size used, otherwise boundary-related artefacts are produced. In this case, a Gauss filter and an attenuation factor of 50\% were used. The resulting curves decrease in smaller steps than those obtained using the FFT technique, but no abrupt steps were observed at the highest wavelengths of the synthesised profiles. The \( R_q \) values become zero at twice the highest profile wavelength. A comparison of the \( R_q \) values at the same wavelength calculated by the three filtering techniques indicate the highest value for the FFT technique and the lowest for the AFT.

Furthermore it is possible to apply a band-pass filter on the profile, having a lower limit corresponding to the resolution and an upper limit corresponding to the...
The philosophy discussed above for the Fourier transformation and the window-roughness concept holds in the same way for the different filtering techniques. In the limit case (band-pass-filter width \( \rightarrow 0 \)), both "window values" (FFT and COF) should be equal and define a correct window-roughness curve vs. wavelength. The defined integral of this function between two chosen limits is equal to the roughness for the analysed profile determined between the boundaries of the lower limit (resolution) and the upper limit (waviness).

6.3.3 The inverse FFT, an application to the window-roughness

An application of the window-roughness approach is the inverse FFT. FFT-transformed profiles are inverse transformed in the wavelength domain of interest. The result is a low-, high- or band-pass filter applied to the original profile. Figure 45 demonstrates the application of inverse transformation of the FFT to the synthetic profile in Figure 41a cutting off the lower wavelength range \( \lambda_{\text{cut-off}} = 2, 16, 32, 64, 128, 256, 512 \) and \( 1024 \) \( \mu \text{m} \). Table XXIII shows the \( R_q \) values for the different inverse transformed profiles calculated using equation 27. Filtering within the ranges 2 to 2048 \( \mu \text{m} \) and 16 to 2048 \( \mu \text{m} \), 32 to 2048 \( \mu \text{m} \) and 64 to 2048 \( \mu \text{m} \), 256 to 2048 \( \mu \text{m} \) and 512 to 2048 \( \mu \text{m} \) respectively showed no change in the inverse transformed profiles and roughness. This corresponds to the power spectrum in Figure 41b and the dependence of the roughness \( R_q \) on the wavelength in Figure 41c.
Fig. 45: The inverse FFT transformed profiles in different ranges of window-roughness from the profile I in Figure 41a (see also Table XXI).
<table>
<thead>
<tr>
<th>Wavelength Range [μm]</th>
<th>Rq Value [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 to 2048</td>
<td>1.811</td>
</tr>
<tr>
<td>4 to 2048</td>
<td>1.811</td>
</tr>
<tr>
<td>8 to 2048</td>
<td>1.811</td>
</tr>
<tr>
<td>16 to 2048</td>
<td>1.811</td>
</tr>
<tr>
<td>32 to 2048</td>
<td>1.668</td>
</tr>
<tr>
<td>64 to 2048</td>
<td>1.668</td>
</tr>
<tr>
<td>128 to 2048</td>
<td>0.884</td>
</tr>
<tr>
<td>256 to 2048</td>
<td>0.707</td>
</tr>
<tr>
<td>512 to 2048</td>
<td>0.707</td>
</tr>
<tr>
<td>1024 to 2048</td>
<td>0</td>
</tr>
</tbody>
</table>

**Tab. XXIII:** List of Rq values calculated for the different inverse FFT transformed profiles of the synthetic profile in Figure 40a using equation 27.

### 6.3.4 Evaluation of three-dimensional areas

The formalism discussed above can be extended to the three-dimensional case. In the Fourier transform concept the resolution can be represented as concentric circles with the centre at \( \lambda_x = \lambda_y = 0 \), in the x/y wavelength or spatial frequency plane as shown in Figure 46. The wavelength-dependent roughness is then proportional to the integral of the coefficients inside this circle. The weighting factor of the resolution changes in the window-roughness concept corresponds to the integral over the annulus centred on zero in the x/y wavelength or spatial frequency plane with radius \( r \) to \( r+dr \). This corresponds to all vectors in the x/y wavelength or spatial frequency plane with length equal to the wavelength or spatial frequency range with the origin at zero.

Using the COF and AFT filtering techniques, a two-dimensional filter with a dimension that changes after each gliding filtering step is applied. After each filtering step, the surface roughness parameter has to be calculated. It is straightforward to use a square matrix filter, although a "round" kernel filter would be more appropriate. In the band-pass case, the surface has to be treated first with the lower and then with...
the upper surface filter and the obtained filtered topographies subtracted from each other.

It is also possible in the three-dimensional case to apply the filtering in the FFT space and to inverse transform the filtered FFT into real space. The result is a filtered topography that depends on the filter used to treat the FFT coefficients. From this filtered surface the roughness parameters for different windows can be calculated.

![Image of concentric circles in the Fourier transform concept]

**Fig. 46:** In the Fourier transform concept the resolution can be represented as concentric circles with the centre at \( \lambda_x = \lambda_y = 0 \), in the x/y wavelength plane.

### 6.4 Surface treatment transfer functions

In the area of surface engineering, several consecutive surface treatment processes are often applied to achieve the required surface properties of the material or product. The surface topography may thereby be modified by each treatment, requiring careful control of the parameters and quality in each individual step. Examples are:
1. Coating by electroplating, plasma spraying or lacquering onto surface-structured substrates, resulting in topographic changes related to both the substrate surface structure and the (macro and micro) throwing power of the applied surface coating technique.

2. Combinations of different surface roughening techniques, such as machining, shot blasting, etching, providing surface topographic effects in different dimensional ranges.

During such surface treatments the surface topography is often transformed in a resolution-dependent manner. It is proposed to use a new "transfer function" concept to follow quantitatively, and in a resolution-dependent way, the effect of each subsequent surface modification step. This may be helpful, both for the quality control of product surfaces and for the systematic development of specific surface structures based on combinations of existing surface treatment methods.

Referring to equation 25, we can define sets of FFT C_n^X coefficients for the surfaces after each surface modification step X:

C_n^A = set of FFT coefficients for surface produced in surface treatment step A
C_n^B = set of FFT coefficients for surface produced in surface treatment steps A+B
C_n^C = set of FFT coefficients for surface produced in surface treatment steps A+B+C etc.

"Multiplicative transfer functions" M_Y/X are defined based on the following ratios of FFT coefficients:

\[ M_{B/A} = \frac{C_n^B}{C_n^A} \]
\[ M_{C/B} = \frac{C_n^C}{C_n^B} \]
\[ M_{C/A} = \frac{C_n^C}{C_n^A} = M_{C/B} \cdot M_{B/A} \]  \hspace{1cm} (29)

etc.

Such transfer functions can be used to characterise the resolution-dependent "topographical fingerprint" of a particular surface treatment process, and, once
known, can be used to back-calculate the effect of this surface treatment on starting surfaces with different topographies. For example, the effect of micro- and macro-throwing power of coating processes, such as electroplating or lacquering, in gradually levelling off substrate surface roughness can be followed in a quantitative way. A practical example will be shown and discussed in section 7.2.4.

In general, however, consecutive surface treatments are unlikely to merely level off or amplify the surface topography of the base material, but will add their own specific surface roughness characteristics with different amplitude and spatial frequency/wavelength contributions. In such a case — in addition to multiplicative factors — additive transfer terms (\(c_n^B, c_n^C\), etc.) have to be considered as well:

\[
M^{B/A} = \left[ \frac{C_n^B}{C_n^A} + c_n^B \right]
\]
\[
M^{C/B} = \left[ \frac{C_n^C}{C_n^B} + c_n^C \right]
\]
\[
M^{C/A} = \left[ \frac{C_n^C}{C_n^B} \times \left\{ \frac{C_n^B}{C_n^A} + c_n^B \right\} + c_n^C \right] = C_n^C/C_n^B \times M^{B/A} + c_n^C
\]

To determine the additive transfer terms for a particular surface treatment process, starting substrates as flat as possible have to be used and the topography determined individually before and after each particular surface treatment step.

Two drawbacks of the transfer function concept should be mentioned:

1. Since the transfer function involves ratios of coefficients, statistical scatter in the data are amplified. For statistically significant transfer function values, rather large surface areas, characteristic of the chosen surface treatment process, have to be measured with adequate lateral and vertical resolution.

2. Large data sets have to be handled with the consequence of increased computation time, particularly in the case of three-dimensional surface topographies.

The techniques described can be very useful, but have to be carefully evaluated in the context of the specific applications and questions raised.

6. Evaluation of surface topography

119
6.5 Application of the wavelength-dependent roughness evaluation to a real model surface

The micromachined steel surface (Figure 47a), used as a calibration reference for topographical instruments, is characterised by two superimposed surface structures with periodicities of the order of 100 µm and 4 µm, respectively. This is clearly visible in the 2-D laser scan profile taken perpendicular to the machining direction over a length of 4.096 mm with a lateral resolution of 1 µm (Figure 47a) as well as from the FFT power spectrum versus the profile wavelength, which is dominated by the two basic wavelengths (Figure 47b).

![Fig. 47: a) SEM image of the micromachined steel surface and a part of 2-D LPM profile taken perpendicular to the machining direction.](image)

6. Evaluation of surface topography
Furthermore the FFT power spectrum shows three distinct peaks around the wavelength of 4 μm. Figure 47c shows the dependence of the $R_q$ value on the profile wavelength $\lambda$ using the FFT technique ($\lambda$ is fixed at three times the resolution limit). The $R_q$ value starts from the highest wavelength distribution at the standardised $R_q$ value ($R_q = 3.47 \mu m$) and falls at the position corresponding to the first basic wavelength (97.5 μm) and again in three steps at the positions corresponding to the lower wavelength distribution.

![FFT power spectrum and $R_q$ value graph](image)

Fig. 47: b) The square of the FFT power spectrum versus the logarithm of the profile wavelength of the 2-D LPM profile. c) The comparison of the dependence of the roughness $R_q$ on the profile wavelength for the micromachined steel surface using the FFT and COF technique.

If the high-pass filter (COF) is applied (Figure 47c) the curve starts at the same $R_q$ value ($R_q = 3.47 \mu m$) as obtained using the FFT technique and falls off continuously.
in small steps over a large range (appr. 250 µm to 20 µm). In the range between 20 and 3 µm, the curve falls over three steps and ends at the same Rq value (Rq = 0.41 µm) at which the FFT-based curve drops off. Using the COF technique, no abrupt steps are indicated around 100 and 4 µm. It follows that in the case of the high-pass filter, the most characteristic information of the profile is lost. Another way to characterise the profile is the window-roughness concept. Figure 47d and e illustrate the results of the inverse FFT and COF techniques when separately treating the two surface structures by dividing up the calculated wavelength range into A (113.8 µm - 85.3 µm) and B (4.31 µm - 3.81 µm). In the case of the COF technique a wavelength range A* (250.0 µm to 12.0 µm) and B (9 µm to 0.5 µm) had to be chosen for the two ranges A and B described above in order to get correct results.

![Graphs showing iFFT transformed profiles and COF profiles for ranges A and B](image)

**Fig. 47:** d) Inverse FFT transformed profiles in the wavelength ranges of A (85.3 µm to 113.8 µm) and B (3.81 µm to 4.31 µm), respectively. e) COF profiles in the same wavelength ranges A and B.

Both methods allow the substructure-specific roughness parameters Ra, Rq, RzDINr, Sm, Sk, and Lr to be determined with a Gauss filter, an attenuation factor of 50% and
In the range A (113.8 μm - 85.3 μm), the inverse FFT and the COF filtered profile are very similar and the corresponding roughness values show only small differences between the two mathematical procedures for $R_a$, $R_q$, $R_{z\text{DIN}}$, $S_m$, and $L_r$. However, the differences are larger in the range B (4.31 μm - 3.81 μm) for $R_a$, $R_q$, $R_{z\text{DIN}}$, $S_k$, and $L_r$ due to two reasons: 1) The band-pass filter has to be chosen at appr. 1/7 of the lower wavelength and twice the higher wavelength to filter in the predefined ranges A and B. 2) The band-pass filter does not correspond to a set of orthonormal functions like the sine and cosines curves of the Fourier transformation.

<table>
<thead>
<tr>
<th>Wavelength range</th>
<th>Roughness parameters</th>
<th>Roughness values (FFT technique)</th>
<th>Roughness values (COF technique)</th>
<th>Wavelength range</th>
<th>Roughness parameters</th>
<th>Roughness values (standard norm DIN4768)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (113.8-85.3 μm)</td>
<td>$R_a$ [μm]</td>
<td>3.10</td>
<td>3.01</td>
<td>original (3-2048μm)</td>
<td>$R_a$ [μm]</td>
<td>3.10</td>
</tr>
<tr>
<td></td>
<td>$R_q$ [μm]</td>
<td>3.45</td>
<td>3.36</td>
<td></td>
<td>$R_q$ [μm]</td>
<td>3.47</td>
</tr>
<tr>
<td></td>
<td>$R_{z\text{DIN}}$ [μm]</td>
<td>9.83</td>
<td>9.71</td>
<td></td>
<td>$R_{z\text{DIN}}$ [μm]</td>
<td>11.49</td>
</tr>
<tr>
<td></td>
<td>$S_m$ [mm]</td>
<td>0.105</td>
<td>0.100</td>
<td></td>
<td>$S_m$ [mm]</td>
<td>0.086</td>
</tr>
<tr>
<td></td>
<td>$S_k$</td>
<td>-0.04</td>
<td>0.04</td>
<td></td>
<td>$S_k$</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>$L_r$</td>
<td>1.02</td>
<td>1.02</td>
<td></td>
<td>$L_r$</td>
<td>1.18</td>
</tr>
<tr>
<td>B (4.31-3.81 μm)</td>
<td>$R_a$ [μm]</td>
<td>0.265</td>
<td>0.34</td>
<td></td>
<td>$R_a$ [μm]</td>
<td>0.2048</td>
</tr>
<tr>
<td></td>
<td>$R_q$ [μm]</td>
<td>0.323</td>
<td>0.44</td>
<td></td>
<td>$R_q$ [μm]</td>
<td>0.2048</td>
</tr>
<tr>
<td></td>
<td>$R_{z\text{DIN}}$ [μm]</td>
<td>1.45</td>
<td>2.45</td>
<td></td>
<td>$R_{z\text{DIN}}$ [μm]</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>$S_m$ [mm]</td>
<td>0.004</td>
<td>0.004</td>
<td></td>
<td>$S_m$ [mm]</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>$S_k$</td>
<td>0.00</td>
<td>0.30</td>
<td></td>
<td>$S_k$</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>$L_r$</td>
<td>1.09</td>
<td>1.16</td>
<td></td>
<td>$L_r$</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Table XXIV: List of the roughness values $R_a$, $R_q$, $R_{z\text{DIN}}$, $S_m$, $S_k$, and $L_r$ calculated in the wavelength ranges A (113.8-85.3 μm) and B (4.31-3.81 μm) with a Gauss filter and an attenuation factor of 50% at the cut-off of 0.82 mm as well as the parameters determined according to DIN4768.

In summary, the concept of wavelength-dependent roughness evaluation is shown to be a useful approach in describing surface topographies, with the advantage that contributions in different wavelength ranges can be separately estimated. This possibility allows technological surface properties to be correlated with roughness contributions in different wavelength ranges (see section 7.2.4 and 7.2.5). Furthermore, the window-roughness concept provides the opportunity to correlate in vitro and/or in vivo biological performance data with surface topographical data in the various size ranges of biological relevance (see section 7.4).
7. Results and discussion

Before cell culture tests were carried out, the chemical composition and the topography of the implant surfaces were determined and are discussed in the following sections 7.1 and 7.2.

7.1 Chemical characterisation of the implant surfaces

7.1.1 Chemical composition of polished cpTi, Ti6Al7Nb and Ti6Al4V surfaces after different cleaning regimens

Discs of cpTi, Ti6Al7Nb and Ti6Al4V were polished as described in section 4.1. After that, the samples were cleaned following the prescription discussed in section 4.2. All polished samples were packed in Al-foil and sterilised within the autoclave at 180°C for 3h (see section 4.3).

Figure 48 shows typical XPS survey spectra of cpTi after polishing and the final surface-cleaning treatment (oxygen plasma) and storage in ultra-pure water. Ti, O, and C were detected on all surfaces. Both spectra were dominated by Ti and O emission intensities of the naturally formed TiO₂ layer (see below). The relatively strong C signal, detected after polishing, is typical for adsorbed organic molecules and always present on high surface energy oxide films, which have been exposed and stored under atmospheric conditions. Low concentrations of N, Si, Ca, Pb, Zn and Cu (<1.0at%), probably due to the mechanical polishing, were detected on untreated, polished cpTi surfaces. Si, subsequently found to be associated in polydimethylsiloxane (PDMS), was determined by ToF-SIMS (Figure 49). It was a frequently detected surface contamination.

Table XXV shows the surface composition (at%) of the cpTi surface as determined by XPS after polishing and the three surface-cleaning steps a) cleaning with organic solvents (hexane, acetone and ethanol) b) passivation in 30% HNO₃ for
1h and c) oxygen-plasma cleaning and storing in ultra-pure water (18.2 MΩcm). Table XXVI summarises the measured binding energies for Ti, and its corresponding chemical states.

![Typical XPS survey spectra of a) polished and b) cleaned cpTi surface.](image)

**Fig. 48:** Typical XPS survey spectra of a) polished and b) cleaned cpTi surface.

7. Results and discussion
Fig. 49: Positive ToF-SIMS spectrum of a polydimethylsiloxane (PDMS) contaminated, polished cpTi surface.
Fig. 49: Positive ToF-SIMS spectrum of a polydimethylsiloxane (PDSM) contaminated, polished cpTi surface.

<table>
<thead>
<tr>
<th>Element</th>
<th>Polished [at%]</th>
<th>Organic Solvent [at%]</th>
<th>Passivation in 30% HNO₃ [at%]</th>
<th>O₂ Plasma [at%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>18.4 ± 1.6</td>
<td>21.5 ± 1.1</td>
<td>26.1 ± 0.9</td>
<td>27.8 ± 0.8</td>
</tr>
<tr>
<td>O</td>
<td>46.8 ± 1.9</td>
<td>51.5 ± 2.0</td>
<td>54.4 ± 2.0</td>
<td>58.8 ± 1.5</td>
</tr>
<tr>
<td>C</td>
<td>30.9 ± 2.1</td>
<td>25.1 ± 2.2</td>
<td>19.0 ± 2.9</td>
<td>12.8 ± 1.8</td>
</tr>
<tr>
<td>N</td>
<td>0.6 ± 0.2</td>
<td>0.3 ± 0.1</td>
<td>0.5 ± 0.1</td>
<td>0.6 ± 0.2</td>
</tr>
<tr>
<td>Si</td>
<td>1.0 ± 0.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ca</td>
<td>0.9 ± 0.3</td>
<td>0.2 ± 0.1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pb</td>
<td>0.3 ± 0.2</td>
<td>0.3 ± 0.2</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Zn</td>
<td>0.7 ± 0.6</td>
<td>0.6 ± 0.3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cu</td>
<td>0.4 ± 0.1</td>
<td>0.5 ± 0.1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O/Ti Ratio</td>
<td>2.54 ± 0.14</td>
<td>2.39 ± 0.12</td>
<td>2.08 ± 0.03</td>
<td>2.12 ± 0.04</td>
</tr>
<tr>
<td>Oxide-layer Thickness [nm]</td>
<td>4.3 ± 0.2</td>
<td>4.3 ± 0.2</td>
<td>4.3 ± 0.2</td>
<td>5.1 ± 0.1</td>
</tr>
</tbody>
</table>

Tab. XXV: Surface composition (at%), atomic ratio O/Ti and oxide layer thickness (nm) of cpTi after polishing followed by the three surface-cleaning steps a) cleaning with organic solvents b) passivation in 30% HNO₃ for 1h and c) oxygen plasma cleaning and storing in ultra-pure water (18.2 MΩcm). Mean values of 5 samples ± standard deviation.

7. Results and discussion
<table>
<thead>
<tr>
<th>Element</th>
<th>Binding Energy [eV]</th>
<th>Chemical State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti (2p&lt;sub&gt;3/2&lt;/sub&gt;)</td>
<td>459.1 ± 0.2</td>
<td>Ti (IV), TiO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Ti (2p&lt;sub&gt;3/2&lt;/sub&gt;)</td>
<td>457.3 ± 0.3</td>
<td>Ti (III), TiO&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>Ti (2p&lt;sub&gt;3/2&lt;/sub&gt;)</td>
<td>455.7 ± 0.2</td>
<td>Ti (II), TiO</td>
</tr>
<tr>
<td>Ti (2p&lt;sub&gt;3/2&lt;/sub&gt;)</td>
<td>454.1 ± 0.2</td>
<td>Ti (Mettall)</td>
</tr>
<tr>
<td>Ti (2p&lt;sub&gt;1/2&lt;/sub&gt;)</td>
<td>464.8 ± 0.2</td>
<td>Ti (IV), TiO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Ti (2p&lt;sub&gt;1/2&lt;/sub&gt;)</td>
<td>462.7 ± 0.3</td>
<td>Ti (III), TiO&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>Ti (2p&lt;sub&gt;1/2&lt;/sub&gt;)</td>
<td>461.3 ± 0.2</td>
<td>Ti (II), TiO</td>
</tr>
<tr>
<td>Ti (2p&lt;sub&gt;1/2&lt;/sub&gt;)</td>
<td>460.3 ± 0.2</td>
<td>Ti (Mettall)</td>
</tr>
<tr>
<td>Al (2p)</td>
<td>74.8 ± 0.3</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>Nb (3d)</td>
<td>207.8 ± 0.1</td>
<td>Nb&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
</tr>
<tr>
<td>V (2p) *)</td>
<td>516.4 ± 0.4</td>
<td>V-Oxide</td>
</tr>
<tr>
<td>O (1s)</td>
<td>530.6 ± 0.1</td>
<td>O, TiO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>C (1s)</td>
<td>285.0 ± 0.1</td>
<td>C-C</td>
</tr>
</tbody>
</table>

*Tab. XXVI: The binding energies (eV) of Ti, Al, Nb and V and their corresponding chemical states. Mean values of 5 samples ± standard deviation. *) detected with monochromated excitation radiation.

After cleaning with the organic solvents (see Table XXV), Si traces were removed, Ca, N and C were decreased, and O and Ti increased. The passivation in 30% HNO<sub>3</sub> for 1h efficiently removed the contaminants Ca, Pb, Zn, and Cu which may have the potential to negatively influence some biological responses such as osseointegration of titanium implants [91]. However, some traces of N from the nitric acid treatment were detected and there was still some C contamination on the surface. After oxygen-plasma cleaning and storing in ultra-pure water, the surfaces were acceptably clean as shown by the XPS spectra. The C signal was reduced due to the removal of hydrocarbon during the oxygen-plasma treatment and the signals of Ti and O were again increased, and some N was still detected.

The polished surface shows an atomic concentration ratio O/Ti of 2.54 ± 0.14, whereas the surfaces after passivation and oxygen plasma treatment indicate a ratio O/Ti of 2.08 ± 0.03 and 2.12 ± 0.04, respectively. The slightly increased atomic concentration ratio for the oxygen plasma treated surface is the direct effect of the
oxygen plasma treatment. However, there were no statistically significant differences of the atomic concentration ratio O/Ti between the passivated and oxygen plasma treated surface. It indicates, that only C in the form of hydrocarbon has been removed by the oxygen plasma treatment.

For untreated and cleaned, polished Ti alloys, all XPS survey spectra show signals of Ti, C, O and Al and additionally Nb on Ti6Al7Nb and V on Ti6Al4V. V could only be detected when using monochromatic excitation radiation. The alloying elements are incorporated in the oxide film in their most stable oxidation states, i.e. Al2O3 and Nb2O5. The situation with V is less clear: the observed binding energy is in a range where different oxidation states [V(III), V(IV) and V(V)] have been reported [100]. Table XXVI shows the measured binding energies for Ti, Al, Nb and V and their corresponding chemical states.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ti6Al7Nb polished [at%]</th>
<th>Ti6Al7Nb O2 plasma cleaned [at%]</th>
<th>Ti6Al4V polished [at%]</th>
<th>Ti6Al4V O2 plasma cleaned [at%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>19.5 ±0.4</td>
<td>23.1 ±0.2</td>
<td>14.1 ±0.8</td>
<td>25.2 ±0.7</td>
</tr>
<tr>
<td>Al</td>
<td>4.1 ±0.3</td>
<td>4.3 ±0.5</td>
<td>3.9 ±0.4</td>
<td>4.1 ±0.5</td>
</tr>
<tr>
<td>Nb</td>
<td>0.9 ±0.1</td>
<td>1.3 ±0.1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>V *)</td>
<td>—</td>
<td>—</td>
<td>0.2 ±0.1</td>
<td>0.3 ±0.1</td>
</tr>
<tr>
<td>O</td>
<td>52.4 ±0.9</td>
<td>56.7 ±0.8</td>
<td>46.8 ±1.0</td>
<td>59.7 ±0.9</td>
</tr>
<tr>
<td>C</td>
<td>18.3 ±1.0</td>
<td>14.0 ±0.7</td>
<td>30.6 ±2.3</td>
<td>10.3 ±0.9</td>
</tr>
<tr>
<td>N</td>
<td>0.5 ±0.2</td>
<td>0.6 ±0.2</td>
<td>0.4 ±0.1</td>
<td>0.4 ±0.2</td>
</tr>
<tr>
<td>Si</td>
<td>1.4 ±0.3</td>
<td>—</td>
<td>1.1 ±0.3</td>
<td>—</td>
</tr>
<tr>
<td>Ca</td>
<td>1.2 ±0.2</td>
<td>—</td>
<td>1.2 ±0.2</td>
<td>—</td>
</tr>
<tr>
<td>Zn</td>
<td>0.8 ±0.2</td>
<td>—</td>
<td>0.8 ±0.3</td>
<td>—</td>
</tr>
<tr>
<td>Cu</td>
<td>0.6 ±0.2</td>
<td>—</td>
<td>0.6 ±0.2</td>
<td>—</td>
</tr>
<tr>
<td>Pb</td>
<td>0.3 ±0.1</td>
<td>—</td>
<td>0.3 ±0.1</td>
<td>—</td>
</tr>
<tr>
<td>Oxide-layer Thickness [nm]</td>
<td>4.5 ±0.2</td>
<td>5.8 ±0.1</td>
<td>4.4 ±0.2</td>
<td>5.5 ±0.1</td>
</tr>
</tbody>
</table>

*Tab. XXVII: Surface composition (at%) and oxide layer thickness (nm) of Ti6Al7Nb and Ti6Al4V after polishing and the surface-cleaning procedure. Mean values of 5 samples ± standard deviation. *) detected with monochromated excitation radiation.

7. Results and discussion
Low-concentration contaminants such as N, Si, Ca, Zn, Cu and Pb (<1.4 at%) were detected on untreated Ti6Al7Nb and Ti6Al4V surfaces (Table XXVII). After the surface-cleaning procedure, the polished Ti6Al7Nb and Ti6Al4V surfaces showed similar changes as the polished cpTi surface. The cleaned surfaces demonstrated reduced C and increased O and Ti surface concentrations. Si, Ca Zn, Cu and Pb were removed from the surface. However, some traces of N from the nitric acid treatment were still detected.

Sittig et al. [86, 97] reported that on polished and 30% HNO₃ passivated Ti6Al7Nb surfaces the Al concentration (wt%) is increased at the surface, while the concentration of Nb at the surface is similar to that in the bulk. The pickled (pickling bath contains 0.18 M HF and 1.88 M HNO₃, applied at 20°C) Ti6Al7Nb samples showed, on the other hand, a significantly higher amount of Nb at the surface. In the case of Ti6Al4V, the Al surface concentration was higher while the V concentration was lower at the surface as compared to the bulk. Pickling increased the surface concentration of V above that of the polished sample. Scanning Auger Microscopy investigations showed a distribution of Ti, Al and Nb reflecting the bulk microstructure [87]. Therefore, in the case of Ti6Al7Nb and Ti6Al4V, the isoelectric point (IEP) of TiO₂ (IEP is between pH 5 and 7) [59] would be modified by the presence of Al (IEP of Al₂O₃ is about pH 8) [57], Nb (IEP of Nb₂O₅ is about pH 4.5) or V (IEP of V₂O₅ is between 1 and 2.5) [61].

Figure 50 shows a typical positive ToF-SIMS spectrum of a polished and cleaned Ti6Al7Nb surface. The corresponding positive ToF-SIMS spectrum of an untreated, polished surface was similar to that shown for untreated, polished cpTi in Figure 49. Before cleaning, the surface was dominated by common atmospheric contaminants such as C₂H₃⁺, C₂H₅⁺, C₃H₅⁺, C₂H₃O⁺, C₄H₇⁺, C₄H₉⁺. No Nb-fragments were detected. After cleaning, the major peak was Ti⁺ (isotope m/z = 46, 47, 48, 49 and 50). The 49Ti⁺ peak seems to be higher than the theoretically expected peak due to the fact that it is the sum of 49Ti⁺ and 48TiH⁺. All detected Ti-fragments can be found by adding n(TiO₂) to Ti⁺, TiO⁺ or TiO₂H⁺. The alloying elements were also detected as Al⁺, Nb⁺, NbO⁺ and NbO₂⁺. The common atmospheric contaminants were significantly smaller compared to those found on untreated, polished surfaces. The positive ToF-SIMS spectra of surface-cleaned cpTi and Ti6Al4V are comparable. The
same Ti- and Al-fragments were found as on the Ti6Al7Nb surface. In the case of Ti6Al4V, only Al⁺ ions were detected.

![Positive ToF-SIMS spectra of polished and cleaned Ti6Al7Nb surface.](image)

*Fig. 50: Positive ToF-SIMS spectra of polished and cleaned Ti6Al7Nb surface.*

*Figure 51 shows the corresponding negative ToF-SIMS spectra of the polished and cleaned Ti6Al7Nb surface. The titanium oxide fragments can be found by adding...*

7. Results and discussion
n(TiO₂) to TiO₂⁻ or TiO₃H⁻. The alloying elements were also detected as AlO⁻, NbO₂⁻ and NbO₃⁻. The common atmospheric contaminants such as C₂H⁺, C₂OH⁺, CHO₂⁻, C₂H₃O₂⁻, CNO⁻ as well as O⁻, OH⁻, O₂⁻ and Cl⁻ were also detected. The corresponding negative ToF-SIMS spectra of cpTi and Ti₆Al₄V are comparable. However, no V fragments were detected on Ti₆Al₄V.

Fig. 51: Negative ToF-SIMS spectra of polished and cleaned Ti₆Al₇Nb surface.
Table XXVIII lists the major positive fragments of the untreated and cleaned Ti6Al7Nb surface.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Fragments</th>
<th>Untreated Ti6Al7Nb</th>
<th>Cleaned Ti6Al7Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Measured mass [m/z]</td>
<td>Error [ppm]</td>
</tr>
<tr>
<td>15</td>
<td>CH₃⁺</td>
<td>15.0236</td>
<td>-1</td>
</tr>
<tr>
<td>27</td>
<td>Al⁺</td>
<td>26.9835</td>
<td>-74</td>
</tr>
<tr>
<td>27</td>
<td>C₂H₃⁺</td>
<td>27.0235</td>
<td>-2</td>
</tr>
<tr>
<td>28</td>
<td>Si⁺</td>
<td>27.9949</td>
<td>-56</td>
</tr>
<tr>
<td>29</td>
<td>C₂H₅⁺</td>
<td>29.0393</td>
<td>-5</td>
</tr>
<tr>
<td>39</td>
<td>C₃H₇⁺</td>
<td>39.0238</td>
<td>-8</td>
</tr>
<tr>
<td>40</td>
<td>K⁺</td>
<td>39.9635</td>
<td>+12</td>
</tr>
<tr>
<td>41</td>
<td>C₂H₅⁺</td>
<td>41.0392</td>
<td>-3</td>
</tr>
<tr>
<td>43</td>
<td>CH₃Si⁺</td>
<td>42.9980</td>
<td>+8</td>
</tr>
<tr>
<td>43</td>
<td>C₂H₃O⁺</td>
<td>43.0197</td>
<td>-31</td>
</tr>
<tr>
<td>43</td>
<td>C₃H₇⁺</td>
<td>43.0555</td>
<td>-16</td>
</tr>
<tr>
<td>48</td>
<td>Ti⁺</td>
<td>47.9512</td>
<td>-47</td>
</tr>
<tr>
<td>55</td>
<td>C₄H₉⁺</td>
<td>55.0558</td>
<td>-1</td>
</tr>
<tr>
<td>57</td>
<td>C₅H₁₀⁺</td>
<td>57.0719</td>
<td>-17</td>
</tr>
<tr>
<td>64</td>
<td>TiO⁺</td>
<td>63.9450</td>
<td>-14</td>
</tr>
<tr>
<td>73</td>
<td>C₃H₇Si⁺</td>
<td>73.0502</td>
<td>+16</td>
</tr>
<tr>
<td>81</td>
<td>TiO₂H⁺</td>
<td>80.9493</td>
<td>-16</td>
</tr>
<tr>
<td>93</td>
<td>Nb⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td>109</td>
<td>NbO⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td>125</td>
<td>NbO₂⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td>128</td>
<td>Ti₂O₂⁺</td>
<td>127.9043</td>
<td>+8</td>
</tr>
<tr>
<td>147</td>
<td>C₅H₁₃OSi₂⁺</td>
<td>147.0729</td>
<td>+28</td>
</tr>
<tr>
<td>161</td>
<td>Ti₂O₄H⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td>207</td>
<td>C₅H₁₃O₃Si₃⁺</td>
<td>207.0327</td>
<td>+1</td>
</tr>
<tr>
<td>208</td>
<td>Ti₃O₄⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td>224</td>
<td>Ti₃O₅⁺</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7. Results and discussion
### Tab. XXVIII: Positive fragments of the untreated and cleaned Ti6Al7Nb surface.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Fragments</th>
<th>Untreated Ti6Al7Nb</th>
<th>Cleaned Ti6Al7Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Measured mass [m/z]</td>
<td>Error [ppm]</td>
</tr>
<tr>
<td>241</td>
<td>TiO₆H⁺</td>
<td>240.8276</td>
<td>+ 12</td>
</tr>
<tr>
<td>281</td>
<td>C₇H₂₁O₄Si₄</td>
<td>281.0367</td>
<td>25</td>
</tr>
<tr>
<td>288</td>
<td>TiO₆⁺</td>
<td>287.7753</td>
<td>+ 21</td>
</tr>
</tbody>
</table>

### Tab. XXIX: Negative fragments of the untreated and cleaned Ti6Al7Nb surface.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Fragment</th>
<th>Untreated Ti6Al7Nb</th>
<th>Cleaned Ti6Al7Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Measured mass [m/z]</td>
<td>Error [ppm]</td>
</tr>
<tr>
<td>16</td>
<td>O⁻</td>
<td>15.9944</td>
<td>+ 31</td>
</tr>
<tr>
<td>17</td>
<td>OH⁻</td>
<td>17.0023</td>
<td>28</td>
</tr>
<tr>
<td>25</td>
<td>C₂H⁻</td>
<td>25.0081</td>
<td>-10</td>
</tr>
<tr>
<td>32</td>
<td>O₂⁻</td>
<td>31.9896</td>
<td>8</td>
</tr>
<tr>
<td>35</td>
<td>Cl⁻</td>
<td>34.9690</td>
<td>-3</td>
</tr>
<tr>
<td>41</td>
<td>C₂OH⁻</td>
<td>41.0034</td>
<td>-16</td>
</tr>
<tr>
<td>42</td>
<td>CNO⁻</td>
<td>41.9987</td>
<td>-17</td>
</tr>
<tr>
<td>43</td>
<td>AlO⁻</td>
<td>42.9753</td>
<td>-3</td>
</tr>
<tr>
<td>45</td>
<td>CHO₂⁻</td>
<td>44.9981</td>
<td>-9</td>
</tr>
<tr>
<td>60</td>
<td>SiO₂⁻</td>
<td>59.9658</td>
<td>+ 15</td>
</tr>
<tr>
<td>61</td>
<td>SiO₂H⁻</td>
<td>59.9746</td>
<td>+ 13</td>
</tr>
<tr>
<td>80</td>
<td>TiO₂⁻</td>
<td>79.9453</td>
<td>+ 43</td>
</tr>
<tr>
<td>97</td>
<td>TiO₂H⁻</td>
<td>96.9408</td>
<td>+ 12</td>
</tr>
<tr>
<td>125</td>
<td>NbO₂⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>141</td>
<td>NbO₃⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>Ti₉O₄⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>177</td>
<td>Ti₉O₅H⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>257</td>
<td>Ti₉O₆H⁻</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7. Results and discussion
Table XXIX lists the major negative fragments of the untreated and cleaned Ti6Al7Nb surfaces.

In summary, positive and negative ToF-SIMS spectra show a comparatively clean surface with low hydrocarbon contamination. These results qualitatively confirm the corresponding XPS data.

**Surface oxide stoichiometry**

*Figure 52* shows the high-resolution Ti 2p spectrum of a polished and cleaned cpTi surface. The high-resolution spectra of the Ti alloys are comparable. The dominant Ti 2p3/2 peak is at a binding energy of 459.1 eV and can be assigned to Ti (IV) (= TiO2). The weaker peak at 454.1 eV is typical for metallic Ti. The observed chemical shift of 5 eV between the oxide peak and the metal peak agrees well with the expected value for TiO2 and Ti [100, 102, 174, 175]. Furthermore, a shoulder at 457.3 eV is clearly visible and can be assigned to Ti (III) (= Ti2O3) [160, 162-164]. A small peak was generally observed at 455.7 eV. It can be assigned to Ti(II) (= TiO) [174, 176-178].

![Fig. 52: High resolution Ti 2p spectrum of the polished and cleaned cpTi surface.](image)

7. Results and discussion
The deconvolution of the Ti (2p) peak was systematically carried out, based on the components listed in Table XXIV. Whether the lower valence states Ti (III) and Ti (II) are due to defined suboxide phases or to non-stoichiometric defect states of the TiO₂ cannot be determined from XPS measurements. Angle-dependent XPS measurements indicate the presence of a gradiated stoichiometry, with a gradient Ti (IV) – Ti(III) – Ti(II) – Ti(metal), as one moves from the oxide/air interface to the metal substrate [97].

Oxide-layer thickness

The oxide-layer thickness for of the untreated and cleaned, polished surfaces of cpTi and its alloys were calculated according to \textit{equation 10} using the XPS intensity ratio Ti(metal)/Ti(oxide). The reproducibility of the thickness measurement was typically ± 0.1 nm, but the absolute thickness is not exactly known. The oxide-layer thickness was determined to be 4 to 5 nm for polished, non-cleaned cpTi and its alloys and 5 to 6 nm for polished and cleaned samples (see Table XXV and XXVII). If exposed to oxygen plasma, the thickness of the oxide layer increases quickly, growing to about 5.1 nm, 5.8 nm, and 5.5 nm for cpTi, Ti6Al7Nb and Ti6Al4V, respectively, within the first minute (Table XXX).

<table>
<thead>
<tr>
<th>Time of Oxygen Plasma Treatment [min.]</th>
<th>Oxide-layer Thickness of cpTi [nm]</th>
<th>Oxide-layer Thickness of Ti6Al7Nb [nm]</th>
<th>Oxide-layer Thickness of Ti6Al4V [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>4.9 ± 0.1</td>
<td>5.5 ± 0.1</td>
<td>5.3 ± 0.1</td>
</tr>
<tr>
<td>1</td>
<td>5.1 ± 0.1</td>
<td>5.7 ± 0.1</td>
<td>5.5 ± 0.1</td>
</tr>
<tr>
<td>2</td>
<td>5.1 ± 0.1</td>
<td>5.8 ± 0.1</td>
<td>5.5 ± 0.1</td>
</tr>
<tr>
<td>10</td>
<td>5.1 ± 0.1</td>
<td>5.8 ± 0.1</td>
<td>5.5 ± 0.1</td>
</tr>
</tbody>
</table>

\textit{Tab. XXX:} Oxide-layer thickness depends on the time of exposure to the oxygen plasma.
Furthermore, the oxide-layer thickness of cpTi, and Ti6Al7Nb surfaces, which were not treated with oxygen plasma, depends on the time of exposure to air [86, 97]. The evolution of the oxide-layer thickness on polished, not oxygen plasma treated cpTi and Ti6Al7Nb surfaces comply with the generic logarithmic equation due to Uhlig [179], which gives typical rates for the formation of thin passive layers on metal. After one year, an oxide-layer thickness of 5 to 6 nm was measured, comparable to that produced by exposure to the oxygen plasma for one minute.

XPS measurements indicate that the passivation in 30% HNO₃ does not increase the oxide-layer thickness. However, the expected passivation of local defects such as flaws and voids would not be detected by XPS as the percentage of the area affected because it is likely to be much smaller than 1%.

**Sterilisation of cpTi surfaces**

Autoclave sterilisation (180°C, 3h) of polished and cleaned cpTi surfaces increased the hydrocarbon contamination and decreased Ti and O (Table XXXI). The oxide-layer thickness was also slightly increased. Similar results were reported by Keller et al. [180].

<table>
<thead>
<tr>
<th>Element</th>
<th>O₂ Plasma [at%]</th>
<th>Autoclave Sterilisation [at%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>27.8 ± 0.8</td>
<td>23.6 ± 0.5</td>
</tr>
<tr>
<td>O</td>
<td>58.8 ± 1.5</td>
<td>52.7 ± 0.8</td>
</tr>
<tr>
<td>C</td>
<td>12.8 ± 1.8</td>
<td>22.9 ± 1.3</td>
</tr>
<tr>
<td>N</td>
<td>0.6 ± 0.2</td>
<td>0.8 ± 0.3</td>
</tr>
<tr>
<td>O/Ti ratio</td>
<td>2.12 ± 0.04</td>
<td>2.23 ± 0.02</td>
</tr>
<tr>
<td>Oxide-layer thickness [nm]</td>
<td>5.1 ± 0.1</td>
<td>5.4 ± 0.1</td>
</tr>
</tbody>
</table>

Tab. XXXI: Surface composition (at%) and oxide layer thickness (nm) of cpTi after the surface-cleaning procedure and the sterilisation within the autoclave at 180°C for 3h. Mean values of 5 samples ± standard deviation.

7. Results and discussion
7.1.2 Chemical composition of polished CoCrMo surfaces after different cleaning treatment steps

CoCrMo discs were polished as described in section 4.1. After that, the samples were cleaned following the prescription given in section 4.2. The polished samples were packed in Al-foil and sterilised within the autoclave at 180°C for 3h (see section 4.3).

Table XXXII shows the surface composition (at%) of untreated and treated, polished CoCrMo as determined by XPS after polishing and the surface-cleaning procedure. The Co and a component of the O emission intensities are due to the naturally formed CoO layer. The alloying elements are incorporated in the oxide film in their most stable oxidation states, i.e. Cr$_2$O$_3$ and MoO$_3$. The relatively high concentration of C, detected after polishing, is typical for adsorbed organic molecules and is always present on high surface energy oxide films that have been exposed and stored under atmospheric conditions. Low concentrations of Ca and Zn (≤2.5at%), probably due to mechanical polishing, were detected on untreated, polished cpTi surfaces. No Si and N were detected on polished surfaces. After the surface-cleaning procedure, Ca and Zn were removed, and the major part of the oxide-layer was detected as Cr$_2$O$_3$ [17].

<table>
<thead>
<tr>
<th>Element</th>
<th>Polished CoCrMo [at%]</th>
<th>O$_2$ Plasma Cleaned CoCrMo [at%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>10.7 ± 0.2</td>
<td>7.5 ± 0.6</td>
</tr>
<tr>
<td>Cr</td>
<td>5.9 ± 0.5</td>
<td>20.5 ± 0.5</td>
</tr>
<tr>
<td>Mo</td>
<td>0.9 ± 0.1</td>
<td>2.4 ± 0.2</td>
</tr>
<tr>
<td>O</td>
<td>52.9 ± 1.6</td>
<td>53.4 ± 2.2</td>
</tr>
<tr>
<td>C</td>
<td>26.4 ± 1.8</td>
<td>16.2 ± 2.0</td>
</tr>
<tr>
<td>Ca</td>
<td>0.9 ± 0.3</td>
<td>—</td>
</tr>
<tr>
<td>Zn</td>
<td>2.3 ± 0.2</td>
<td>—</td>
</tr>
<tr>
<td>Oxide-layer thickness [nm]</td>
<td>5.0 ± 0.1</td>
<td>5.8 ± 0.1</td>
</tr>
</tbody>
</table>

Tab. XXXII: Surface composition (at%) and oxide-layer thickness (nm) of CoCrMo after polishing and the surface-cleaning procedure. Mean values of 5 samples ± standard deviation.
Table XXXIII summarises the measured binding energies for Co, Cr, and Mo and their corresponding chemical states.

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding Energy [eV]</th>
<th>Chemical State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co (2p3/2)</td>
<td>780.6± 0.2</td>
<td>CoO</td>
</tr>
<tr>
<td>Cr (2p3/2)</td>
<td>574.1 ± 0.2</td>
<td>Cr (III), Cr2O3</td>
</tr>
<tr>
<td>Cr (2p3/2)</td>
<td>576.9 ± 0.2</td>
<td>Cr (metal)</td>
</tr>
<tr>
<td>Cr (2p1/2)</td>
<td>583.3 ± 0.2</td>
<td>Cr (III), Cr2O3</td>
</tr>
<tr>
<td>Cr (2p1/2)</td>
<td>856.7 ± 0.2</td>
<td>Cr (metal)</td>
</tr>
<tr>
<td>Mo (3d5/2)</td>
<td>232.4 ± 0.1</td>
<td>MoO3</td>
</tr>
</tbody>
</table>

Tab. XXXIII: The binding energies of Co, Cr and Mo and their corresponding chemical states. Mean values of 5 samples ± standard deviation.

Figure 53 shows the high-resolution Cr 2p spectrum of a polished and cleaned CoCrMo surface. The dominant Cr 2p3/2 peak was found at a binding energy of 576.9 eV and can be assigned to Cr (III) (= Cr2O3) [100, 181-183]. Furthermore, a shoulder at 574.1 eV is clearly visible and is typical for metallic Cr [100, 184]. The observed chemical shift of 2.8 eV between the oxide peak and the metal peak agrees well with the expected value for Cr2O3 [100]. The deconvolution of the Cr (2p) peak

Fig. 53: High-resolution Cr2O3 2p spectrum of the polished and cleaned CoCrMo surface.

7. Results and discussion
was systematically carried out, based on the components listed in Table XXIII. The oxide-layer thickness was determined to be about 5 nm for polished and untreated and about 5.8 nm for polished and cleaned CoCrMo surfaces (see Table XXXII).

7.1.3 Chemical composition of implant surfaces after blasting, blasting + etching, cpTi plasma spraying and HA plasma spraying

Finely and coarsely blasted cpTi, Ti6Al7Nb, Ti6Al4V and CoCrMo

Discs of cpTi, Ti6Al7Nb, Ti6Al4V and CoCrMo were finely (with glass beads) and coarsely (with alumina particles) blasted as described in section 4.1. Subsequent ultrasonic cleaning was carried out in a commercial detergent (see section 4.2). All finely and coarsely blasted surfaces were sterilised by γ-irradiation (see section 4.3).

Figure 54 to 56 show the XPS results of the finely and coarsely blasted cpTi, Ti6Al7Nb, Ti6Al4V and CoCrMo surfaces after the γ-sterilisation. Si, Na, Ca and Al from the blasting process as well as the contaminants C, and, to some extent, O and N were detected. Compared to the untreated, polished surfaces, Ti and O were decreased and C was increased. The atomic Al and Si concentrations were very high. Furthermore, there were no statistically significant differences for the Al concentration among the coarsely blasted and for the Si concentration among the finely blasted cpTi, Ti6Al7Nb, Ti6Al4V and CoCrMo surfaces, respectively. Nb was only detected on the coarsely blasted surface. In the case of Ti6Al4V, no V could be detected. Figure 57 a and b show the SEM and BSE (backscattered secondary electron) images of the coarsely blasted cpTi surface. In the case of the BSE image, the black areas can be assigned to alumina from the blasting process. In the lower magnification, the BSE image shows a surface largely covered with alumina particles. Similar results were obtained on finely blasted surfaces, which were largely covered with glass beads. Imaging analysis using the software analySIS® Pro 2.11
indicated for both cases, that about 16 – 18 % of the surfaces were covered either by alumina particles or by glass beads.

Fig. 54: Surface composition (at%) of finely blasted cpTi, Ti6Al7Nb and Ti6Al4V. Mean values of 5 samples ± standard deviation.

Fig. 55: Surface composition (at%) of coarsely blasted cpTi, Ti6Al7Nb and Ti6Al4V. Mean values of 5 samples ± standard deviation.
Fig. 56: Surface composition (at%) of finely and coarsely blasted CoCrMo. Mean values of 5 samples ± standard deviation.

Fig. 57a: SEM images of a coarsely blasted Ti6Al7Nb surface.
Fig. 57b: BSE (backscattered secondary electron) images of a coarsely blasted Ti6Al7Nb surface. Black particles can be assigned to alumina from the blasting process.
Coarsely blasted + etched cpTi (SLA) and titanium plasma sprayed cpTi (TPS) surfaces

The coarsely blasted (with alumina particles) + etched cpTi (SLA) as well as the titanium plasma sprayed cpTi (TPS) were surface treated and cleaned as described in section 4.1 and 4.2. After that, the surfaces were packed in Al-foil and sterilised within the autoclave at 180°C for 3h (see section 4.3).

Table XXIV shows the surface composition (at%) of SLA and TPS as determined by XPS after the oxygen plasma treatment. The results are similar to those detected on polished and cleaned cpTi. In the case of SLA the subsequent etching process (HCl/H2SO4) dissolved or removed the particles implanted by the blasting process (see above). However, a small amount of Al was still detected. In the case of TPS, a higher amount of N and Al was also detected. The high resolution N 1s spectrum showed a double peak at the binding energies of 396.9 ± 0.2 eV and 400.8 ± 0.2 eV, which can be assigned to TiN (nitride) and N contamination, respectively [100]. The amount of N contamination is about 0.4 ± 0.2 at%. The detected Al was probably due to the alumina blasting process (see also Figure 58).

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding Energy [eV]</th>
<th>SLA [at%]</th>
<th>TPS [at%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>459.1 ± 0.2</td>
<td>27.3 ± 0.8</td>
<td>25.8 ± 0.6</td>
</tr>
<tr>
<td>O</td>
<td>530.6 ± 0.1</td>
<td>58.9 ± 0.7</td>
<td>56.5 ± 0.7</td>
</tr>
<tr>
<td>C</td>
<td>285.6 ± 0.2</td>
<td>13.5 ± 0.5</td>
<td>12.4 ± 0.4</td>
</tr>
<tr>
<td>N</td>
<td>396.9 ± 0.2</td>
<td>—</td>
<td>2.0 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>400.8 ± 0.2</td>
<td>—</td>
<td>0.4 ± 0.2</td>
</tr>
<tr>
<td>Al</td>
<td>74.8 ± 0.3</td>
<td>0.3 ± 0.1</td>
<td>2.9 ± 0.8</td>
</tr>
</tbody>
</table>

Tab. XXXIV: Binding energies (eV) and surface composition (at%) of SLA (blasted + etched cpTi) SLA and TPS (titanium plasma sprayed cpTi) after oxygen plasma cleaning. Mean values of 5 samples ± standard deviation.

7. Results and discussion
Figure 58 show the SEM and BSE images of TPS. The cracks in the coating layer are typical of the plasma-spray process. The black particle visible in the BSE image can be assigned to alumina from the blasting process, which preceded the plasma sprayed process.

Fig. 58: a) SEM and b) BSE images of a TPS.
Air plasma sprayed (APS) hydroxyapatite (HA)

Air-plasma-sprayed (APS) hydroxyapatite (HA) was produced as described in section 4.1. Then, the surfaces were packed in Al-foil and sterilised by $\gamma$-irradiation with 30 kGy (see section 4.3).

Table XXXV shows the XPS results of the HA surface after the sterilisation. The XPS spectrum is dominated by O, Ca and P. Also the common atmospheric contaminants C and, in some extent, O were detected. The atomic ratio of Ca/P is about 1.59, close to the theoretical ratio of 1.67 for pure HA [28].

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding Energy [eV]</th>
<th>Surface Composition [at%]</th>
<th>Ca / P ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>530.5 ± 0.2</td>
<td>48.17 ± 0.38</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>284.1 ± 0.2</td>
<td>21.99 ± 0.94</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>132.5 ± 0.2</td>
<td>11.49 ± 0.28</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>346.5 ± 0.2</td>
<td>18.34 ± 0.29</td>
<td>1.59 ± 0.03</td>
</tr>
</tbody>
</table>

Tab. XXXV: Binding energy (eV), surface composition (at%) and atomic ratio Ca/P of air plasma sprayed HA. Mean values of 5 samples ± standard deviation.
7.2 Topographical characterisation of the implant surfaces

The topographical characterisations of the implant surfaces were carried out with a mechanical stylus, a non-contact laser profilometer (LPM), an interference microscope (IM) and the method of stereo-SEM. The different methods, together with their advantages and limitations, were described in Chapter 5. To compare the performances of the different instruments, an amplitude-wavelength plot is drawn in Figure 59. The two axes represent the resolution (line closer to the origin) and the range (line further away from the origin) of the instruments both in vertical and lateral directions. Each block in the figure indicates the working area of the used instrument. From any working point in the area vertically and horizontally, the resolutions and working ranges at this working point are given.

In order to be able to compare surface roughness values obtained with different instruments it must be ensured that the measurements cover the same spatial wavelength domain. Furthermore, the same filter and cut-off wavelength have to be applied on the profiles and areas for all roughness calculations, independent of the instrument used. The cut-off, which has to be chosen, will be given by the
measurement with the largest working area. Otherwise, part of the roughness may be lost. Therefore, in my thesis, all roughness parameters discussed in the following sections, were calculated with a Gauss filter and an attenuation factor of 50% at the cut-off wavelength, $\lambda_c$, of 0.58 mm (for all coarsely blasted, etched, structured + etched, SLA, TPS and HA surface) and 0.29 mm (for all polished and finely blasted surfaces), respectively, obtained from the LPM measurements. In the case of LPM, profiles were measured with a resolution of 1000 points/mm over a distance of 4.096 mm (see Table XV) for all coarsely blasted, etched, structured + etched, SLA, TPS and HA surfaces and 2.048 mm for the finely blasted and polished surfaces. Then, the cut-off was set at 1/7 of the scan length according to norm DIN 4678 [117]. However, the chosen measurement conditions for LPM measurements were different to those defined in DIN 4678 [117]. Consequently, the cut-off wavelengths had to be different as well. A comparison of the roughness values obtained according DIN 4678 [117] and under our specific conditions will be discussed in the sections 7.2.3 and 7.2.4. The cut-off wavelengths 0.58 mm and 0.29 mm were also applied to the profiles and areas determined with the IM and stereo-SEM method.

Before experimental roughness values recorded with the different instruments were compared, the height calibration of each technique was checked using a calibration sample (Rauhnormal RNDH3 Serie. Nr.: 0325) produced by Thyssen Hommelwerke GmbH (German calibration service), Germany. This standard is a micromachined steel surface with the following characteristic roughness parameters: $R_{\text{max}} = 9.99 \mu m$, $R_{z,\text{DIN}} = 9.87 \mu m$ and $R_a = 3.049 \mu m$, based on a cut-off of 0.8 mm. The obtained data from the different instruments fit the characteristic data of the calibration surface within the experimental errors. LPM measurements indicated a $R_{\text{max}} = 10.81 \mu m$, $R_{z,\text{DIN}} = 10.39 \mu m$ and $R_a = 3.10 \mu m$ whereas IM measurements indicated a $R_{\text{max}} = 10.41 \mu m$, $R_{z,\text{DIN}} = 10.28 \mu m$ and $R_a = 3.03 \mu m$.
7.2.1 Comparison of mechanical stylus and non-contact laser profilometry

In this section, topographies of polished, finely blasted and coarsely blasted Ti6Al7Nb, Ti6Al4V and CoCrMo, as well as TPS surfaces, were investigated using a mechanical stylus profilometer and a non-contact laser profilometer (LPM). For all surfaces, area measurements were done over a 0.5 mm x 0.5 mm square with both instruments. In the case of the mechanical stylus, the resolutions of 2 µm and 4 µm in the X- and Y- directions were chosen. In the case of LPM, the resolution in the X- and Y- directions was 2 µm (as described in sections 5.3.2 and 5.4.2). To compare the roughness obtained by the two methods, the same areas were measured. Figure 60 shows the surface topography of TPS obtained by the mechanical stylus method as well as by LPM. The topography determined with the mechanical stylus seems to be smoother, due to the contacting envelope [115] caused by the stylus tip (see also section 5.3.1).

The integral 3-D roughness values were calculated with the software provided by UBM with a Gaussian filter and an attenuation factor of 50% at the cut-off wavelength in X- and Y-directions of 0.58 µm for coarsely blasted and TPS surfaces and 0.29 µm for polished and finely blasted surfaces (see sections 5.3.2 and 5.4.2).
Fig. 60: Surface topography of the same area of TPS obtained by a) mechanical stylus and b) non-contact laser profilometer (LPM).

Table XXXVI summarises the calculated integral 3-D roughness values. For TPS as well as coarsely blasted and finely blasted surfaces, the amplitude roughness values $R_a$, $R_q$, $R_t$ and $R_{2DIN}$ as well as the relative area $L_r$ calculated from the LPM data are higher than those calculated from the stylus data, because the LPM has an optically induced artefact signal caused by steep local slopes in the surface being measured [111-114, 120]. A minor effect has the higher lateral and vertical resolutions. The false signal obtained at these steps can exceed several microns in height. More artefacts occur if steep local slopes are located at sharp edges as has been found on finely blasted or coarsely blasted surfaces (see Figure 57a). Fewer artefacts are detected (compare Figure 60b and 61b) on porous surfaces with rounded features, such as TPS (see Figure 58a). On the other hand, the mechanical stylus technique has limitations in the measurement of the height of features on porous surfaces. In the case of TPS, the $R_a$ and $R_q$ values were similar, calculated from LPM and stylus data. In general, the integral 2-D and 3-D roughness values calculated from the stylus data tend to be low because of the envelope effect. For all polished surfaces, the roughness values were similar, calculated from LPM and mechanical stylus data, except the skewness, $S_k$, and the curtosis, $K$, of the profiles. The skewness, $S_k$, is
the amplitude distribution skew. Sk is zero when the amplitude distribution is symmetrical. It is not zero when the profile amplitudes as well as the amplitude density curve are asymmetric, e.g. profiles with "plateaus" and single deep valleys have a negative skew, profiles with very intense peaks have a positive skew. The curtosis is the comparison of the profile curve with Gaussian amplitude and characterises the density as "smooth" or "with peaks". The Gaussian amplitude density curve has a curtosis of $K = 3$, smoother profiles have a $K < 3$, steeper profiles have a $K > 3$.

Fig. 61: Surface topography of the same area of the coarsely blasted Ti6Al4V obtained by a) mechanical stylus and b) non-contact laser profilometer (LPM).
<table>
<thead>
<tr>
<th>Surface and Method</th>
<th>R_a</th>
<th>R_q</th>
<th>R_t</th>
<th>R_{Z100}</th>
<th>S_k</th>
<th>K</th>
<th>L_r</th>
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<tr>
<td>TPS</td>
<td>7.17</td>
<td>8.36</td>
<td>24.10</td>
<td>11.84</td>
<td>0.20</td>
<td>1.66</td>
<td>1.17</td>
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<td>7.13</td>
<td>8.95</td>
<td>41.67</td>
<td>21.57</td>
<td>0.26</td>
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<td>1.93</td>
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<tr>
<td>c.b. Ti6Al7Nb</td>
<td>2.66</td>
<td>3.22</td>
<td>14.67</td>
<td>7.42</td>
<td>-0.082</td>
<td>0.53</td>
<td>1.11</td>
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<tr>
<td>Mech. Stylus</td>
<td>4.48</td>
<td>5.69</td>
<td>22.63</td>
<td>10.68</td>
<td>-1.06</td>
<td>37.02</td>
<td>1.72</td>
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</tr>
<tr>
<td>c.b. Ti6Al4V</td>
<td>2.05</td>
<td>2.43</td>
<td>10.16</td>
<td>5.56</td>
<td>-0.76</td>
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<td>1.09</td>
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<td>4.96</td>
<td>22.90</td>
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<td>6.35</td>
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<tr>
<td>c.b. CoCrMo</td>
<td>2.70</td>
<td>3.38</td>
<td>14.06</td>
<td>8.08</td>
<td>0.12</td>
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<tr>
<td>f.b. Ti6Al7Nb</td>
<td>0.84</td>
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<td>f.b. CoCrMo</td>
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<td>0.58</td>
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<td>1.77</td>
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<td>59.34</td>
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<td>0.90</td>
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<td>0.04</td>
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<td>254.95</td>
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<td>4.67</td>
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<tr>
<td>pol. CoCrMo</td>
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<td>0.03</td>
<td>0.14</td>
<td>0.09</td>
<td>-0.03</td>
<td>3.10</td>
<td>1.00</td>
</tr>
<tr>
<td>Mech. Stylus</td>
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<td>0.02</td>
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<td>0.07</td>
<td>-5.99</td>
<td>353.43</td>
<td>1.00</td>
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</table>

Table XXXVI: List of the 3-D surface integral amplitude roughness values of the same surface areas obtained with the mechanical stylus method and the LPM. A Gaussian filter and an attenuation factor of 50% at the cut-off wavelength in X- and Y-directions of 0.58 μm for coarsely blasted and TPS surfaces and 0.29 μm for polished and finely blasted surfaces were chosen.

The values for skewness (S_k) of each surface showed the same symmetry of the areas, calculated from LPM and mechanical stylus data, even though the skewness is dependent on the amplitude of the profiles and therefore on the artefacts of the

7. Results and discussion
laser. However, measurements of curtosis (K) is much more dependent on the amplitude (see definition in section 6.1), and therefore more sensitive to artefacts. In particular for LPM measurements, the results of the curtosis should be carefully interpreted.

In summary, mechanical stylus and LPM yield similar topography parameters for polished surfaces. However, in the case of finely and coarsely blasted and plasma sprayed surfaces, the integral 2-D and 3-D roughness values calculated from the stylus data were probably too low, because of the envelope effect [111, 114, 115]. On the other hand, LPM measurements of such surfaces often show optically induced artefact signals caused by steep local slopes in the surface, which can exceed several microns in height [111-114, 120]. Furthermore, in both cases, the lateral resolution was not high enough to detect small topographical features of less than 1 μm. Therefore, in the next section a comparison of non-contact Laser profilometry (LPM), interference microscopy (IM), stereo-SEM and atomic force microscopy (AFM) will be discussed.

7.2.2 Comparison of non-contact laser profilometry (LPM), interference microscopy (IM), stereo-SEM and atomic force microscopy (AFM)

In this section, topographies of alumina particle blasted + etched (SLA) and structured + etched cpTi surfaces (see section 4.1) were investigated using non-contact laser profilometry (LPM), interference microscopy (IM) and stereo-SEM. Figures 62 and 63 show the SLA as well as the structured + etched surfaces obtained by LPM, IM and SEM. The same areas of about 100 μm x 77 μm were investigated. The LPM measurements were performed with a resolution of 1 μm and 2 μm in X- and Y-direction, respectively. The surface topographies obtained by IM were measured with a 50x objective with a resolution of 0.4 μm. Stereo-SEM images were obtained by tilting the object by ± 3° out of the initial position.

7. Results and discussion
Fig 62: a) SEM-, b) interference microscope- (IM) and c) non-contact laser profilometer (LPM) images of the same area of the SLA surface.
Fig. 63: SEM-, interference microscope- (IM) and non-contact laser profilometer (LPM) images of the same area of the structured + etched surface.
In comparison, SEM images (Figures 62a and 63a) show topographical features such as edges, pits and holes more clearly and give a better three-dimensional impression than the IM or LPM images (Figures 62b-c and 63b-c). In the case of SLA, two parts of topography contributions are visible in the SEM: one in the range of 20 – 40 \( \mu \text{m} \) (produced by the alumina blasting process and the subsequent removal of the alumina particles by the acid etching process), and the other in the range of about 0.5 - 2 \( \mu \text{m} \) (produced by the acid etching process). In the case of the structured etched surface, there are also two parts of topography contribution: one from the pits (30 \( \mu \text{m} \) in diameter) produced by electrochemical micromachining [96] (see chapter 4), and the other in the range of about 0.5 - 2 \( \mu \text{m} \) (produced by the acid etching process). IM and LPM images can easily be viewed computationally as 3-D plots. 2-D and 3-D roughness calculations are feasible, although 3-D LPM measurements require extensive data acquisition time (typically two hours for an area measurement of 500 x 500 \( \mu \text{m} \) square with a resolution of 2 \( \mu \text{m} \) in each direction) to scan images and to calculate 3-D roughness parameters. The stereo-SEM images were obtained computationally by a parallax calculation using analySIS\textsuperscript{\textregistered} Pro software as discussed in section 5.6.2. The computational time for the profile calculations is approximately one minute.
Fig. 64: 3-D images of the same area of the structured + etched surface using a) stereo-SEM, b) interference microscope (IM) and non-contact laser profilometer (LPM).
Figure 64 shows the reconstructed stereo-SEM image of the structured + etched surface (Figure 64a) as well as the corresponding three-dimensional plots of the IM and LPM image (Figure 64b and 64c).

Table XXXVII lists the corresponding integral amplitude 3-D roughness parameters $R_a$, $R_q$, and $R_t$ of the SLA and the structured + etched surface obtained with IM as well as with LPM and calculated with the provided software WYKO Vision 32 version 2.000 and UMB version 1.5, respectively. With the stereo-SEM method, only 2-D profiles can be calculated as discussed in section 5.6.2.

<table>
<thead>
<tr>
<th>Surface Topography</th>
<th>Interference Microscope (IM)</th>
<th>Non-contact Laser profilometry (LPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_a$ [µm]</td>
<td>$R_q$ [µm]</td>
</tr>
<tr>
<td>SLA</td>
<td>4.22</td>
<td>5.41</td>
</tr>
<tr>
<td>structured + etched</td>
<td>4.24</td>
<td>4.87</td>
</tr>
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</table>

Tab. XXXVII: List of the 3-D surface integral amplitude roughness values $R_a$, $R_q$ and $R_t$ of the same surface areas obtained with the IM as well as with the LPM

IM versus LPM give similar $R_a$ and $R_q$ values for the structured + etched surface, but differ for the SLA surface. For both the SLA and structured + etched surface, $R_t$ differed between the two methods. The differences resulted from the different lateral and vertical resolution of the two methods, as well as the roughness calculation procedures of the two software packages (see also Table XXXVIII).

To perform a more appropriate comparison between LPM, IM and stereo-SEM measurements, the same profiles of the SLA as well as of the structured + etched surface were selected from the three-dimensional data set determined with the three methods. The profiles are shown in Figures 65. The shapes of all profiles were very similar, although the profiles obtained from the stereo-SEM (Figure 65c) showed many more features than those from LPM and IM (Figures 65a and b), an observation that was subjectively evident in Figures 62 and 63.
A quantitative description of the profiles shown in Figures 65 is given by the calculated integral 2-D roughness parameters in Table XXXVIII. The roughness values were calculated as outlined in sections 5.4.2, 5.5.2 and 5.6.2.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>SLA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IM ¹)</td>
</tr>
<tr>
<td>Ra [µm]</td>
<td>6.22</td>
</tr>
<tr>
<td>Rq [µm]</td>
<td>7.51</td>
</tr>
<tr>
<td>Rt [µm]</td>
<td>29.48</td>
</tr>
<tr>
<td>RzDIN [µm]</td>
<td>---</td>
</tr>
<tr>
<td>Sm [mm]</td>
<td>---</td>
</tr>
<tr>
<td>Sk</td>
<td>---</td>
</tr>
<tr>
<td>K</td>
<td>---</td>
</tr>
<tr>
<td>Lr</td>
<td>---</td>
</tr>
<tr>
<td>Rpk [µm]</td>
<td>---</td>
</tr>
<tr>
<td>Rk [µm]</td>
<td>---</td>
</tr>
<tr>
<td>Rvk [µm]</td>
<td>---</td>
</tr>
<tr>
<td>Mn(%)</td>
<td>---</td>
</tr>
<tr>
<td>Mr2(%)</td>
<td>---</td>
</tr>
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</table>

<table>
<thead>
<tr>
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<th>structured + etched</th>
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<tr>
<td>K</td>
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<td>Lr</td>
<td>---</td>
</tr>
<tr>
<td>Rpk [µm]</td>
<td>---</td>
</tr>
<tr>
<td>Rk [µm]</td>
<td>---</td>
</tr>
<tr>
<td>Rvk [µm]</td>
<td>---</td>
</tr>
<tr>
<td>Mn(%)</td>
<td>---</td>
</tr>
<tr>
<td>Mr2(%)</td>
<td>---</td>
</tr>
</tbody>
</table>

Tab. XXXVIII: Integral 2-D roughness values of SLA and structured + etched profiles. ¹) IM profiles calculated with the WYKO Vision 32 software ²) IM profiles calculated with the UBM software ³) Stereo-SEM profiles calculated with the UBM software ⁴) LPM profiles calculated with the UBM software.
Differences in the integral roughness values were found between the same profiles for the three topographic measurement techniques. These differences result from the different software calculations and characteristics of the instruments. For example, the same SLA and structured + etched profiles determined with the IM were calculated by the WYKO Vision 32 software and the UBM software. The results were quite different in some aspects. If the data from the stereo-SEM and IM profiles of SLA profiles were processed with the UBM software, they yielded similar amplitude, spacing and hybrid roughness values. Also the calculated bearing ratio curves (see section 6.1) characterised by $R_{pk}$, $R_k$, $R_{pk}$, $M_{11}$, and $M_{12}$ were similar. Nevertheless, even when using the same software and calculation parameters, some differences remained because of instrumental effects. In particular the highest $R_t$ and $K$ values for the LPM profiles are related to artefacts of the laser as discussed in section 7.2.1. Also $R_{pk}$ and $R_{pk}$ and consequently $M_{11}$ and $M_{12}$ are dependent on the amplitude of the profiles and therefore on artefacts of the laser as shown in case of the structured + etched surface. However, the bearing ratio curve showed no dependence on the lateral resolution. Because according to its definition, the bearing ratio curve has been influenced by the height distribution of the profile (see definition in section 6.1). On the other hand, the stereo-SEM approach, which has the highest lateral resolution, yielded longer $L_r$ values than the IM and LPM methods. Because the lateral resolution (or sampling length) acts as a kind of averaging filter and has a direct influence on the relative length of a profile or an area. Figure 66 illustrates this effect: a) detail of the stereo-SEM profile of the SLA with a lateral resolution of 0.064 μm (shown in Figure 65) has been compared with b) that of the LPM profile with a lateral resolution of 1 μm and c) the stereo-SEM profile after a 16-point average filter has been applied. The dependence of integral roughness parameters on artefacts [111-115, 120], lateral and vertical resolution [111, 114, 142, 144-147] as well as the calculation parameters such as filter, attenuation factor, cut-off settings and calculation length [113, 142, 146, 185] had also been noted previously.

7. Results and discussion
Fig. 66: Lateral resolution (or sampling length) acts as a kind of averaging filter: a) detail of the stereo-SEM profile of the SLA (shown in Figure 64) compared with b) that of the LPM profile and c) the stereo-SEM profile after a 16-point average filter has been applied on.
Despite these sources of error and the limitation in characterisation of topographies with integral roughness parameters, the results of all methods are comparable. The accuracy obtained from the different topographic measurement techniques can be determined by comparison of the structured + etched surface whose controlled dimensions before etching were obtained by electrochemical micromachining [96]. The heights and diameters of the holes of this surface, expressed by the roughness parameters $R_t$ and $S_m$, were calculated for profiles obtained from the three methods using UBM software and were found ($R_t = 14.9 \mu m$ to $18.8 \mu m$; $S_m = 32$ to $34 \mu m$) to be in the expected ranges given that the height and diameter of the holes before etching were $15 \mu m$ and $30 \mu m$, respectively. That means that the IM as well as the stereo-SEM method can be used as complementary methods to the LPM. Whereas LPM is used to measure the topographies in the range of a few micron to milimeter, the IM has its particular merits for measuring topography features in the range of 0.5 to 300 $\mu m$ and the stereo-SEM method in the range of around 50 nm to 100 $\mu m$.

AFM studies showed that SLA and the structured + etched surface had a height distribution that was too large for AFM measurements. For example Figure 67 shows an AFM scan of the SLA surface over an area of 141.6 x 141.6 $\mu m$ square. The true surface is strongly distorted due to limitations in Z-direction and tip envelope effects. Therefore, no more AFM studies were performed on such surfaces.

However, independent of the instrument used, the smaller topography contribution in the range of about 2 $\mu m$ (produced by the etching step), could not be sufficiently characterised with the integral roughness parameters for both the SLA and the structured + etched surface, although the lateral and vertical resolutions of IM and stereo-SEM are high enough to determine these features. For example, the $S_m$ values of 0.026 to 0.028 $\mu m$ and 0.023 to 0.034 $\mu m$ or the $R_t$ values of 12.54 to 16.56 $\mu m$ and 14.93 to 18.84 $\mu m$ for SLA and the structured + etched surface, respectively, did not characterise sufficiently reflect the structure in this scale range. In the case of SLA, these values characterised the topography contribution produced by the alumina blasting process and the subsequently removal of the alumina particles by the etching process. In the case of the structured + etched surface, the values of $S_m$ and $R_t$ characterised the pits produced by the electrochemical micromachining. Therefore, another method has to be used for the evaluation and
calculation of surface topographies. In the next section, the wavelength-dependent roughness evaluation will be demonstrated as a possible method to characterise small surface features independent of the rougher component.

Fig. 67: AFM image of SLA. The height distribution of that surface is too large for AFM studies. Some parts of the surface were too deep to be measured.

7.2.3 Wavelength-dependent roughness evaluation of alumina particles blasted, etched and blasted + etched (SLA) cpTi surfaces

The SLA surface was investigated to illustrate the effect on cpTi surfaces of two consecutive surface-structuring processes resembling those used in some dental implants, and which are known to lead to particularly effective bone integration and implant stability [5-7, 9]. In this sequence, the titanium surface is first treated by particle-blasting with alumina beads, followed by a chemical etch process with a hot solution of HCl/H₂SO₄ for several minutes that removes the alumina particles and superimposes an appr. 10 to 20-times finer structure on top of the blasted surface (see also section 4.1). The result is a topography with two characteristic contributions
in the range of 20 – 40 μm (produced by the blasting and the adjacent removing of the particles in the etching process) and the range of about 0.5 - 2 μm (produced by the etching process). The stereo-SEM images in Figure 68 illustrate these two ranges.

Fig. 68: The blasting and etching processes of SLA result in a topography with two characteristic contributions in the range of a) 20 – 40 μm and b) about 0.5 - 2 μm as shown in the stereo-SEM images.
Following surface treatment, seven random 2-D profiles of blasted (with alumina particles), etched and SLA surfaces were measured with the LPM according to DIN4768 (section 5.4.2). Figure 69 shows the SEM images of each surface type together with part of their 2-D LPM profiles. No major differences are immediately evident between the blasted and SLA profiles. However the standard integral roughness values $R_a$ and $R_q$ of the two surfaces are different.

Fig. 69: SEM images of the blasted (with alumina particles), the etched and SLA surface and part of their 2-D LPM profiles.

7. Results and discussion
<table>
<thead>
<tr>
<th>Type of cpTi Surface</th>
<th>Roughness Parameters</th>
<th>Roughness Values (Standard Norm DIN4768)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Blasted</strong></td>
<td>( R_a ) [( \mu \text{m} )]</td>
<td>4.40 ± 0.18</td>
</tr>
<tr>
<td></td>
<td>( R_q ) [( \mu \text{m} )]</td>
<td>5.66 ± 0.23</td>
</tr>
<tr>
<td></td>
<td>( R_l ) [( \mu \text{m} )]</td>
<td>46.65 ± 5.01</td>
</tr>
<tr>
<td></td>
<td>( R_{z_{\text{DIN}}} ) [( \mu \text{m} )]</td>
<td>33.97 ± 1.70</td>
</tr>
<tr>
<td></td>
<td>( S_m ) [( \text{mm} )]</td>
<td>0.070 ± 0.004</td>
</tr>
<tr>
<td></td>
<td>( S_k )</td>
<td>-0.29 ± 0.20</td>
</tr>
<tr>
<td></td>
<td>( K )</td>
<td>4.03 ± 0.62</td>
</tr>
<tr>
<td></td>
<td>( L_r )</td>
<td>1.16 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>( R_{pk} ) [( \mu \text{m} )]</td>
<td>5.10 ± 0.81</td>
</tr>
<tr>
<td></td>
<td>( R_{vk} ) [( \mu \text{m} )]</td>
<td>6.70 ± 0.70</td>
</tr>
<tr>
<td></td>
<td>( R_k ) [( \mu \text{m} )]</td>
<td>5.38 ± 0.23</td>
</tr>
<tr>
<td></td>
<td>( M_{11} ) [%]</td>
<td>9.60 ± 1.32</td>
</tr>
<tr>
<td></td>
<td>( M_{12} ) [%]</td>
<td>87.76 ± 1.50</td>
</tr>
<tr>
<td><strong>Etched</strong></td>
<td>( R_a ) [( \mu \text{m} )]</td>
<td>0.96 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>( R_q ) [( \mu \text{m} )]</td>
<td>1.22 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>( R_l ) [( \mu \text{m} )]</td>
<td>9.01 ± 0.61</td>
</tr>
<tr>
<td></td>
<td>( R_{z_{\text{DIN}}} ) [( \mu \text{m} )]</td>
<td>7.90 ± 0.29</td>
</tr>
<tr>
<td></td>
<td>( S_m ) [( \text{mm} )]</td>
<td>0.013 ± 0.000</td>
</tr>
<tr>
<td></td>
<td>( S_k )</td>
<td>-0.16 ± 0.08</td>
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<td></td>
<td>( K )</td>
<td>3.47 ± 0.15</td>
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<tr>
<td></td>
<td>( L_r )</td>
<td>1.26 ± 0.01</td>
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<tr>
<td></td>
<td>( R_{pk} ) [( \mu \text{m} )]</td>
<td>1.16 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>( R_{vk} ) [( \mu \text{m} )]</td>
<td>1.33 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>( R_k ) [( \mu \text{m} )]</td>
<td>1.14 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>( M_{11} ) [%]</td>
<td>9.43 ± 0.50</td>
</tr>
<tr>
<td></td>
<td>( M_{12} ) [%]</td>
<td>88.48 ± 0.93</td>
</tr>
<tr>
<td><strong>SLA</strong></td>
<td>( R_a ) [( \mu \text{m} )]</td>
<td>5.50 ± 0.30</td>
</tr>
<tr>
<td></td>
<td>( R_q ) [( \mu \text{m} )]</td>
<td>6.91 ± 0.39</td>
</tr>
<tr>
<td></td>
<td>( R_l ) [( \mu \text{m} )]</td>
<td>44.99 ± 2.55</td>
</tr>
<tr>
<td></td>
<td>( R_{z_{\text{DIN}}} ) [( \mu \text{m} )]</td>
<td>36.70 ± 1.63</td>
</tr>
<tr>
<td></td>
<td>( S_m ) [( \text{mm} )]</td>
<td>0.075 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>( S_k )</td>
<td>-0.14 ± 0.17</td>
</tr>
<tr>
<td></td>
<td>( K )</td>
<td>3.12 ± 0.25</td>
</tr>
<tr>
<td></td>
<td>( L_r )</td>
<td>1.17 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>( R_{pk} ) [( \mu \text{m} )]</td>
<td>6.14 ± 0.53</td>
</tr>
<tr>
<td></td>
<td>( R_{vk} ) [( \mu \text{m} )]</td>
<td>7.17 ± 1.09</td>
</tr>
<tr>
<td></td>
<td>( R_k ) [( \mu \text{m} )]</td>
<td>7.19 ± 0.56</td>
</tr>
<tr>
<td></td>
<td>( M_{11} ) [%]</td>
<td>8.86 ± 0.89</td>
</tr>
<tr>
<td></td>
<td>( M_{12} ) [%]</td>
<td>89.19 ± 2.11</td>
</tr>
</tbody>
</table>

**Tab XXXIX:** List of the integral roughness values from 2-D LPM profiles of the blasted, etched and SLA surface calculated according to norm DIN 4768 (n=7 for each surface; mean values ± standard deviations).
Table XXXIX summarises the results of the integral roughness values for the three surfaces. No differences could be observed for the integral roughness values $R_t$, $R_{zdIN}$, $S_m$, $S_k$, $K$, $L_r$ as well as $R_{pk}$ and $R_{vk}$ and consequently $M_{r1}$ and $M_{r2}$ between the blasted and SLA surfaces, although in particular the mean groove distance $S_m$ is visibly different in the SEM images. The reason for this finding is that the LPM method has a lateral resolution of 2 μm that is in the same range as the fine structure produced by the etching is. Therefore, fine structures smaller than 2 μm could not be effectively measured with LPM. An effect of the etching process of the blasted surface was probably indicated by $R_a$ and $R_q$. Except for the roughness parameter $S_k$, $K$, $M_{r1}$ and $M_{r2}$, all roughness values for the etched surface are different to those of the blasted and SLA surfaces.

In summary, an additive effect for the etching treatment of the blasted surface could be observed for the amplitude parameters $R_a$ and $R_q$ as well as for the bearing ratio curve (see Figure 70), but not for $R_l$ and $R_{zdIN}$, the spacing parameter $S_m$ and the hybrid parameters $S_k$ and $L_r$. However, the standard integral roughness parameters,

7. Results and discussion
obtained from LPM profiles according to DIN 4768, were of limited value for the
description of the blasted, etched and SLA surface as well as the influence of the
etching process on the blasted surface because the fine roughness features,
measured in the low micron and submicron range, were hidden by the coarser
contributions to roughness. Furthermore, features \( \leq 2 \mu m \) could not be measured
with LPM because of the lateral resolution limit of the instrument.

In order to get more specific information on the effect of each treatment step,
the dependence of the roughness \( R_q \) on the profile wavelength was evaluated using
\textit{equation 27 (FFT)} and the high-pass filter (COF) (see sections 6.2 and 6.3). Seven
profiles of each type of surface were measured over a scan length of 4.096 mm with
a resolution of 1 \( \mu m \). The waviness of the LPM profiles was subtracted with a cut-off
of 0.58 \( \mu m \) as discussed in section 5.4.2. \textit{Figure 71 shows} for the blasted, etched
and SLA surfaces both the FFT and COF evaluated averaged curves \( R_q = f (\lambda) \). For
the blasted and etched surfaces, the values of \( R_q \) (calculated by FFT) start at the
standard roughness values and below a wavelength of 0.58 mm (blasted surface)
and about 0.2 mm (etched surface), respectively, steadily decreases with decreasing
wavelength \( \lambda \). The two curves cross each other at a wavelength of 4 \( \mu m \). In the case
of the SLA surface, the curve evaluated with the FFT technique also decreases
below a wavelength of 0.58 mm, starting at the standard roughness value and
crossing the curve of the blasted surface twice at wavelengths of 65 \( \mu m \) and 7.4 \( \mu m \),
respectively. The wavelength-dependent roughness within that window (65.0 and
7.4 \( \mu m \)) shows decreasing \( R_q \) with decreasing \( \lambda \) for SLA surface compared to blasted
surface. The probable explanation is that the etching process removed the alumina
beads from the blasting process and smoothed the sharp edges of the surface at the
same time (\textit{see Figure 69}). Below 7.4 \( \mu m \) there is again an increase of \( R_q \) due to the
superimposed structure produced by the etching process.

For the etched surface the curves of the FFT and the COF technique are very
similar above a wavelength of 30 \( \mu m \). Below this value the COF curve falls stepwise.
In the case of the blasted surface, the two curves are equal above a wavelength of
700 \( \mu m \). Below that value the COF curve steadily decreases to a wavelength of
approximately 90 \( \mu m \) and then falls off stepwise. For the SLA surface the curve
obtained by the COF technique is always lower compared to the curve obtained by

7. \textit{Results and discussion}
the FFT technique and starts to decrease stepwise in the same range as the curve for the blasted surface. The two curves cross each other at a wavelength of approximately 260 μm. Below a wavelength of 10 μm, the COF technique will be uncertain.

**Fig. 71:** Comparison of the dependence of the roughness $R_q$ on the profile wavelength for blasted, etched and SLA surfaces calculated using the FFT (Fast Fourier Transformation) and below COF (high-pass filter) technique ($n = 7$ profiles).
More detailed insight into the influence of each treatment step can be obtained in calculating the transfer functions between the different surfaces as discussed in section 6.4 (see equation 29). The transfer functions were calculated by the ratio of FFT coefficients of the different surfaces after each treatment step. Figure 72a shows

![Graph showing FFT power spectra of different surfaces](image)

**Fig. 72** a) The square of the FFT power spectra of the polished, etched, blasted and SLA surface versus the logarithm of the profile wavelength b) The "multiplicative transfer functions" between the different surface treatment steps.

7. Results and discussion
the square of the FFT power spectrum of the polished, etched, blasted and SLA surfaces and Figure 72b the different transfer functions. There were two first-order transfer functions (SLA/blasted; blasted/polished) and one second-order function (SLA/polished). The first-order transfer functions characterise the effects of each single treatment step, the second order transfer function characterises the effect of the overall surface treatment process.

The alumina particles blasting process increased the amplitude of the contributions to the roughness by a factor of fifty up to a wavelength of 100 μm and by a factor of twenty between 100 μm and 1 mm. The etching of the blasted surface increased the amplitude by a factor of 1.2 up to a wavelength of 6 μm and by a factor of 1.5 between 60 μm and 1 mm. Between 6 μm and 60 μm, there was a reduction of the amplitude by a factor of 0.8, which is already discussed above (see Figure 71).

The total effect of the blasting and etching processes was the multiplication of the two individual first-order transfer functions. Therefore, the blasting and etching process increased the amplitude of the contributions to the roughness by a factor of fifty up to a wavelength of 5 μm, by a factor of forty between 5 μm and 45 μm and by a factor of thirty between 100 μm and 1 mm.

The calculated transfer function is characteristic for a particular surface treatment system such as the system applied for SLA. Within certain limits it is independent of the surface to which it is applied.

Once the transfer function for a system is defined, it can be applied to different starting surfaces to predict the final result. If, on the other hand, the final result is specified, one can define topography limits for the starting surface.

In the present surface treatment system the concept of a simple "multiplicative transfer function" is applied, since, as a first approximation, only a proportional increasing of the roughness is expected. In the more general case for which roughness contributions are added in one or several steps, an "additive term" should be added to the transfer function. This term could be experimentally determined as discussed in section 6.4.

To expand the accessible wavelength range from 3 μm to the submicron range, the three surfaces were also investigated with IM and stereo-SEM. Seven
random 2-D profiles of each surface type were obtained and the waviness subtracted (see sections 5.4.2, 5.5.2 and 5.6.2).

*Figure 73* shows the comparison of the wavelength-dependent roughness evaluation of SLA profiles obtained with LPM, IM and stereo-SEM. Before calculation, the waviness of all profiles was subtracted with a cut-off of 0.58 mm. The averaged curves $R_q = f(\lambda)$ of the profiles of each method always start at the standard roughness values and below a wavelength of 0.58 mm steadily decrease with decreasing wavelength $\lambda$. Between a wavelength of about 40 $\mu$m to 4 $\mu$m, the curves $R_q = f(\lambda)$ of the LPM and IM profiles are congruent. The curves of the IM profiles and the stereo-SEM profiles cross each other at a wavelength of 0.75 $\mu$m. Above 0.75 $\mu$m, the curve of the stereo-SEM profile shows constantly lower wavelength-dependent roughness values compared to the other two. The dramatically decreasing of the roughness values of each curve are due to their instrumental resolution limits, which were in this case 0.19 $\mu$m, 0.4 $\mu$m and 3 $\mu$m for stereo-SEM, IM and LPM, respectively. Of coarse, with a higher magnification, the resolution of the stereo-SEM will increase as shown in *Figure 74* for the etched surface.

![Figure 73: The comparison of the wavelength-dependent roughness evaluation of the SLA surface using seven profiles measured with LPM, IM and stereo-SEM.](image)
Figure 74 compares the averaged curves $R_q = f(\lambda)$ of the blasted, etched and SLA surface obtained from seven LPM and stereo-SEM profiles (IM data not shown). The curves $R_q = f(\lambda)$ evaluated from the LPM profiles have been discussed above (see Figure 71). For the blasted surface obtained with the stereo-SEM, the curve $R_q = f(\lambda)$ starts at the wavelength of 50 \( \mu \)m with a higher value than the SLA surface and decreases with decreasing $\lambda$. Between wavelengths of 10 \( \mu \)m to 4 \( \mu \)m, the curves for the blasted and SLA surfaces are congruent. Below 4 \( \mu \)m the wavelength-dependent roughness demonstrated lower $R_q$ values with decreasing $\lambda$ for the SLA surface compared to the blasted surface. In the case of the etched surface obtained from the stereo-SEM, the curve starts at a wavelength of 50 \( \mu \)m with the same $R_q$ value as evaluated from the LPM profiles. Below 4 \( \mu \)m the curves of the SLA and the etched surface are congruent. That means that in the range below 4 \( \mu \)m only the effects of the etching process are evident on the SLA and etched surface. The resolution limit of the stereo-SEM is related to the magnification. For example the etched surface was determined with a magnification of 2000x, whereas the magnification used on

Fig. 74: The comparison of the dependence of the roughness $R_q$ on the profile wavelength for blasted, etched and SLA surface using seven profiles of each type of surface measured with LPM and stereo-SEM.
SLA and blasted surfaces was 1000x. This study indicates, that the observed structure of the etching is independent on the magnification, otherwise the etched and SLA curve were not be congruent below 4 µm.

The results obtained from the wavelength-dependent roughness evaluation is a useful approach in describing and analysing surface topographies, because it enables the effect of two or more consecutive surface-structuring processes to be investigated and discussed. Furthermore, the results indicated that because of the different working ranges (see Figure 59) and artefacts of the different instruments, more than one method of analysis is needed to characterise rough surfaces. In my thesis, LPM, IM as well as the stereo-SEM method have been used to characterise the total surface topography from the macrometer- to the nanometer-range. In the case of LPM and IM, 2-D and 3-D topographical data were obtained, whereas with the stereo-SEM method only 2-D data could be calculated, because of the height calculation based on the X-shift (see section 5.5.6.2).

7.2.4 Window-roughness evaluation of implant surfaces

As discussed above, the standard roughness parameter sets are of very limited value in describing the complex surface structures present on surface-treated titanium implants, since the surfaces often show a variety of topographical features in different dimensional ranges that are all believed to be relevant to the interaction of the surface with biomolecules such as proteins, with cells and with tissue [42]. For example, atomic defects and surface roughness on the nanometer scale may interact with functional groups in proteins. At the macroscopic end of the scale range, surface irregularities or deliberately produced structures on the 10 mm scale, may influence the behaviour of cells and mechanical effects on tissue interactions [72]. Since there exists biological structural elements at all length scales in the range < 1 nm to 0.1 mm, it seems reasonable to assume that biomaterial surface structures in the same dimensionality range may be important for the overall interaction between
cells/tissue and biomaterial surfaces [42]. The window roughness concept, discussed in section 6.3.3, is a useful approach for the calculation of amplitude, spacing as well as hybrid parameters in different wavelength ranges.

Seven profiles of each implant surface investigated in my thesis were measured with the LPM. In addition, the blasted, etched and SLA cpTi surfaces were also investigated using IM and stereo-SEM. The measuring conditions and data processing for the waviness subtraction and window roughness evaluation are described in chapter 5. The seven profiles of each type of surface were FFT-transformed and again inverse transformed with iFFT in wavelength ranges of interest as discussed in section 6.3.3. After that, the roughness parameters of the iFFT profiles were calculated. The following window ranges were chosen because of the lateral resolution and working range of the different instruments (Figure 59) used in my thesis.

- 500 - 50 μm: roughness range important for the mechanical interlocking of tissue with the biomaterial surface [42]
- 50 - 10 μm: size range typical of the dimension of cells, important for the interaction of individual cells with surface features such as cavities [42]
- 10 - 3 μm: range of some sub-cellular components such as focal adhesion; also relevant for the organisation of adsorbed biomolecule layers [42]
- 3 - 0.4 μm: size range important for interactions of proteins or macrophages with surface features [42]

The results of the window roughness evaluation will be discussed for the SLA surface based on the LPM, IM and stereo-SEM data used for the wavelength-dependent roughness evaluation shown in Figure 73. In that figure the total, accessible wavelength range for each method is shown. The window roughness evaluations were done within the ranges defined above. Figure 75 shows a FFT filtered IM profile of the SLA surface including the window ranges. Figure 76 shows the original SEM image and an example of an IM profile together with the FFT filtered SEM images and IM profiles in the wavelength ranges 50 - 10 μm, 10 - 3 μm and 3 - 0.4 μm. Table XL lists the corresponding differential 2-D roughness parameters for the four

7. Results and discussion

176
window ranges and the original profiles, which include all wavelengths. The results of LPM measurements for all other surfaces are listed in appendix 1.

Fig. 75: FFT filtered IM profile of the SLA surface including the window ranges of 50–10 μm, 10–3 μm and 3–0.4 μm.

7. Results and discussion
In general, for each evaluated window range, the amplitude parameters \( R_a, R_q, R_t, R_{2DIN} \) and the spacing parameter \( S_m \) decreased with increasing lateral resolution, while the hybrid parameter \( L_r \) increased. The hybrid parameters \( S_k \) and \( K \) as well as the material ratio parameters \( R_{pk} \) and \( R_{vk} \), and consequently \( M_{r1} \) and \( M_{r2} \), indicated no difference with increasing lateral resolution. Similar results were discussed in section 7.2.1 and 7.2.2, where the different methods were compared. All roughness parameters except \( S_k, K, M_{r1} \) and \( M_{r2} \) were different in the different ranges of the LPM profiles. In the case of the IM profiles, the roughness parameters \( R_a, R_q, S_m, R_{pk}, R_{vk} \) and \( R_k \) were different in all calculated window ranges, whereas the roughness value \( R_t \) only indicated differences in the ranges 0.4 – 3 \( \mu \)m and 10 – 50 \( \mu \)m. The amplitude parameter \( R_{2DIN} \) and the hybrid parameter \( L_r \) were not different in the ranges 3 – 10 \( \mu \)m and 10 – 50\( \mu \)m and 0.4 – 3 \( \mu \)m and 3 – 10 \( \mu \)m, respectively.
<table>
<thead>
<tr>
<th>Method</th>
<th>Roughness Parameter</th>
<th>Roughness Values Range</th>
<th>Roughness Values Range</th>
<th>Roughness Values Range</th>
<th>Roughness Values Range</th>
<th>Roughness Values Original Profiles</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPM 1)</td>
<td>$R_a$ [µm]</td>
<td>0.15 ± 0.02</td>
<td>0.86 ± 0.10</td>
<td>2.68 ± 0.94</td>
<td>—</td>
<td>4.61 ± 1.08</td>
</tr>
<tr>
<td></td>
<td>$R_t$ [µm]</td>
<td>0.26 ± 0.07</td>
<td>1.19 ± 0.20</td>
<td>3.33 ± 1.13</td>
<td>—</td>
<td>5.76 ± 1.45</td>
</tr>
<tr>
<td></td>
<td>$R_k$ [µm]</td>
<td>6.22 ± 3.26</td>
<td>12.16 ± 6.51</td>
<td>15.78 ± 5.25</td>
<td>—</td>
<td>25.34 ± 6.08</td>
</tr>
<tr>
<td></td>
<td>$R_{DIN}$ [µm]</td>
<td>2.89 ± 0.83</td>
<td>7.09 ± 1.68</td>
<td>11.29 ± 3.06</td>
<td>—</td>
<td>16.60 ± 3.35</td>
</tr>
<tr>
<td></td>
<td>$S_m$ [mm]</td>
<td>0.002 ± 0.000</td>
<td>0.005 ± 0.001</td>
<td>0.029 ± 0.004</td>
<td>—</td>
<td>0.022 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>$K$</td>
<td>47.37 ± 39.35</td>
<td>7.39 ± 5.85</td>
<td>2.73 ± 0.29</td>
<td>—</td>
<td>2.51 ± 0.55</td>
</tr>
<tr>
<td></td>
<td>$L_t$</td>
<td>1.70 ± 0.13</td>
<td>1.87 ± 0.15</td>
<td>1.22 ± 0.08</td>
<td>—</td>
<td>2.06 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>$R_{pk}$ [µm]</td>
<td>0.36 ± 0.08</td>
<td>1.56 ± 0.47</td>
<td>2.49 ± 0.48</td>
<td>—</td>
<td>4.53 ± 2.18</td>
</tr>
<tr>
<td></td>
<td>$R_{vk}$ [µm]</td>
<td>0.35 ± 0.06</td>
<td>1.29 ± 0.37</td>
<td>3.55 ± 1.51</td>
<td>—</td>
<td>6.24 ± 4.48</td>
</tr>
<tr>
<td></td>
<td>$R_k$ [µm]</td>
<td>0.13 ± 0.02</td>
<td>0.99 ± 0.08</td>
<td>3.21 ± 1.30</td>
<td>—</td>
<td>5.34 ± 1.51</td>
</tr>
<tr>
<td></td>
<td>$M_1$ [%]</td>
<td>13.02 ± 1.47</td>
<td>12.46 ± 2.23</td>
<td>10.41 ± 3.82</td>
<td>—</td>
<td>11.79 ± 6.93</td>
</tr>
<tr>
<td></td>
<td>$M_2$ [%]</td>
<td>85.71 ± 0.94</td>
<td>88.74 ± 2.22</td>
<td>85.87 ± 4.46</td>
<td>—</td>
<td>86.57 ± 5.45</td>
</tr>
<tr>
<td>IM (UBM) 2)</td>
<td>$R_a$ [µm]</td>
<td>0.14 ± 0.02</td>
<td>0.76 ± 0.01</td>
<td>1.84 ± 0.46</td>
<td>—</td>
<td>2.44 ± 0.63</td>
</tr>
<tr>
<td></td>
<td>$R_t$ [µm]</td>
<td>0.22 ± 0.06</td>
<td>0.97 ± 0.02</td>
<td>2.31 ± 0.59</td>
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<td>3.17 ± 0.92</td>
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<tr>
<td></td>
<td>$R_k$ [µm]</td>
<td>3.59 ± 2.22</td>
<td>7.43 ± 0.51</td>
<td>10.65 ± 3.06</td>
<td>—</td>
<td>18.76 ± 5.34</td>
</tr>
<tr>
<td></td>
<td>$R_{DIN}$ [µm]</td>
<td>2.14 ± 1.05</td>
<td>5.01 ± 0.13</td>
<td>6.92 ± 1.59</td>
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<td>10.87 ± 1.48</td>
</tr>
<tr>
<td></td>
<td>$S_m$ [mm]</td>
<td>0.002 ± 0.000</td>
<td>0.005 ± 0.000</td>
<td>0.029 ± 0.002</td>
<td>—</td>
<td>0.013 ± 0.005</td>
</tr>
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<td></td>
<td>$S_k$</td>
<td>-0.14 ± 0.24</td>
<td>0.08 ± 0.27</td>
<td>0.14 ± 0.46</td>
<td>—</td>
<td>-0.20 ± 0.37</td>
</tr>
<tr>
<td></td>
<td>$K$</td>
<td>7.92 ± 2.43</td>
<td>3.75 ± 0.42</td>
<td>2.84 ± 0.18</td>
<td>—</td>
<td>3.65 ± 1.56</td>
</tr>
<tr>
<td></td>
<td>$L_t$</td>
<td>1.84 ± 0.19</td>
<td>1.66 ± 0.05</td>
<td>1.12 ± 0.04</td>
<td>—</td>
<td>2.32 ± 0.28</td>
</tr>
<tr>
<td></td>
<td>$R_{pk}$ [µm]</td>
<td>0.28 ± 0.08</td>
<td>1.09 ± 0.16</td>
<td>2.26 ± 0.92</td>
<td>—</td>
<td>3.09 ± 0.90</td>
</tr>
<tr>
<td></td>
<td>$R_{vk}$ [µm]</td>
<td>0.27 ± 0.06</td>
<td>0.96 ± 0.22</td>
<td>2.29 ± 0.53</td>
<td>—</td>
<td>3.85 ± 3.05</td>
</tr>
<tr>
<td></td>
<td>$R_k$ [µm]</td>
<td>0.15 ± 0.01</td>
<td>0.96 ± 0.07</td>
<td>2.17 ± 0.56</td>
<td>—</td>
<td>2.72 ± 0.57</td>
</tr>
<tr>
<td></td>
<td>$M_1$ [%]</td>
<td>12.31 ± 0.81</td>
<td>10.89 ± 2.65</td>
<td>15.23 ± 4.26</td>
<td>—</td>
<td>12.77 ± 1.73</td>
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<tr>
<td></td>
<td>$M_2$ [%]</td>
<td>87.07 ± 1.06</td>
<td>91.26 ± 2.98</td>
<td>90.59 ± 2.01</td>
<td>—</td>
<td>87.36 ± 2.01</td>
</tr>
</tbody>
</table>

Tab. XL: List of the roughness values from LPM, IM and stereo-SEM profiles of the SLA surface for the original profile and the four different scale ranges 500 - 50 µm, 50 - 10 µm, 10 - 3 µm and 3 - 0.4 µm calculated with the UBM software (n=7 for each surface; mean values ± standard deviations). 1) LPM profiles calculated with the UBM software. 2) IM profiles calculated with the UBM software. 3) stereo-SEM profiles calculated with the UBM software.

7. Results and discussion
The material ratio parameters \( M_{r1} \) and \( M_{r2} \) did not differ between the various window ranges. In the case of the stereo-SEM profiles, no differences have been observed in each range for \( S_k \), \( M_{r1} \) and \( M_{r2} \) as well as for \( R_t \) and \( K \) in the range 3 -10 \( \mu \)m and 10 - 50 \( \mu \)m and \( L_r \) in the range 0.4 - 3 \( \mu \)m and 3 - 10 \( \mu \)m, respectively.

The ratio of \( R_t/S_m \) can be used to characterise the holes and pits of the SLA surface. In the case of the holes produced by the blasting and the subsequent etching process, the ratios were found to be between 0.65 and 0.37 calculated from the different methods in the range 10 to 50 \( \mu \)m. In the case of the small pits produced by the etching the ratios were between 3.11 and 1.80 calculated in the range 0.4 to 3 \( \mu \)m. That values indicate that in this range depth of the pits was greater than the diameter of the pits.

A comparison of the roughness parameters of the LPM, IM and stereo-SEM measurements in each range indicated no differences in both ranges 3 - 10 \( \mu \)m and 10 - 50 \( \mu \)m for LPM and IM as well as in the ranges 0.4 - 3 \( \mu \)m and 10 - 50 \( \mu \)m for IM and stereo-SEM. A comparison of the roughness values \( R_q^2 \) and \( R_a^2 \) in the different ranges of each method with those determined for the original profile indicated an additive effect for each range (see equation 27). In the case of LPM, the sum of \( R_q^2 \) and \( R_a^2 \) was similar to \( R_q^2 \) and \( R_a^2 \) of the original profile. However, in the case of IM and stereo-SEM the results differed more, because some wavelength contributions were not within the defined window ranges and therefore their \( R_q^2 \) and \( R_a^2 \) contributions were missed.

In summary, the roughness parameters \( R_a \), \( R_q \), \( R_t \), \( R_{2DIN} \), \( S_m \), \( R_{pk} \), \( R_{vk} \) and \( R_k \) indicate the smallest values in the range with the lowest wavelengths, whereas \( L_r \) has in this range the highest value. Furthermore, the window roughness evaluation indicated that the roughness parameters \( R_t \), \( R_{2DIN} \) and \( K \) in particular are highly sensitive to artefacts, whereas the skewness \( S_k \) is less sensitive to artefacts and the different window ranges. The roughness parameters \( R_a \), \( R_q \), \( S_m \) and \( L_r \) as well as the material ratio curve are useful to describe 2-D profiles in the different wavelength ranges. Above 3 \( \mu \)m LPM and IM data are similar, below 3 \( \mu \)m IM and stereo-SEM data. However, IM shows less artefacts compare to LPM. Stereo-SEM enables high-lateral-resolution 2-D profiles to be calculated.

It has often been assumed that specific size features in different dimensions of
the surface have specific effects on the biological processes [42]. But the characterisation of these features by standard integral roughness parameters as well as standard methods such as mechanical stylus or LPM is still insufficient (as discussed in section 7.2.2 and 7.2.3). The wavelength-dependent roughness evaluation developed in this thesis appears to be a useful approach in describing surface topographies, and has the advantage that feature contributions in different wavelength ranges can be separately estimated. The present data calculated by the window roughness concept provide the opportunity to correlate the different effects of macro- to nanostructure of varying dimensions on biological processes.

7.2.5 SEM studies: angle dependent stereo-SEM and comparison of SEM and back-scattered electron (BSE) using stereo mode

In this section, the dependence of the computational profiles on the stereo angle will be discussed. Furthermore, a comparison of SEM and back-scattered electron (BSE) images using the stereo method will be given. These investigations were done with the structured + etched surface.

It is well known that the tilt angle influences the height resolution [130], as discussed in section 5.6.2 (Figure 36). Theoretically, the best resolution will be given, when the tilt angle is 90° (see equation 20). However, very large angles would create stereoscopic gaps and other related mapping problems, while very small angles give unreliable heights. For a given surface topography, a practical compromise between the two extremes is, therefore, necessary. Ghosh and El Ghazali [186] reported that a tilt angle between 8° and 20° would generally give adequate results, the optimum being usually between 10° and 15°. In general, for smoother surfaces, a larger angle will be chosen, and for a rough surface with high peaks, a small angle will be preferred.

The structured + etched surface was investigated with a stereo angle of ± 3° and ± 4.9° out of the initial position, respectively. The tilting limit of the Philips 30XL
are $+70^\circ$ and $-4.9^\circ$. The SEM images were acquired with a beam energy of 20 kV at a working distance of 10 mm. *Figure 77* shows the SEM image of the structured + etched surface. Along the white line, the same profiles were calculated from the two SEM images, which were tilted by either $\pm3^\circ$ or $\pm4.9^\circ$. The calculations were done with the software analySIS® Pro. *Figure 78* shows the calculated profiles. The shape and some features of the profiles were comparable. However, in the case of a stereo angle of $9.8^\circ$, the calculated profile showed a lot of artefacts. That means that for this kind of surface a stereo angle of $9.8^\circ$ already produced some stereoscopic gaps. Similar results were found for SLA, TPS and coarsely blasted surfaces. Therefore, it is safer to work with a stereo angle of $6^\circ$, which produced less artefacts. All other stereo-SEM investigations in my thesis were carried out with a stereo angle of $6^\circ$.

The SEM image of the structured + etched surface (*Figure 77*) shows that the etching process attacked the grain boundaries. The etched structure in the grain boundary regions is much finer.

*Fig. 77:* SEM image of the structured + etched surface. Along the white line, profiles were calculated from the two SEM images, which were tilted out of the initial position either by $\pm3^\circ$ or $\pm4.9^\circ$.

7. Results and discussion
Fig. 78: Same profiles of the structured + etched surface calculated from the two SEM images, which were tilted out of the initial position either by a) ±3° or ±4.9°.

The image information that can be obtained using a SEM depends on both on the type of signal detected and the position within a specimen where the signal has originated. Decreases the primary beam energy decreases the beam penetration. Selected investigations with low (<5kV) beam energies for imaging with secondary
electrons (SE) were carried out to obtain SEM images with increased surface sensitivity [187-189]. In contrast, back-scattered electrons (BSE) are well known for material contrast and topographic contrast imaging.

In this study, the stereo-SEM and stereo-BSE images were compared and the corresponding profiles were calculated with the software analySIS® Pro. The images were obtained with the Hitachi S-4100 FESEM fitted with an Autrata yttrium aluminium garnet (YAG) detector for the BSE imaging. A stereo angle of ±3° out of the initial position and beam energy of 4 and 20 kV at a working distance of 10 mm were used for SE and BSE imaging. Figures 79 and 80 show the stereo-SEM and stereo-BSE images. Figure 79a and 80a show the stereo-SEM and stereo-BSE images obtained with the common beam energy of 20 kV. In general images are similar, but more topographical information was obtained with the lower beam energy (4 kV). In particular the stereo-BSE image showed more details of the topography. This appears to be an anomaly, since it is expected that higher beam energies should result in a smaller spot size and less chromatic aberration. The explanation for this result probably lies in the complexities of beam-sample interaction at such low energies [190]. The stereo-BSE image at the energy of 4 kV clearly showed a different orientation of the grains (Figure 81). It is well known that etching and pickling processes are dependent on the grain orientation.

The same profiles were always calculated from the two SEM or BSE images obtained either with a beam energy of 20 kV or 4 kV (Figure 82). The best computational profile resulted from the SE images, which was obtained with the commonly used beam energy of 20 kV. The highest tendency to artefacts was observed for the profile based on the BSE data, obtained with beam energy of 4 kV. Although the stereo-BSE images gave much more visible detail of the topography, the contrast of the images was lower than in the case of SE images. Because the software needs good contrast for the calculation of the profiles, SE images are preferred for height profile measurements. Furthermore, SE images obtained with beam energy of 20 kV had more contrast than those obtained with lower beam energy.

7. Results and discussion
Fig. 79: Stereo-SEM images of the structured + etched surface obtained with a stereo angle of 6°. A beam energy of a) 20 kV and b) 4 kV and a working distance of 10 mm were used.

7. Results and discussion
Fig. 80: Stereo-BSE images of the structured + etched surface obtained with a stereo angle of 6°. Beam energy of a) 20 kV and b) 4 kV and a working distance of 10 mm were used.
Fig. 81: The stereo-BSE image obtained with the beam energy of 4 kV clearly shows the orientation of the grains made evident by the etching process.

Fig. 82: Same profiles of the structured + etched surface calculated from the stereo-SEM and stereo-BSE images shown in Fig. 79 and 80. a) SE mode with 20 kV, b) SE mode with 4 kV, c) BSE mode with 20 kV and d) BSE mode with 4 kV.
In summary, the stereo-angle-dependent studies indicated that a stereo angle of 9.6° produced some stereoscopic gaps on surfaces such as coarsely blasted, structured + etched TPS as well as SLA. Therefore, on those kinds of surfaces it is more appropriate to work with a stereo angle of 6°. Stereo-BSE images at low beam energy (4 kV) show for more details of the topography than the comparable stereo-SEM images. However, the calculated profiles indicate fewer artefacts if they are obtained from the tilt SEM images with a higher beam energy (20 kV), because the SEM images have a higher contrast, which was needed for the calculations.
7.3 Biological characterisation of the implant surfaces using MC3T3E1 cell line and rat bone marrow cells

This work was performed in collaboration with the chair of Biocompatible Materials Science and Engineering of ETHZ led by Prof. Dr. E. Wintermantel). Ms. Viola Schlosser and Dr. Arie Bruinink were responsible for the experimental studies.

The objective of the work was to study the effect of polished, finely blasted and coarsely blasted cpTi, Ti6Al7Nb, Ti6Al4V, CoCrMo surfaces, respectively, as well as TPS, SLA, HA, etched cpTi, structured cpTi and structured + etched cpTi on the proliferation and differentiation of bone cells. Another aim was to compare the response of cells of the osteoblastic cell line MC3T3-E1 with those of adult primary rat bone marrow cells (RBM). The MC3T3 cell line was chosen because it is one of the most commonly used cell lines in studies related to load-bearing implants and bone diseases. RBM were used since most bone-replacement materials are implanted in an adult bone and therefore are in direct contact with bone marrow. Characterisation of the effect on both types of cell cultures enabled us: (a) to compare our data with existing literature based on both types of cultures and (b) to define a platform on which data of osteoblastic cell lines and those of primary cell cultures can be compared. The latter platform will help to clarify those processes taking place at bone implant surfaces that discriminate between the ability of surfaces to be osteogenic surfaces.

7.3.1 Materials and methods

Cloned, osteoblast-like MC3T3-E1 cells originally derived from new born mouse calvaria were maintained in α-Minimum Essential Medium (α-MEM, Gibco, Basel, Switzerland) containing 10% heat-inactivated fetal calf serum (FCS) at 37°C, 5% CO₂ and 95% air. MC3T3-E1 cells were subcultured until passage numbers of 25-30 in PSN (antibiotics cocktail)-free α-MEM culture medium. For experiments, cells were
harvested by trypsinization (Trypsin-EDTA solution, Gibco, Basel, Switzerland), counted by using a Coulter Counter (Coulter® Z1, Coulter Electronics Ltd., Luton, Beds., USA), and cooled in ice until use.

Primary rat bone marrow cells (RBM) were freshly isolated from femoral and tibial bone of adult male Wistar rats. Tibiae and femora were dissected longitudinally after removal of the periosteum and bone marrow was collected using a scalpel. The bone marrow was resuspended in phosphate-buffered saline (PBS, pH 7.4), supplemented with 10% antibiotics (PSN antibiotic mixture, Gibco, Basel, Switzerland, consisting of 5 mg/ml penicillin, 5 mg/ml streptomycin, 1 mg/ml Neomycin). This cell suspension was filtered through a 200-μm-mesh nylon filter to remove bone fragments and coagula. After centrifugation of 60 g at 4°C for 10 minutes, the cell pellet was resuspended in culture medium (α-MEM), supplemented with 10% heat inactivated fetal calf serum and 1% PSN.

Tissue-culture polystyrene surfaces were used as controls. Polished, finely blasted, coarsely blasted cpTi, Ti6Al7Nb and Ti6Al4V as well as TPS, HA, SLA, etched and structured + etched surfaces were used in the cell culture tests. Finely and coarsely blasted surfaces as well as HA were γ-sterilised, polished, SLA, TPS, etched and structured + etched surfaces were sterilised within the autoclave at 180°C for 3h. They were immersed with 400 μl 70% ethanol per well in a 24-well plate. One milliliter containing 500'000 RBM or 40'000 MC3T3-E1 cells was added to each sample. Medium was exchanged at days 2 and 5 (MC3T3-E1) and at days 5 and 11 (RBM) after seeding. Cultures were kept at 37°C, in a humidified 5% CO2 atmosphere. After 7 (MC3T3-E1) and 14 (RBM) days of in vitro cultivation, the cells were analysed for ALP activity [191], DNA content [18], and total protein content [18]. A second series of test samples was fixed with 3% glutaraldehyde in PBS and prepared for scanning electron microscopy (SEM). Basal cell functions were estimated by measuring protein content culture new well (Pierce BCA assay) and mitochondrial activity (MTT-dehydrogenase activity) [18].

Bone-tissue formation depends on the generation of adequate cellular signals that tend to reduce the encapsulation of the surface by fibroblasts and dedifferentiated bone cells and shifts the balance between bone formation and resorption towards bone formation. The cell type responsible for bone resorption is
the osteoclast, whereas bone formation is accomplished by osteoblasts. Osteoclast activity can be characterised by determining Tartrate Resistant Acidic Phosphatase (TRAP), whereas an equivalent number for osteoblasts is Alkaline Phosphatase (ALP) activity. Cell proliferation was estimated by measuring cell culture DNA content (Sigma Hoechst assay). Degree of differentiation was assessed by determining ALP activity [191]. Three parameters, DNA, ALP/DNA, and Protein/DNA, were calculated. The DNA value is proportional to the total number of cells. ALP/DNA is a parameter for evaluation of the cell differentiation. The ratio Protein/DNA is related to the cell size.

7.3.2 Cell culture tests and SEM investigations

MC3T3-E1 cell culture results

The morphological investigations of in vitro cultivated MC3T3-E1 cells using SEM indicated that after 7 days incubation, the degree of cell spreading varied with the different surface topographies. The cells on the coarsely blasted and TPS surfaces were evenly spread and were often seen to form bridges between domains of the surface irregularities. The cells had been generally observed in large clusters, even though the coverage of the surface was not complete. Cells formed multi-layers. These indicated in particular the relatively higher degree of proliferation for the TPS surface (Figure 84a). On the finely blasted surfaces, as well as on the structured surfaces, cell spreading appeared more regular and smoother. Polished samples indicated a more or less complete monolayer of cells. No major differences in cell morphology were observed for cpTi, Ti6Al7Nb, Ti6Al4V and CoCrMo within one type of surface treatment. Figure 83 represents these observations. It shows the cell morphology of MC3T3-E1 cells on a) coarsely blasted, b) finely blasted and c) polished Ti6Al7Nb surface after 7 days incubation.

7. Results and discussion
Fig. 83: Cell morphology of MC3T3-E1 cells on a) coarsely blasted, b) finely blasted and c) polished Ti6Al7Nb surface after 7 days of incubation, imaged by Scanning Electron Microscopy (SEM).

Figures 84 and 85 summarised the preliminary results of the biochemical investigations of MC3T3-E1 cells cultivated in vitro for 7 days on different surfaces. Two different investigations were carried out. In both cases, three independent
experiments with 6 samples of each type of surface were investigated. In the first experiment polished, finely and coarsely blasted surfaces of each cpTi, Ti6Al7Nb, Ti6Al4V and CoCrMo, respectively, together with TPS were compared. In the second experiment TPS was compared with polished cpTi as well as with cpTi surfaces with different structures. In the first experiment, the DNA data indicated that TPS and the control surface (polystyrene) had more proliferation compared to the other surfaces (Figures 84a). However, no other large differences for cell number were found between the polished, finely and coarsely blasted surfaces. Also, no differences among the different surfaces could be found for cell differentiation (ALP/DNA) and cell size (Protein/DNA). In the second experiment, a tendency to decrease in cell number was observed for all investigated surfaces, compared to the control surface. Cell differentiation, as assessed by the ALP/DNA value for the structured and TPS surfaces, was less than the control surface, which did not differ from the polished surface. The cell size estimated by the Protein/DNA value indicated no differences between the control surface and the other surfaces.

7. Results and discussion
Fig. 84: Mc3T3-E1 cells cultivated in vitro for 7 days on polished (pol), finely (fb) and coarsely (cb) blasted cpTi, Ti6Al7Nb, Ti6Al4V and CoCrMo surfaces, respectively, as well as on polystyrene control surface and TPS. The results of a) cell number (DNA), b) cell differentiation (ALP/DNA) and c) cell size (Protein/DNA) are shown (n=18, mean values ± standard deviation).
Fig. 85: Mc3T3-E1 cells cultivated in vitro for 7 days on polished (pol) cpTi, different structured cpTi (e.g., 20/30 means: pits with a diameter of 30 μm and the space between the pits in X- and Y-direction 20 μm), TPS as well as on polystyrene control surfaces. The results of cell number (DNA), cell differentiation (ALP/DNA) and cell size (Protein/DNA) are shown (n=18, mean values ± standard deviation).
RBM (rat bone marrow) cell culture results

The cell morphologies of RBM cells on polished, etched, different structured, structured + etched, and SLA after 14 days incubation were investigated using SEM. The structured surfaces were electrochemically microstructured resulting in geometric patterns of circular pits. The first series had pits with a diameter of 50 μm, a depth of 20 μm, separated only by a sharp edge, where the circumferences close together. The second series had pits with a diameter of 30 μm, a depth of 20 μm, separated by a 20 μm space between. The edges were either rounded or sharp. The third series with a diameter of 30 μm, a depth of 20 μm, separated by a 20 μm space between and with sharp edges was etched in a hot solution of HCl/H₂SO₄ for a few minutes (the same etching process as used for the etched and SLA surfaces). The degree of cell spreading varied with the different surface topographies. The cell morphologies of the polished, finely blasted and coarsely blasted surfaces were comparable to those shown in Figure 83. Figure 86 shows the cell morphologies of
RBM cells on a) SLA, b) structured + etched, c) etched, d-f) structured and g) polished cpTi surfaces. The cells on the SLA surface (a) were evenly spread and were often seen to form bridges between domains of the surface irregularities. Contacts of the cells with the surface were observed on surface features with a high slope. The cells had been generally observed in large clusters, even though the coverage of the surface by cells was not complete. Cells formed multi-layers. Similar behaviour was observed on the structured + etched surface (b). On the etched surface (c), some cell clusters were observed. On structured surfaces, the cell
densities were higher. If the surfaces were manufactured with pits with sharp edges
(d and e), the cells bridged the gaps. However, gaps in the coverage of the surface
by cells were observed. If the edges were rounded (f) cells adapted to the pits and
the cell-layer was more or less complete. Polished cpTi samples (g) indicated a more
or less complete monolayer of cells. No obvious differences on cell morphologies
were found between the structured surface with pits with a diameter of 50 \( \mu \text{m} \) and a
depth of 20 \( \mu \text{m} \) separated only by a sharp edge (d) and the surface with pits 30 \( \mu \text{m} \)
depth of 20 \( \mu \text{m} \) that were separated by a 20 \( \mu \text{m} \) space (e).

Figures 87 and 88 summarised the preliminary results of the biochemical
investigations of RBM cells cultivated in vitro for 14 days on different surfaces. Two
different investigations were carried out. In both cases, three independent
experiments with 6 samples of each type of surface were investigated. In the first
experiment polished, finely and coarsely blasted cpTi, Ti6Al7Nb, Ti6Al4V and
CoCrMo surfaces, respectively, together with TPS were compared. In the second
experiment polished cpTi surfaces were compared with different structured, etched,
and structured + etched cpTi surfaces as well as SLA.

In the first experiment, the assayed cell number (DNA) and cell sizes
(Protein/DNA) of polished, finely and coarsely blasted CoCrMo surfaces indicated a
decrease relative to the control surface (tissue culture polystyrene). However, no

![Graph showing DNA results](Image)
Fig. 87: RBM (rat bone marrow) cells cultivated in vitro for 14 days on polished (pol), finely (fb) and coarsely (cb) blasted cpTi, Ti6Al7Nb, Ti6Al4V and CoCrMo surfaces, respectively, as well as on polystyrene control surface and TPS. The results of a) cell number (DNA), b) cell differentiation (ALP/DNA) and c) cell size (Protein/DNA) are shown (n=18, mean values ± standard deviation).
significant differences could be observed among the surface of cpTi and its alloys. A decrease, relative to the control tissue culture polystyrene surface, in cell differentiation (ALP/DNA) was observed for the finely and coarsely blasted surfaces as well as for TPS. No differences were found between the polished samples of cpTi and its alloys as well as CoCrMo. Cell number (DNA), ALP and protein decreased on HA, compared to TPS.

Fig. 88: RBM (rat bone marrow) cells cultivated in vitro for 14 days on polished (pol) cpTi, different structured cpTi (e.g. 20/30 means: pits with a diameter of 30 μm and the space between the pits in X- and Y-direction 20 μm), etched, SLA as well as on polystyrene control surfaces. The results of a) cell number (DNA), and b) cell differentiation (ALP/DNA) and cell size (Protein/DNA) are shown (n=18, mean values ± standard deviation).
In the second experiment, a decrease in cell number, cell differentiation (ALP/DNA) and cell size (Protein/DNA) was observed for all investigated surfaces compared to the control surface. The ratio used to indicate cell differentiation (ALP/DNA) was much less for cells grown on etched and structured + etched surface than for the other surfaces.

In summary, RBM cells appeared to be more sensitive to surface topography and composition with regard to cell number (DNA) and cell differentiation (ALP/DNA) than the MC3T3-E1 cell line. However, more studies have to be carried out to obtain response to the investigated surfaces so that appropriate detailed statistical comparisons can be made.

7.4 Correlation between the window-roughness results and the biological data

The wavelength-dependent roughness evaluation has been shown to be a useful approach in the describing surface topographies, with the advantage that feature contributions in different wavelength ranges can be separately estimated (section 7.2.4). The calculated window roughness data (listed either in section 7.2.4 or in the appendix 1) in this thesis provide the opportunity to correlate the different effects of macro- to nanostructure of varying dimensions with biological responses (see also section 7.3). In particular, the RBM cell studies indicated a possible relationship between cell number (DNA) and cell differentiation (ALP/DNA) with type of topography. Buser et al. [5] and Wong et al. [6] reported an increase of bone contact with increased roughness estimated by the $R_a$ value. In the study of Buser et al. [5] HA, SLA, TPS, blasted (with alumina particles) cpTi and polished cpTi surfaces were investigated. In the study of Wong et al. [6] finely and coarsely blasted cpTi, Ti6Al7Nb and Ti6Al4V surfaces as well as SLA were investigated. Therefore, it was of interest to determine whether there was a correlation between their in vivo data and the roughness data for the different window ranges of their surfaces.
For the correlation calculations, the software S-Plus Version 4.5 was used. First a correlation between the different roughness parameters was carried out. It was of interest to know what correlations exist between the different roughness parameters. This allowed us to reduce the number of roughness parameters, within the same parameter group describing roughness (amplitude, spacing, or hybrid or bearing parameters) and which correlated well with each other. A strong correlation between $R_a$ and $R_q$ resulted as expected from the definition of the two parameters. Furthermore, all calculated amplitude parameters ($R_a$, $R_q$, $R_{zDL}$, $R_{\text{max}}$ and $R_t$) as well as the bearing curve parameters $R_{pk}$, $R_{vk}$ and $R_k$ showed a correlation with each other for each window range and the original profile, which included all wavelengths. In the case of the original profiles including all wavelengths after cut-

![Fig. 89: Scatter plot of all roughness values calculated for all investigated surfaces in the ranges of 3 – 10 µm, 10 – 50 µm and 50 – 500 µm as well as for the original profiles including all wavelengths.](image)

7. Results and discussion
off filtering and the range of 50 – 500 μm, the amplitude parameters also correlated to the mean groove distance $S_m$. An example is given for SLA, where in the 10 – 50 μm and 50 – 500 μm range the ratio of $R_t/S_m$ was between 0.65 and 0.37 and for the range 0.4 – 3 μm between 3.11 and 1.80. Figure 89 shows the scatter plot of this correlation including all data of each range and the original profiles including all wavelengths. For the correlation between the roughness values and the biological data, the following roughness parameters were used: $R_a$, $S_k$, $S_m$, $K$, $L_r$, $D$, $R_t$, $M_{r1}$, $M_{r2}$ and $R_k$.

For the correlation of the window roughness values with the biological results the following model was used:

$$X = \begin{bmatrix} R_{a1} & S_{k1} & S_{m1} & K_1 & \ldots & R_{k1} \\ R_{a2} & S_{k2} & S_{m2} & K_2 & \ldots & R_{k2} \\ R_{a3} & S_{k3} & S_{m3} & K_3 & \ldots & R_{k3} \\ R_{a4} & S_{k4} & S_{m4} & K_4 & \ldots & R_{k4} \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ R_{an} & S_{kn} & S_{mn} & K_n & \ldots & R_{kn} \end{bmatrix}$$

$$Y = \begin{bmatrix} Y_1 \\ Y_2 \\ Y_3 \\ Y_4 \\ \vdots \\ Y_n \end{bmatrix}$$

where $X$ is the matrix of independent variables (topographical properties) and $Y$ is the vector of dependent variables of one biological data set.

In the case of RBM cells, an increase of the cell differentiation (ALP/DNA) was correlated with a decrease in the $R_a$, $R_t$, $R_k$, $L_r$ and $S_m$ values in the range of 3 – 10 μm. In the ranges of 10 – 50 μm and 50 – 500 μm, only $S_m$ correlated with the cell differentiation. In the case of the original profiles, no correlation could be found. That means, that the cell differentiation is only dependent on the microrange between 3 – 10 μm, but not on the standard calculated profile roughness of the original profiles including all wavelengths. Therefore, no correlation between the cell
differentiation and the topography can be observed, if common integral roughness parameters were calculated. We are only able to observe a correlation with the wavelength-dependent roughness evaluation using the window roughness concept. The dependence is more pronounced, when only the cpTi and its alloy surfaces (i.e. excluding the data from CoCrMo and HA surfaces) were used for the correlation. However, for cell number (DNA) and cell size (protein/DNA) no correlation could be found. In the case of MC3T3-E1 cells no correlation could be found between cell number (DNA), cell differentiation (ALP/DNA), and cell size (protein/DNA) with the topographical data in the different window ranges as well as the original profiles. That finding indicates that the RMB cells are more sensitive to surface topography than the MC3T3-E1 cells.

In the study of Buser et al [5] and Wong et al. [6], bone contact increased with increasing Ra of the different surfaces, determined by mechanical stylus measurements. In our studies, bone contact data published by Buser et al. [6] also increased with increasing Ra calculated from the original profiles of the different surfaces. Furthermore, our studies also indicated an increase of bone contact with increasing Sm, Ri and Rk of the original profile, which included all wavelengths, and a decrease with increasing Sk and K (Figure 90). In the range of 50 – 500 µm except for Sk the same correlation could be observed as for the original profile. In the range of 10 – 50 µm a decrease of bone contact with Sk and K was found. In the range 3 – 10 µm the bone contact only indicated a correlation to Sk. Thus it appears that topographical features in the size range of 50 – 500 µm are the prime influences of the formation of bone contact with implants in vivo. Similar results were obtained by the correlation of the bone contact data published by Wong et al. [6] and our window-roughness data. As the commonly used integral roughness values obtained by mechanical stylus are accurate in the macrorange of the surface topography, it is not surprising that a correlation of bone contact and roughness were found by Buser et al. [5] and Wong et al. [6]
Fig. 90: Scatter plot of the roughness values calculated for the original profiles including all wavelengths and the bond contact data published by Buser et al. [5].

It must be emphasised that the current study is based on exploratory data that was originally obtained for other purposes. Thus, this exploratory study examined all potential correlations and laid the foundations for future studies in which specific hypotheses could be tested. Nevertheless, the study indicates that primary RBM (rat bone marrow) cells are more sensitive to topography than the cell-line MC3T3-E1. This result agrees with earlier studies [192, 193], in which transformed cell-lines were less sensitive to topographic stimuli than primary cells. It is also evident that the window roughness approach enables one to distinguish the effects of surface roughness in different size ranges.

Thus, for RBM cells, a correlation was found between the roughness $R_a$, $R_t$, $R_k$, $L_r$, and $S_m$ values and cell differentiation (ALP/DNA) in the range of 3 –10 μm. In the ranges of 10 – 50 μm and 50 – 500 μm, a correlation was only found between $S_m$.
and cell differentiation. No correlation at all was found between the common integral roughness parameters of the original profiles and cell differentiation. Thus it appears that topographical features in the size range of $3 - 10 \, \mu m$ mainly influence the differentiation (ALP/DNA) of RBM cells in vitro.

A correlation was found between the bone contact and the roughness parameters $R_a$, $S_m$, $R_t$ and $R_k$ (either calculated as common integral roughness parameters or in the range of $50 - 500 \, \mu m$ (except for $S_k$)), but no correlation was found between the bone contact and the roughness values in the range $3 - 10 \, \mu m$. Thus it appears that topographical features in the macro range are the prime influences of the formation of bone contact with implants in vivo.
8. Summary and outlook

In this work, the oxide layers of cpTi, Ti6Al7Nb, Ti6Al4V and CoCrMo, which form the surface layer of the implants, were investigated by XPS and ToF-SIMS. In the case of titanium, the native oxide layers of all three investigated materials consisted mainly of TiO$_2$ and the thickness was 4-6 nm. Suboxides such as Ti$_2$O$_3$ and TiO were present at the oxide/metal interface. In the case of Ti6Al7Nb and Ti6Al4V, the alloying elements were detected on the surface in oxidised form as Al$_2$O$_3$, Nb$_2$O$_5$ and VO$_x$. In the case of CoCrMo, the native oxide layer consisted mainly of Co$_2$O$_3$ and the thickness was 5-6 nm.

Finely and coarsely blasted surfaces were covered in the range of 16–18% of the surface with blasting particles such as glass beads and alumina particles, respectively. Also titanium plasma sprayed (TPS) surfaces were found to contain some Al, probably due to a previous alumina blasting process. In the case of HA, the detected atomic ratio of Ca/P of about 1.59 is close to the theoretical ratio of 1.67 of pure HA.

Non-contact laser profilometry (LPM) was found to be a useful method to characterise topographical features in the millimeter to micrometer range, whereas interference microscopy (IM) and stereo-SEM extended the accessible range into the sub-micrometer region. Stereo-SEM was particularly useful for quantifying topographies with complex, strongly corrugated ('sharp') and high-aspect-ratio properties with only minor risk of artefacts and 'distortions' of the true profiles. The techniques LPM, IM and stereo-SEM generally complemented each other in the study of rough surfaces across a wide range of dimensions.

Independent of the instrument used, the evaluation of topographical data in terms of standardised 'integral' amplitude roughness parameters such as $R_a$, $R_q$ or $R_{2\text{DIN}}$ were often found of limited value for the description of real implant surfaces. For example, fine roughness features in the low micron- or submicron-range that may be important for performance in a given application, were often hidden by the coarser contributions to roughness. This is often a major limitation in conventional topography evaluation, and therefore a general interest exists in describing surface topographies with wavelength-dependent functions rather than with integral topographical
parameters.

Wavelength-dependent roughness evaluation was demonstrated to be a useful approach in describing surface topographies, with the advantage that feature contributions in different wavelength ranges can be separately estimated. Additionally, the technique was demonstrated to be a useful quantitative indicator of the individual effects of consecutive surface treatment processes and to be useful in the development of surface treatment processes and in quality control (e.g., SLA process, section 7.2.3). The present data calculated by the window roughness concept (section 7.2.4) provide the opportunity to correlate the different effects of macro- to nanostructure of varying dimensions on the biological processes.

Preliminary cell culture studies demonstrated that RBM cells appeared to be more sensitive than the MC3T3-E1 cell line to surface composition and topography as assessed by effects on cell number (DNA) and cell differentiation (ALP/DNA). The following correlations between surface topography and biochemical data obtained from primary RBM cell culture studies were found:

- In the range of 3 – 10 μm, a correlation was found between the roughness parameters \( R_a, R_t, R_k, L_r \) and \( S_m \) and cell differentiation (ALP/DNA). Cell differentiation increased with increasing \( R_a, R_t, R_k, L_r \) and \( S_m \) values.
- In the ranges of 10 – 50 μm and 50 – 500 μm, a correlation was only found between \( S_m \) and the cell differentiation.
- No correlation at all was found between the roughness parameters and cell differentiation, when the values were calculated over the total wavelength range.

Thus it appears that topographical features in the size range of 3 – 10 μm are particularly relevant in influencing the differentiation (ALP/DNA) of RBM cells in vitro.

Furthermore, correlations between surface topography and bone contact were found, when the in vivo data of Buser et al. [5] and Wong et al. [6] were analysed by the wavelength-dependent method:
• For integral roughness parameters calculated over the total wavelength range and those calculated in the range of 50 – 500 μm, a correlation was found between the bone contact and the roughness parameters $R_a$, $S_m$, $R_t$, $R_k$, $S_k$ and $K$. Bone contact increased with increasing $R_a$, $S_m$, $R_t$ and $R_k$ values, and decreased with increasing $S_k$ and $K$ values.

• In the range of 3 – 10 μm, no correlation was found between the bone contact and the roughness values.

Thus it appears that topographical features in the size range of 50 – 500 μm are the prime factor influencing the formation of bone contact with implants in vivo.

In the future, more studies have to be carried out to obtain response to the investigated surfaces so that appropriate detailed statistical comparisons can be made. Furthermore, the wavelength-dependent roughness evaluation can be applied on micro- and nanofabricated surfaces, which are used for study cell motility, shape, size, orientation and cytoskeletal organisation. Another approach of the wavelength-dependent roughness evaluation will be to control other surface treatment processes such as TiO$_2$ blasting, etching with different electrolytes, and so forth. The application of the transfer functions can be used to characterise the resolution-dependent "topographical fingerprint" of a particular surface treatment process, and, once known, can be used to back-calculate the effect of this surface treatment on starting surfaces with different topographies.

Possible applications of the wavelength-dependent roughness evaluation and the window roughness concept outside the implant area will be in the areas of formability, adhesion, tribology (wear and lubrication), joining techniques (such as bond wiring) or optics.
9. References


9. References
9. References


9. References
[117] DIN 4768, Determination of surface roughness values of the parameters $R_a$, $R_z$, $R_{\text{max}}$ by means of electrical contact (stylus) instruments; terminology, measuring conditions, Beuth Verlag GmbH, Berlin 1990.
[125] I.F. Ferguson; Scanning Electron Microscopy: Applications and Techniques; Warringto, 1976

9. References 215

9. References


10. Appendix

<table>
<thead>
<tr>
<th>Original Profile</th>
<th>polished cpTi</th>
<th>filely-blasted cpTi</th>
<th>coarsely-blasted cpTi</th>
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<tbody>
<tr>
<td></td>
<td>average</td>
<td>sdev</td>
<td>average</td>
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<tr>
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<tr>
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<td>0.000</td>
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<tr>
<td>RzDIN[μm]</td>
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</tr>
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<td>Rk [μm]</td>
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<td>0.01</td>
<td>1.43</td>
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| Range 3 - 10 μm  |               |                     |                       |                      |
|------------------|---------------|---------------------|-----------------------|
|                  | average       | sdev                | average               | sdev                |
| Ra [μm]          | 0.03          | 0.00                | 0.58                  | 0.03                | 0.96                | 0.05                |
| Rq [μm]          | 0.04          | 0.01                | 0.79                  | 0.04                | 1.29                | 0.06                |
| Sk               | 0.20          | 0.49                | -0.10                 | 0.21                | -0.02               | 0.07                |
| Sm [mm]          | 0.000         | 0.000               | 0.008                 | 0.001               | 0.007               | 0.00                |
| RzDIN[μm]        | 0.40          | 0.07                | 5.84                  | 0.34                | 10.42               | 0.93                |
| K                | 13.07         | 5.58                | 5.76                  | 0.74                | 5.42                | 0.79                |
| Rmax [μm]        | 0.52          | 0.14                | 7.90                  | 1.02                | 14.17               | 2.04                |
| LR               | 1.00          | 0.00                | 1.34                  | 0.03                | 1.59                | 0.03                |
| Rt [μm]          | 0.56          | 0.16                | 8.18                  | 0.98                | 14.19               | 2.01                |
| Mr1 [%]          | 14.60         | 0.78                | 12.46                 | 1.07                | 11.27               | 0.77                |
| Mr2 [%]          | 85.11         | 0.24                | 87.29                 | 0.78                | 88.20               | 1.01                |
| Rpk [μm]         | 0.07          | 0.01                | 0.97                  | 0.08                | 1.61                | 0.10                |
| Rvk [μm]         | 0.07          | 0.01                | 1.01                  | 0.08                | 1.58                | 0.15                |
| Rk [μm]          | 0.02          | 0.00                | 0.65                  | 0.04                | 1.12                | 0.08                |

Tab. XLI: Window-roughness values of polished, finely-blasted and coarsely-blasted cpTi calculated for the original profile, including all wavelengths, and for the range 3 – 10 μm. Original profiles were determined by LPM.
<table>
<thead>
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<th>Range</th>
<th>polished cpTi</th>
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<th>coarsely-blasted cpTi</th>
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<td>0.08</td>
<td>4.00</td>
</tr>
<tr>
<td>K</td>
<td>4.62</td>
<td>1.86</td>
<td>3.02</td>
</tr>
<tr>
<td>Rmax [μm]</td>
<td>0.25</td>
<td>0.17</td>
<td>5.46</td>
</tr>
<tr>
<td>Lr</td>
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<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Rt [μm]</td>
<td>0.26</td>
<td>0.17</td>
<td>5.55</td>
</tr>
<tr>
<td>Mr1 [%]</td>
<td>11.36</td>
<td>2.25</td>
<td>9.19</td>
</tr>
<tr>
<td>Mr2 [%]</td>
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<td>2.29</td>
<td>88.81</td>
</tr>
<tr>
<td>Rpk [μm]</td>
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<td>0.03</td>
<td>0.90</td>
</tr>
<tr>
<td>Rvk [μm]</td>
<td>0.05</td>
<td>0.04</td>
<td>0.97</td>
</tr>
<tr>
<td>Rk [μm]</td>
<td>0.03</td>
<td>0.01</td>
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Tab. XLII: Window-roughness values of polished, finely-blasted and coarsely-blasted cpTi calculated for the ranges 10 – 50 μm and 50 – 500 μm. Original profiles were determined by LPM.
<table>
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<tr>
<th>Original Profile</th>
<th>polished Ti6Al7Nb average</th>
<th>sdev</th>
<th>finely-blasted Ti6Al7Nb average</th>
<th>sdev</th>
<th>coarsely-blasted Ti6Al7Nb average</th>
<th>sdev</th>
</tr>
</thead>
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<td>1.51</td>
<td>0.28</td>
<td>4.11</td>
<td>0.25</td>
</tr>
<tr>
<td>Rq [μm]</td>
<td>0.01</td>
<td>0.00</td>
<td>2.13</td>
<td>0.53</td>
<td>5.47</td>
<td>0.32</td>
</tr>
<tr>
<td>Sk</td>
<td>0.61</td>
<td>2.34</td>
<td>-0.08</td>
<td>0.73</td>
<td>-0.37</td>
<td>1.02</td>
</tr>
<tr>
<td>Sm [mm]</td>
<td>0.000</td>
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<td>0.001</td>
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<td>0.004</td>
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<td>RzDIN[μm]</td>
<td>0.11</td>
<td>0.05</td>
<td>12.49</td>
<td>2.78</td>
<td>31.39</td>
<td>2.85</td>
</tr>
<tr>
<td>K</td>
<td>26.61</td>
<td>25.19</td>
<td>6.97</td>
<td>3.86</td>
<td>6.48</td>
<td>2.94</td>
</tr>
<tr>
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</tr>
<tr>
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<td>0.00</td>
<td>1.45</td>
<td>0.04</td>
<td>1.74</td>
<td>0.04</td>
</tr>
<tr>
<td>Rt [μm]</td>
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<td>0.12</td>
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<td>44.99</td>
<td>8.95</td>
</tr>
<tr>
<td>Mr1 [%]</td>
<td>10.06</td>
<td>1.34</td>
<td>10.33</td>
<td>1.28</td>
<td>9.21</td>
<td>2.37</td>
</tr>
<tr>
<td>Mr2 [%]</td>
<td>89.13</td>
<td>1.89</td>
<td>86.75</td>
<td>1.07</td>
<td>86.50</td>
<td>2.46</td>
</tr>
<tr>
<td>Pp [μm]</td>
<td>0.01</td>
<td>0.01</td>
<td>2.86</td>
<td>1.62</td>
<td>5.28</td>
<td>1.45</td>
</tr>
<tr>
<td>Rv [μm]</td>
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<td>1.01</td>
<td>7.06</td>
<td>2.06</td>
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<tr>
<td>Rk [μm]</td>
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<td>1.67</td>
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<td>4.81</td>
<td>0.45</td>
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**Range 3 - 10 μm**

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<th>finely-blasted Ti6Al7Nb sdev</th>
<th>coarsely-blasted Ti6Al7Nb sdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra [μm]</td>
<td>0.01</td>
<td>0.00</td>
<td>0.67</td>
</tr>
<tr>
<td>Rq [μm]</td>
<td>0.01</td>
<td>0.00</td>
<td>0.89</td>
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<tr>
<td>Sk</td>
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<td>1.81</td>
<td>-0.06</td>
</tr>
<tr>
<td>Sm [mm]</td>
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<td>0.000</td>
<td>0.007</td>
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<td>RzDIN[μm]</td>
<td>0.08</td>
<td>0.04</td>
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<tr>
<td>K</td>
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<td>26.42</td>
<td>4.69</td>
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<td>Lr</td>
<td>1.00</td>
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<td>1.42</td>
</tr>
<tr>
<td>Rt [μm]</td>
<td>0.15</td>
<td>0.09</td>
<td>8.52</td>
</tr>
<tr>
<td>Mr1 [%]</td>
<td>10.79</td>
<td>0.85</td>
<td>11.79</td>
</tr>
<tr>
<td>Mr2 [%]</td>
<td>88.08</td>
<td>1.21</td>
<td>88.25</td>
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<tr>
<td>Pp [μm]</td>
<td>0.01</td>
<td>0.00</td>
<td>1.05</td>
</tr>
<tr>
<td>Rv [μm]</td>
<td>0.01</td>
<td>0.00</td>
<td>1.11</td>
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<tr>
<td>Rk [μm]</td>
<td>0.01</td>
<td>0.00</td>
<td>0.78</td>
</tr>
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</table>

*Tab. XLIII:* Window-roughness values of polished, finely-blasted and coarsely-blasted Ti6Al7Nb calculated for the original profile, including all wavelengths, and for the range 3 – 10 μm. Original profiles were determined by LPM.
<table>
<thead>
<tr>
<th>Range</th>
<th>polished Ti6Al7Nb average</th>
<th>sdev</th>
<th>finely-blasted Ti6Al7Nb average</th>
<th>sdev</th>
<th>coarsely-blasted Ti6Al7Nb average</th>
<th>sdev</th>
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</thead>
<tbody>
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<td></td>
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<td></td>
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<td>Ra [µm]</td>
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<td>0.00</td>
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<td>0.01</td>
<td>0.00</td>
<td>1.18</td>
<td>0.27</td>
<td>3.07</td>
<td>0.24</td>
</tr>
<tr>
<td>Sk</td>
<td>0.05</td>
<td>0.50</td>
<td>0.00</td>
<td>0.28</td>
<td>0.04</td>
<td>0.61</td>
</tr>
<tr>
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<td>0.000</td>
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<td>0.002</td>
<td>0.026</td>
<td>0.002</td>
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<td>0.04</td>
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<td>2.90</td>
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<td>2.92</td>
<td>7.67</td>
<td>5.16</td>
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<td>31.27</td>
<td>10.00</td>
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<tr>
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<td>0.00</td>
<td>1.06</td>
<td>0.02</td>
<td>1.27</td>
<td>0.02</td>
</tr>
<tr>
<td>Rt [µm]</td>
<td>0.06</td>
<td>0.04</td>
<td>12.11</td>
<td>4.78</td>
<td>31.85</td>
<td>9.59</td>
</tr>
<tr>
<td>Mr1 [%]</td>
<td>10.99</td>
<td>1.31</td>
<td>11.42</td>
<td>1.02</td>
<td>10.98</td>
<td>1.32</td>
</tr>
<tr>
<td>Mr2 [%]</td>
<td>88.32</td>
<td>1.86</td>
<td>87.76</td>
<td>1.62</td>
<td>86.96</td>
<td>1.61</td>
</tr>
<tr>
<td>Rp [µm]</td>
<td>0.01</td>
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<td>1.53</td>
<td>0.56</td>
<td>3.74</td>
<td>0.63</td>
</tr>
<tr>
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<td>1.59</td>
<td>0.45</td>
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<td>0.52</td>
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<tr>
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<td>0.00</td>
<td>0.94</td>
<td>0.11</td>
<td>2.54</td>
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</tr>
<tr>
<td>50 - 500 µm</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Ra [µm]</td>
<td>0.00</td>
<td>0.00</td>
<td>0.97</td>
<td>0.25</td>
<td>3.22</td>
<td>0.46</td>
</tr>
<tr>
<td>Rq [µm]</td>
<td>0.01</td>
<td>0.00</td>
<td>1.32</td>
<td>0.44</td>
<td>4.09</td>
<td>0.62</td>
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<td>0.38</td>
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<td>0.011</td>
<td>0.103</td>
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<td>RzDIN[µm]</td>
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<td>2.15</td>
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<td>4.66</td>
<td>2.30</td>
<td>3.53</td>
<td>0.97</td>
</tr>
<tr>
<td>Rmax [µm]</td>
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<td>0.00</td>
<td>8.27</td>
<td>4.09</td>
<td>23.29</td>
<td>4.16</td>
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<tr>
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<td>0.00</td>
<td>1.01</td>
<td>0.00</td>
<td>1.04</td>
<td>0.01</td>
</tr>
<tr>
<td>Rt [µm]</td>
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<td>0.01</td>
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<td>4.86</td>
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<tr>
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<td>1.91</td>
<td>10.32</td>
<td>2.75</td>
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</tr>
<tr>
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<td>0.00</td>
<td>1.06</td>
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Tab. XLIV: Window-roughness values of polished, finely-blasted and coarsely-blasted Ti6Al7Nb calculated for the ranges 10 – 50 µm and 50 – 500 µm. Original profiles were determined by LPM.
<table>
<thead>
<tr>
<th>Original Profile</th>
<th>polished Ti6Al4V average</th>
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<th>coarsely-blasted Ti6Al4V average</th>
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<td>sdev</td>
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<td>Ra [μm]</td>
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<td>0.00</td>
<td>1.50</td>
</tr>
<tr>
<td>Sk</td>
<td>-0.22</td>
<td>0.60</td>
<td>-0.74</td>
</tr>
<tr>
<td>Sm [mm]</td>
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<td>0.000</td>
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<td>RzDIN[μm]</td>
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<tr>
<td>K</td>
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<td>6.79</td>
<td>5.93</td>
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<tr>
<td>Rmax [μm]</td>
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<td>0.07</td>
<td>13.21</td>
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<td>0.00</td>
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<tr>
<td>Mr1 [%]</td>
<td>9.99</td>
<td>1.79</td>
<td>9.85</td>
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<tr>
<td>Mr2 [%]</td>
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<td>2.26</td>
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<td>1.29</td>
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**Range 3 - 10 μm**

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<td>0.57</td>
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<tr>
<td>Rq [μm]</td>
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<tr>
<td>RzDIN[μm]</td>
<td>0.07</td>
<td>0.02</td>
<td>5.52</td>
</tr>
<tr>
<td>K</td>
<td>18.28</td>
<td>26.11</td>
<td>5.47</td>
</tr>
<tr>
<td>Rmax [μm]</td>
<td>0.12</td>
<td>0.06</td>
<td>7.78</td>
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<tr>
<td>Lr</td>
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<td>0.00</td>
<td>1.35</td>
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<tr>
<td>Rt [μm]</td>
<td>0.13</td>
<td>0.06</td>
<td>7.91</td>
</tr>
<tr>
<td>Mr1 [%]</td>
<td>12.25</td>
<td>2.19</td>
<td>11.73</td>
</tr>
<tr>
<td>Mr2 [%]</td>
<td>89.10</td>
<td>1.09</td>
<td>88.15</td>
</tr>
<tr>
<td>Rpk [μm]</td>
<td>0.01</td>
<td>0.00</td>
<td>0.90</td>
</tr>
<tr>
<td>Rvk [μm]</td>
<td>0.01</td>
<td>0.00</td>
<td>0.98</td>
</tr>
<tr>
<td>Rk [μm]</td>
<td>0.01</td>
<td>0.00</td>
<td>0.66</td>
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</table>

**Tab. XLV:** Window-roughness values of polished, finely-blasted and coarsely-blasted Ti6Al4V calculated for the original profile, including all wavelengths, and for the range 3 – 10 μm. Original profiles were determined by LPM.
<table>
<thead>
<tr>
<th>Range</th>
<th>polished Ti6Al4V</th>
<th>finely-blasted Ti6Al4V</th>
<th>coarsely-blasted Ti6Al4V</th>
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<tbody>
<tr>
<td>10 - 50 μm</td>
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<td></td>
</tr>
<tr>
<td>Ra [μm]</td>
<td>0.01 0.00</td>
<td>0.64 0.11</td>
<td>2.36 0.24</td>
</tr>
<tr>
<td>Rq [μm]</td>
<td>0.01 0.00</td>
<td>0.89 0.20</td>
<td>3.25 0.45</td>
</tr>
<tr>
<td>Sk</td>
<td>-0.09 0.10</td>
<td>-0.66 0.68</td>
<td>0.03 0.26</td>
</tr>
<tr>
<td>Sm [mm]</td>
<td>0.000 0.000</td>
<td>0.033 0.002</td>
<td>0.027 0.001</td>
</tr>
<tr>
<td>RzDIN[μm]</td>
<td>0.06 0.01</td>
<td>5.16 1.45</td>
<td>22.45 4.90</td>
</tr>
<tr>
<td>K</td>
<td>3.56 0.76</td>
<td>8.19 4.86</td>
<td>6.19 1.88</td>
</tr>
<tr>
<td>Rmax [μm]</td>
<td>0.08 0.02</td>
<td>9.02 4.11</td>
<td>32.20 10.05</td>
</tr>
<tr>
<td>Lr</td>
<td>1.00 0.00</td>
<td>1.04 0.01</td>
<td>1.28 0.04</td>
</tr>
<tr>
<td>Rt [μm]</td>
<td>0.08 0.02</td>
<td>9.07 4.05</td>
<td>33.23 9.52</td>
</tr>
<tr>
<td>Mr1 [%]</td>
<td>10.71 2.23</td>
<td>11.04 2.02</td>
<td>11.56 1.48</td>
</tr>
<tr>
<td>Mr2 [%]</td>
<td>88.47 1.66</td>
<td>87.42 1.16</td>
<td>87.22 1.19</td>
</tr>
<tr>
<td>Rpk [μm]</td>
<td>0.01 0.00</td>
<td>0.94 0.45</td>
<td>4.39 1.06</td>
</tr>
<tr>
<td>Rvk [μm]</td>
<td>0.01 0.00</td>
<td>1.30 0.40</td>
<td>4.10 0.93</td>
</tr>
<tr>
<td>Rk [μm]</td>
<td>0.01 0.00</td>
<td>0.72 0.10</td>
<td>2.64 0.19</td>
</tr>
<tr>
<td>50 - 500 μm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ra [μm]</td>
<td>0.01 0.00</td>
<td>0.64 0.14</td>
<td>3.25 0.39</td>
</tr>
<tr>
<td>Rq [μm]</td>
<td>0.01 0.00</td>
<td>0.82 0.18</td>
<td>4.23 0.61</td>
</tr>
<tr>
<td>Sk</td>
<td>0.05 0.21</td>
<td>-0.20 0.36</td>
<td>-0.39 0.27</td>
</tr>
<tr>
<td>Sm [mm]</td>
<td>0.000 0.000</td>
<td>0.124 0.025</td>
<td>0.102 0.009</td>
</tr>
<tr>
<td>RzDIN[μm]</td>
<td>0.03 0.01</td>
<td>3.20 0.76</td>
<td>18.55 3.26</td>
</tr>
<tr>
<td>K</td>
<td>2.89 0.42</td>
<td>3.56 0.43</td>
<td>4.16 1.25</td>
</tr>
<tr>
<td>Rmax [μm]</td>
<td>0.05 0.02</td>
<td>4.72 1.14</td>
<td>26.33 8.75</td>
</tr>
<tr>
<td>Lr</td>
<td>1.00 0.00</td>
<td>1.00 0.00</td>
<td>1.04 0.01</td>
</tr>
<tr>
<td>Rt [μm]</td>
<td>0.05 0.02</td>
<td>4.80 1.10</td>
<td>27.77 8.03</td>
</tr>
<tr>
<td>Mr1 [%]</td>
<td>11.05 2.42</td>
<td>11.15 2.67</td>
<td>10.30 2.77</td>
</tr>
<tr>
<td>Mr2 [%]</td>
<td>90.31 2.40</td>
<td>87.47 4.11</td>
<td>88.77 2.90</td>
</tr>
<tr>
<td>Rpk [μm]</td>
<td>0.01 0.00</td>
<td>0.82 0.26</td>
<td>3.98 1.05</td>
</tr>
<tr>
<td>Rvk [μm]</td>
<td>0.01 0.00</td>
<td>0.94 0.26</td>
<td>5.85 1.48</td>
</tr>
<tr>
<td>Rk [μm]</td>
<td>0.01 0.00</td>
<td>0.76 0.19</td>
<td>3.90 0.51</td>
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</table>

Tab. XLVI: Window-roughness values of polished, finely-blasted and coarsely-blasted Ti6Al4V calculated for the ranges 10 – 50 μm and 50 – 500 μm. Original profiles were determined by LPM.
<table>
<thead>
<tr>
<th>Original Profile</th>
<th>polished CoCrMo average</th>
<th>polished CoCrMo sdev</th>
<th>filely-blasted CoCrMo average</th>
<th>filely-blasted CoCrMo sdev</th>
<th>coarsely-blasted CoCrMo average</th>
<th>coarsely-blasted CoCrMo sdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra [μm]</td>
<td>0.01</td>
<td>0.00</td>
<td>0.81</td>
<td>0.09</td>
<td>3.54</td>
<td>0.22</td>
</tr>
<tr>
<td>Rq [μm]</td>
<td>0.02</td>
<td>0.00</td>
<td>1.05</td>
<td>0.11</td>
<td>4.77</td>
<td>0.41</td>
</tr>
<tr>
<td>Sk</td>
<td>-0.98</td>
<td>2.64</td>
<td>-0.42</td>
<td>0.29</td>
<td>-0.83</td>
<td>0.30</td>
</tr>
<tr>
<td>Sm [mm]</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>RzDIN[μm]</td>
<td>0.13</td>
<td>0.05</td>
<td>6.66</td>
<td>0.70</td>
<td>29.92</td>
<td>2.80</td>
</tr>
<tr>
<td>K</td>
<td>31.56</td>
<td>47.41</td>
<td>4.32</td>
<td>1.05</td>
<td>5.39</td>
<td>0.94</td>
</tr>
<tr>
<td>Rmax [μm]</td>
<td>0.25</td>
<td>0.14</td>
<td>8.40</td>
<td>0.94</td>
<td>36.99</td>
<td>4.35</td>
</tr>
<tr>
<td>Lr</td>
<td>1.00</td>
<td>0.00</td>
<td>1.33</td>
<td>0.05</td>
<td>1.76</td>
<td>0.05</td>
</tr>
<tr>
<td>Rt [μm]</td>
<td>0.27</td>
<td>0.15</td>
<td>8.69</td>
<td>0.91</td>
<td>39.14</td>
<td>4.55</td>
</tr>
<tr>
<td>Mr1 [%]</td>
<td>10.27</td>
<td>2.18</td>
<td>9.35</td>
<td>0.64</td>
<td>9.35</td>
<td>1.71</td>
</tr>
<tr>
<td>Mr2 [%]</td>
<td>87.26</td>
<td>1.37</td>
<td>87.57</td>
<td>0.83</td>
<td>86.04</td>
<td>1.30</td>
</tr>
<tr>
<td>Rpk [μm]</td>
<td>0.02</td>
<td>0.00</td>
<td>0.98</td>
<td>0.17</td>
<td>4.13</td>
<td>0.71</td>
</tr>
<tr>
<td>Rvk [μm]</td>
<td>0.02</td>
<td>0.00</td>
<td>1.31</td>
<td>0.16</td>
<td>7.46</td>
<td>1.74</td>
</tr>
<tr>
<td>Rk [μm]</td>
<td>0.01</td>
<td>0.00</td>
<td>0.98</td>
<td>0.12</td>
<td>4.03</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Range
3 - 10 μm
| Ra [μm]          | 0.01                    | 0.00                 | 0.54                        | 0.07                        | 1.00                        | 0.01                        |
| Rq [μm]          | 0.01                    | 0.00                 | 0.70                        | 0.08                        | 1.36                        | 0.02                        |
| Sk               | 0.41                    | 1.94                 | 0.03                        | 0.18                        | 0.11                        | 0.09                        |
| Sm [mm]          | 0.00                    | 0.00                 | 0.01                        | 0.00                        | 0.01                        | 0.00                        |
| RzDIN[μm]        | 0.10                    | 0.04                 | 4.72                        | 0.31                        | 11.21                       | 0.84                        |
| K                | 53.99                   | 60.43                | 4.20                        | 0.64                        | 5.55                        | 0.81                        |
| Rmax [μm]        | 0.19                    | 0.12                 | 5.82                        | 0.57                        | 14.94                       | 2.07                        |
| Lr               | 1.00                    | 0.00                 | 1.32                        | 0.05                        | 1.64                        | 0.01                        |
| Rt [μm]          | 0.20                    | 0.12                 | 6.12                        | 0.45                        | 14.95                       | 2.06                        |
| Mr1 [%]          | 10.74                   | 1.40                 | 11.61                       | 0.74                        | 11.94                       | 0.25                        |
| Mr2 [%]          | 88.12                   | 1.19                 | 88.87                       | 1.20                        | 88.34                       | 0.79                        |
| Rpk [μm]         | 0.01                    | 0.00                 | 0.83                        | 0.10                        | 1.69                        | 0.04                        |
| Rvk [μm]         | 0.01                    | 0.00                 | 0.76                        | 0.04                        | 1.71                        | 0.02                        |
| Rk [μm]          | 0.01                    | 0.00                 | 0.65                        | 0.09                        | 1.15                        | 0.01                        |

Tab. XLVII: Window-roughness values of polished, finely-blasted and coarsely-blasted CoCrMo calculated for the original profile, including all wavelengths, and for the range 3 – 10 μm. Original profiles were determined by LPM.
<table>
<thead>
<tr>
<th>Range</th>
<th>polished CoCrMo</th>
<th>finely-blasted CoCrMo</th>
<th>coarsely-blasted CoCrMo</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>average</td>
<td>sdev</td>
<td>average</td>
</tr>
<tr>
<td>10 - 50 μm</td>
<td>Ra [μm]</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Rq [μm]</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Sk</td>
<td>-0.34</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>Sm [mm]</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>RzDIN[μm]</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>6.76</td>
<td>7.76</td>
</tr>
<tr>
<td></td>
<td>Rmax [μm]</td>
<td>0.09</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>Lr</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Rt [μm]</td>
<td>0.09</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>Mr1 [%]</td>
<td>11.35</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>Mr2 [%]</td>
<td>88.77</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>Rpk [μm]</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Rvk [μm]</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Rk [μm]</td>
<td>0.01</td>
<td>0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Range</th>
<th>polished CoCrMo</th>
<th>finely-blasted CoCrMo</th>
<th>coarsely-blasted CoCrMo</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>average</td>
<td>sdev</td>
<td>average</td>
</tr>
<tr>
<td>50 - 500 μm</td>
<td>Ra [μm]</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Rq [μm]</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Sk</td>
<td>-0.13</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>Sm [mm]</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>RzDIN[μm]</td>
<td>0.02</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>3.25</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>Rmax [μm]</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Lr</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Rt [μm]</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Mr1 [%]</td>
<td>11.81</td>
<td>2.83</td>
</tr>
<tr>
<td></td>
<td>Mr2 [%]</td>
<td>87.58</td>
<td>3.14</td>
</tr>
<tr>
<td></td>
<td>Rpk [μm]</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Rvk [μm]</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Rk [μm]</td>
<td>0.01</td>
<td>0.00</td>
</tr>
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Tab. XLVIII: Window-roughness values of polished, finely-blasted and coarsely-blasted CoCrMo calculated for the ranges 10 – 50 μm and 50 – 500 μm. Original profiles were determined by LPM.
<table>
<thead>
<tr>
<th>Original Profile</th>
<th>blasted cpTi average</th>
<th>sdev</th>
<th>etched cpTi average</th>
<th>sdev</th>
<th>SLA average</th>
<th>sdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra [μm]</td>
<td>4.07</td>
<td>0.29</td>
<td>0.91</td>
<td>0.02</td>
<td>5.09</td>
<td>0.39</td>
</tr>
<tr>
<td>Rq [μm]</td>
<td>5.34</td>
<td>0.35</td>
<td>1.17</td>
<td>0.03</td>
<td>6.40</td>
<td>0.50</td>
</tr>
<tr>
<td>Sk</td>
<td>-0.40</td>
<td>0.23</td>
<td>-0.15</td>
<td>0.09</td>
<td>-0.06</td>
<td>0.20</td>
</tr>
<tr>
<td>Sm [mm]</td>
<td>0.028</td>
<td>0.002</td>
<td>0.009</td>
<td>0.001</td>
<td>0.030</td>
<td>0.003</td>
</tr>
<tr>
<td>RzDIN[μm]</td>
<td>30.00</td>
<td>1.92</td>
<td>7.99</td>
<td>0.38</td>
<td>31.18</td>
<td>2.87</td>
</tr>
<tr>
<td>K</td>
<td>4.39</td>
<td>1.04</td>
<td>3.65</td>
<td>0.28</td>
<td>3.00</td>
<td>0.41</td>
</tr>
<tr>
<td>Rmax [μm]</td>
<td>37.06</td>
<td>5.33</td>
<td>9.30</td>
<td>0.99</td>
<td>37.09</td>
<td>4.58</td>
</tr>
<tr>
<td>Lr</td>
<td>1.73</td>
<td>0.04</td>
<td>1.54</td>
<td>0.01</td>
<td>1.81</td>
<td>0.01</td>
</tr>
<tr>
<td>Rt [μm]</td>
<td>39.43</td>
<td>5.09</td>
<td>9.89</td>
<td>1.34</td>
<td>40.28</td>
<td>5.43</td>
</tr>
<tr>
<td>Mr1 [%]</td>
<td>10.92</td>
<td>1.41</td>
<td>9.43</td>
<td>0.50</td>
<td>10.11</td>
<td>1.44</td>
</tr>
<tr>
<td>Mr2 [%]</td>
<td>88.26</td>
<td>1.08</td>
<td>88.48</td>
<td>0.93</td>
<td>88.52</td>
<td>2.54</td>
</tr>
<tr>
<td>Rpk [μm]</td>
<td>5.10</td>
<td>0.93</td>
<td>1.16</td>
<td>0.09</td>
<td>5.86</td>
<td>1.62</td>
</tr>
<tr>
<td>Rvk [μm]</td>
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<td>0.82</td>
<td>1.33</td>
<td>0.07</td>
<td>6.20</td>
<td>1.17</td>
</tr>
<tr>
<td>Rk [μm]</td>
<td>4.86</td>
<td>0.38</td>
<td>1.14</td>
<td>0.03</td>
<td>6.41</td>
<td>0.44</td>
</tr>
</tbody>
</table>

**Tab. IL:** Window-roughness values of alumina blasted, etched and SLA cpTi surfaces calculated for the original profile, including all wavelengths, and for the range 3 – 10 μm. Original profiles were determined by LPM.

10. Appendix 226
<table>
<thead>
<tr>
<th>Range</th>
<th>blasted cpTi</th>
<th>etched cpTi</th>
<th>SLA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 - 50 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ra [µm]</td>
<td>2.08 ± 0.16</td>
<td>0.50 ± 0.02</td>
<td>2.01 ± 0.22</td>
</tr>
<tr>
<td>Rq [µm]</td>
<td>2.85 ± 0.24</td>
<td>0.64 ± 0.03</td>
<td>2.56 ± 0.28</td>
</tr>
<tr>
<td>Sk</td>
<td>-0.24 ± 0.27</td>
<td>-0.14 ± 0.10</td>
<td>0.06 ± 0.14</td>
</tr>
<tr>
<td>Sm [mm]</td>
<td>0.027 ± 0.001</td>
<td>0.027 ± 0.001</td>
<td>0.028 ± 0.003</td>
</tr>
<tr>
<td>RzDIN[µm]</td>
<td>18.91 ± 2.21</td>
<td>3.84 ± 0.39</td>
<td>14.17 ± 2.27</td>
</tr>
<tr>
<td>K</td>
<td>5.78 ± 1.58</td>
<td>3.51 ± 0.50</td>
<td>3.40 ± 0.59</td>
</tr>
<tr>
<td>Rmax [µm]</td>
<td>26.71 ± 6.86</td>
<td>4.69 ± 0.84</td>
<td>17.77 ± 4.56</td>
</tr>
<tr>
<td>Lr</td>
<td>1.25 ± 0.02</td>
<td>1.03 ± 0.00</td>
<td>1.18 ± 0.01</td>
</tr>
<tr>
<td>Rt [µm]</td>
<td>27.71 ± 6.46</td>
<td>4.80 ± 0.73</td>
<td>18.42 ± 4.38</td>
</tr>
<tr>
<td>Mr1 [%]</td>
<td>11.75 ± 0.82</td>
<td>9.94 ± 1.16</td>
<td>11.01 ± 1.25</td>
</tr>
<tr>
<td>Mr2 [%]</td>
<td>87.15 ± 0.78</td>
<td>89.33 ± 0.80</td>
<td>90.01 ± 1.60</td>
</tr>
<tr>
<td>Rpk [µm]</td>
<td>3.54 ± 0.40</td>
<td>0.62 ± 0.06</td>
<td>2.74 ± 0.33</td>
</tr>
<tr>
<td>Rvk [µm]</td>
<td>3.90 ± 0.26</td>
<td>0.70 ± 0.10</td>
<td>2.49 ± 0.55</td>
</tr>
<tr>
<td>Rk [µm]</td>
<td>2.32 ± 0.19</td>
<td>0.63 ± 0.02</td>
<td>2.53 ± 0.33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Range</th>
<th>50 - 500 µm</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra [µm]</td>
<td>3.31 ± 0.31</td>
<td>0.27 ± 0.02</td>
<td>4.47 ± 0.39</td>
</tr>
<tr>
<td>Rq [µm]</td>
<td>4.27 ± 0.38</td>
<td>0.34 ± 0.02</td>
<td>5.66 ± 0.45</td>
</tr>
<tr>
<td>Sk</td>
<td>-0.09 ± 0.12</td>
<td>-0.05 ± 0.34</td>
<td>-0.11 ± 0.35</td>
</tr>
<tr>
<td>Sm [mm]</td>
<td>0.105 ± 0.006</td>
<td>0.399 ± 0.134</td>
<td>0.127 ± 0.018</td>
</tr>
<tr>
<td>RzDIN[µm]</td>
<td>18.33 ± 1.36</td>
<td>1.51 ± 0.14</td>
<td>23.25 ± 1.97</td>
</tr>
<tr>
<td>K</td>
<td>3.48 ± 0.71</td>
<td>3.64 ± 1.01</td>
<td>3.20 ± 0.77</td>
</tr>
<tr>
<td>Rmax [µm]</td>
<td>23.30 ± 3.24</td>
<td>2.04 ± 0.32</td>
<td>29.59 ± 3.11</td>
</tr>
<tr>
<td>Lr</td>
<td>1.04 ± 0.00</td>
<td>1.00 ± 0.00</td>
<td>1.05 ± 0.01</td>
</tr>
<tr>
<td>Rt [µm]</td>
<td>25.45 ± 3.46</td>
<td>2.12 ± 0.31</td>
<td>31.90 ± 3.51</td>
</tr>
<tr>
<td>Mr1 [%]</td>
<td>12.47 ± 1.94</td>
<td>10.52 ± 1.58</td>
<td>9.75 ± 3.60</td>
</tr>
<tr>
<td>Mr2 [%]</td>
<td>88.66 ± 1.10</td>
<td>88.05 ± 1.36</td>
<td>87.55 ± 3.21</td>
</tr>
<tr>
<td>Rpk [µm]</td>
<td>4.29 ± 1.05</td>
<td>0.33 ± 0.06</td>
<td>4.87 ± 1.76</td>
</tr>
<tr>
<td>Rvk [µm]</td>
<td>5.08 ± 1.09</td>
<td>0.35 ± 0.07</td>
<td>5.95 ± 1.77</td>
</tr>
<tr>
<td>Rk [µm]</td>
<td>3.92 ± 0.48</td>
<td>0.33 ± 0.03</td>
<td>5.50 ± 0.85</td>
</tr>
</tbody>
</table>

**Tab. L:** Window-roughness values of alumina blasted, etched and SLA cpTi surfaces calculated for the ranges 10 – 50 µm and 50 – 500 µm. Original profiles were determined by LPM.
<table>
<thead>
<tr>
<th>Original Profile</th>
<th>HA average</th>
<th>HA sdev</th>
<th>TPS average</th>
<th>TPS sdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra [µm]</td>
<td>6.74</td>
<td>0.57</td>
<td>5.96</td>
<td>0.51</td>
</tr>
<tr>
<td>Rq [µm]</td>
<td>8.42</td>
<td>0.62</td>
<td>7.63</td>
<td>0.67</td>
</tr>
<tr>
<td>Sk</td>
<td>0.00</td>
<td>0.16</td>
<td>0.21</td>
<td>0.46</td>
</tr>
<tr>
<td>Sm [mm]</td>
<td>0.061</td>
<td>0.010</td>
<td>0.033</td>
<td>0.002</td>
</tr>
<tr>
<td>RzDIN[µm]</td>
<td>39.24</td>
<td>2.11</td>
<td>38.16</td>
<td>3.07</td>
</tr>
<tr>
<td>K</td>
<td>3.02</td>
<td>0.35</td>
<td>3.87</td>
<td>1.91</td>
</tr>
<tr>
<td>Rmax [µm]</td>
<td>46.20</td>
<td>2.80</td>
<td>48.59</td>
<td>9.42</td>
</tr>
<tr>
<td>Lr</td>
<td>1.51</td>
<td>0.01</td>
<td>1.93</td>
<td>0.03</td>
</tr>
<tr>
<td>Rt [µm]</td>
<td>50.25</td>
<td>5.28</td>
<td>51.11</td>
<td>9.80</td>
</tr>
<tr>
<td>Mr1 [%]</td>
<td>9.46</td>
<td>2.30</td>
<td>11.10</td>
<td>2.93</td>
</tr>
<tr>
<td>Mr2 [%]</td>
<td>89.85</td>
<td>2.13</td>
<td>89.07</td>
<td>2.21</td>
</tr>
<tr>
<td>Rpk [µm]</td>
<td>8.54</td>
<td>1.85</td>
<td>8.45</td>
<td>2.94</td>
</tr>
<tr>
<td>Rvk [µm]</td>
<td>7.80</td>
<td>1.39</td>
<td>7.23</td>
<td>1.44</td>
</tr>
<tr>
<td>Rk [µm]</td>
<td>8.60</td>
<td>1.03</td>
<td>7.26</td>
<td>0.52</td>
</tr>
</tbody>
</table>

**Range**

3 - 10 µm

<table>
<thead>
<tr>
<th>Original Profile</th>
<th>HA average</th>
<th>HA sdev</th>
<th>TPS average</th>
<th>TPS sdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra [µm]</td>
<td>0.76</td>
<td>0.04</td>
<td>1.20</td>
<td>0.06</td>
</tr>
<tr>
<td>Rq [µm]</td>
<td>0.97</td>
<td>0.05</td>
<td>1.57</td>
<td>0.09</td>
</tr>
<tr>
<td>Sk</td>
<td>-0.14</td>
<td>0.09</td>
<td>-0.02</td>
<td>0.09</td>
</tr>
<tr>
<td>Sm [mm]</td>
<td>0.008</td>
<td>0.000</td>
<td>0.007</td>
<td>0.000</td>
</tr>
<tr>
<td>RzDIN[µm]</td>
<td>6.89</td>
<td>0.61</td>
<td>11.59</td>
<td>1.12</td>
</tr>
<tr>
<td>K</td>
<td>4.01</td>
<td>1.00</td>
<td>4.18</td>
<td>0.52</td>
</tr>
<tr>
<td>Rmax [µm]</td>
<td>8.77</td>
<td>2.49</td>
<td>13.70</td>
<td>2.14</td>
</tr>
<tr>
<td>Lr</td>
<td>1.34</td>
<td>0.01</td>
<td>1.80</td>
<td>0.03</td>
</tr>
<tr>
<td>Rt [µm]</td>
<td>8.94</td>
<td>2.40</td>
<td>14.39</td>
<td>1.89</td>
</tr>
<tr>
<td>Mr1 [%]</td>
<td>10.49</td>
<td>0.84</td>
<td>11.39</td>
<td>0.82</td>
</tr>
<tr>
<td>Mr2 [%]</td>
<td>89.29</td>
<td>0.69</td>
<td>88.66</td>
<td>0.73</td>
</tr>
<tr>
<td>Rpk [µm]</td>
<td>0.96</td>
<td>0.09</td>
<td>1.80</td>
<td>0.18</td>
</tr>
<tr>
<td>Rvk [µm]</td>
<td>1.10</td>
<td>0.10</td>
<td>1.79</td>
<td>0.18</td>
</tr>
<tr>
<td>Rk [µm]</td>
<td>0.94</td>
<td>0.05</td>
<td>1.44</td>
<td>0.05</td>
</tr>
</tbody>
</table>

**Tab. LI:** Window-roughness values of HA and TPS surfaces, calculated for the original profile, including all wavelengths, and for the range 3 – 10 µm. Original profiles were determined by LPM.
<table>
<thead>
<tr>
<th>Range</th>
<th>HA</th>
<th>TPS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>average</td>
<td>sdev</td>
</tr>
<tr>
<td>10 - 50 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ra [µm]</td>
<td>2.12</td>
<td>0.14</td>
</tr>
<tr>
<td>Rq [µm]</td>
<td>2.72</td>
<td>0.18</td>
</tr>
<tr>
<td>Sk</td>
<td>-0.13</td>
<td>0.09</td>
</tr>
<tr>
<td>Sm [mm]</td>
<td>0.026</td>
<td>0.001</td>
</tr>
<tr>
<td>RzDIN[µm]</td>
<td>15.75</td>
<td>1.50</td>
</tr>
<tr>
<td>K</td>
<td>3.66</td>
<td>0.45</td>
</tr>
<tr>
<td>Rmax [µm]</td>
<td>20.31</td>
<td>2.39</td>
</tr>
<tr>
<td>Lr</td>
<td>1.22</td>
<td>0.02</td>
</tr>
<tr>
<td>Rt [µm]</td>
<td>20.89</td>
<td>2.27</td>
</tr>
<tr>
<td>Mr1 [%]</td>
<td>10.88</td>
<td>1.07</td>
</tr>
<tr>
<td>Mr2 [%]</td>
<td>89.15</td>
<td>0.82</td>
</tr>
<tr>
<td>Rpk [µm]</td>
<td>2.74</td>
<td>0.33</td>
</tr>
<tr>
<td>Rvk [µm]</td>
<td>3.02</td>
<td>0.41</td>
</tr>
<tr>
<td>Rk [µm]</td>
<td>2.62</td>
<td>0.21</td>
</tr>
<tr>
<td>50 - 500 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ra [µm]</td>
<td>5.57</td>
<td>0.56</td>
</tr>
<tr>
<td>Rq [µm]</td>
<td>7.01</td>
<td>0.56</td>
</tr>
<tr>
<td>Sk</td>
<td>0.02</td>
<td>0.16</td>
</tr>
<tr>
<td>Sm [mm]</td>
<td>0.161</td>
<td>0.021</td>
</tr>
<tr>
<td>RzDIN[µm]</td>
<td>28.56</td>
<td>1.71</td>
</tr>
<tr>
<td>K</td>
<td>3.18</td>
<td>0.38</td>
</tr>
<tr>
<td>Rmax [µm]</td>
<td>36.95</td>
<td>1.92</td>
</tr>
<tr>
<td>Lr</td>
<td>1.05</td>
<td>0.01</td>
</tr>
<tr>
<td>Rt [µm]</td>
<td>40.33</td>
<td>4.37</td>
</tr>
<tr>
<td>Mr1 [%]</td>
<td>10.37</td>
<td>1.70</td>
</tr>
<tr>
<td>Mr2 [%]</td>
<td>89.87</td>
<td>2.57</td>
</tr>
<tr>
<td>Rpk [µm]</td>
<td>7.34</td>
<td>1.35</td>
</tr>
<tr>
<td>Rvk [µm]</td>
<td>6.79</td>
<td>1.19</td>
</tr>
<tr>
<td>Rk [µm]</td>
<td>7.02</td>
<td>1.09</td>
</tr>
</tbody>
</table>

*Tab. LII:* Window-roughness values of HA and TPS surfaces calculated for the ranges 10 – 50 µm and 50 – 500 µm. Original profiles were determined by LPM.
Curriculum Vitae

Personal Information

Name: Marco Wieland
Date of birth: April 11, 1968 in Chur
Nationality: Swiss, Citizen of Valendas GR
Marital status: unmarried

Education

1995 – present
PhD thesis at the Laboratory for Surface Science and Technology, Department of Materials, Swiss Federal Institute of Technology Zürich, guided by Prof. Dr. N.D. Spencer and at the EMPA Dübendorf, guided by Dr. M. Wolfensberger.

1989 – 1995
Diploma in Materials Engineering at the Swiss Federal Institute of Technology Zürich.

1984 – 1989
Mature, Typus C at the Kantonsschule Chur

Semester and Diploma works

Nov 1994 – Feb 1995
Plasma-nitriding of commercial pure aluminum (Al 99.3) and the alloy AlMn1.

April 1994 – July 1994
Semester work at the Institute for building materials, material chemistry and corrosion of Prof. Dr. H. Böhni
pH – dependence of copper and its alloys in a solution of 0.1M NaAc

Nov. 1993 – Feb 1994
Semester work at the Chair of nonmetallic materials of Prof. Dr. L. Gauckler
Manufacturing and Characterisation of anodes of nickel-zirconia and nickel-ceria cermets for solid oxide fuel cells.
Publications related to this thesis:

Papers


Posters

