The significance of brittle reaction layers in fusing of dental ceramics to titanium

Mikko Tapani Saloniemi

ACADEMIC DISSERTATION

To be publicly discussed with the permission of the Faculty of Medicine of the University of Helsinki, in the Institute of Dentistry, Lecture Hall 1, Mannerheimintie 172, on December 17th 2010, at 12h00.

Helsinki 2010
Supervised by

Professor Mauno Könönen
Department of Stomatognathic Physiology and Prosthetic Dentistry
Institute of Dentistry, Faculty of Medicine
University of Helsinki, Helsinki, Finland

and

Professor emeritus Jorma Kivilahti
Department of Electronics
Faculty of Electronics, Communications and Automation
Helsinki University of Technology, Espoo, Finland

Reviewed by

Professor Pekka Vallittu
Department of Biomaterials Science
Institute of Dentistry, Faculty of Medicine
University of Turku, Turku, Finland

and

Docent Jarmo Hautaniemi
Faculty of Technology and Maritime Management Rauma (Technology)
Satakunta University of Applied Sciences, Rauma, Finland

Discussed by

Professor Timo Närhi
Department of Prosthetic Dentistry
Institute of Dentistry, Faculty of Medicine
University of Turku, Turku, Finland

ISBN 978-952-10-6716-7 (PDF) Helsinki 2010
ACKNOWLEDGEMENTS

This study was carried out at the Institute of Dentistry in the University of Helsinki and the Department of Electronics in the School of Science and Technology – former Helsinki University of Technology. I wish to thank Finnish Dental Society Apollonia and the Helsinki University Central Hospital for making it financially possible to complete this study.

I would like to express my deep gratitude to my supervisor, Prof. Mauno Könönen. Prof. Könönen demonstrated open-minded confidence in inviting a young student into an important and intriguing research project, and in providing constant encouragement and support. I also wish to thank my other supervisor, Prof. (emer.) Jorma Kivilahti, for his extensive and profound knowledge on material sciences, for our long discussions during the final stages of completing this study, and for providing me with broad access to facilities and equipment. Thanks to the special nature of this joint study, I was able to work as research assistant and researcher in the Helsinki University of Technology, gaining significant interdisciplinary experience from a variety of other projects and studies, as well as teaching experience.

I gratefully acknowledge my skilled referees, Prof. Pekka Vallittu and Docent Jarmo Hautaniemi, for their insightful commentary and constructive criticism. I also wish to thank my honored opponent, Prof. Timo Närhi, for agreeing to take on this task.

To Mr. Jukka Wichmann I owe my sincere thanks for the use of his dental laboratory facilities and for his expert guidance in dental techniques. His constant positive attitude and cheerful disposition made working on this study an enjoyable experience.

My collective thanks go to the personnel of the Helsinki University of Technology, who readily accepted an outsider in their midst and introduced him to the use of advanced analytical equipment, also beyond the button-pushing level. Our cooperation will certainly be of future benefit to dental medicine; the skills I have acquired in the process are also bound to prove invaluable in my research career.

Finally, I would like to apologize to my wife Tiina, our cat Questor and my family for so completely depending on their warm and patient support. My brother Timo bore the brunt of difficult questions and late-night revision sessions, while my father Hannu guided me through the world of academic writing, and my mother and colleague Elina kept alive my faith in practical clinical dentistry.

Mikko Saloniemi
Helsinki, October 2010
TABLE OF CONTENTS

TABLE OF CONTENTS ......................................................................................................................... 4
ABBREVIATIONS .................................................................................................................................. 6
ABSTRACT ............................................................................................................................................. 7
1. INTRODUCTION ................................................................................................................................ 9
2. REVIEW OF THE LITERATURE .................................................................................................... 10
  2.1. Titanium in comparison to other metals in dental metalloceramics ............................................ 10
  2.2. Factors influencing joint integrity ............................................................................................... 14
    2.2.1. Coefficient of thermal expansion (CTE) ............................................................................. 14
    2.2.2. Wetting of titanium surfaces ............................................................................................ 16
    2.2.3. \( \alpha \)-case layer .............................................................................................................. 17
    2.2.4. Oxygen and titanium oxides ............................................................................................ 19
    2.2.5. Titanium silicides ............................................................................................................ 20
  2.3. Methods to increase joint strength .............................................................................................. 22
    2.3.1. Surface roughening ........................................................................................................... 22
    2.3.2. Bonding agents and interlayers ......................................................................................... 23
  2.4. Testing joints between dental ceramics and titanium ................................................................. 27
3. AIMS OF THE STUDY ..................................................................................................................... 30
4. SIGNIFICANCE OF TITANIUM OXIDE LAYERS ....................................................................... 31
  4.1. Materials and methods ................................................................................................................ 32
    4.1.1. Sample fabrication ............................................................................................................. 32
    4.1.2. Sample characterization ................................................................................................... 34
  4.2. Results ....................................................................................................................................... 36
  4.3. Discussion .................................................................................................................................. 39
    4.3.1. On ALD manufactured TiO\(_2\) layers .................................................................................. 39
    4.3.2. On scanning acoustic microscopy ..................................................................................... 39
    4.3.3. On three-point bending testing ......................................................................................... 40
    4.3.4. On titanium and oxygen .................................................................................................. 40
  4.4. Conclusions ................................................................................................................................. 46
5. PHOTONDOUCED SUPERHYDROPHILICITY .............................................................................. 47
  5.1. Materials and methods ................................................................................................................ 49
    5.1.1. Sample fabrication ............................................................................................................. 49
5.1.2. Photoinduced hydrophilicity characterization ................................................................. 50
5.2. Results .................................................................................................................................. 51
5.3. Discussion ............................................................................................................................... 54
  5.3.1. On titanium as photoactive material ................................................................................ 54
  5.3.2. On light source, UV parameters and achieved hydrophilicity ........................................ 56
  5.3.3. On Ti wetting with dental ceramics ................................................................................ 57
5.4. Conclusions ............................................................................................................................ 58

6. SILVER INTERLAYERS ........................................................................................................... 59
  6.1. Materials and methods ........................................................................................................ 60
    6.1.1. Sample fabrication ........................................................................................................ 60
    6.1.2. Sample characterization ............................................................................................... 61
  6.2. Results .................................................................................................................................. 62
  6.3. Discussion ............................................................................................................................... 68
    6.3.1. On the biocompatibility of Ag ...................................................................................... 69
    6.3.2. On oxygen dissolution ................................................................................................. 69
    6.3.3. On plastic deformation and bond strength results ....................................................... 69
    6.3.4. On applicability and blasting particle contamination ................................................... 71
  6.4. Conclusions ............................................................................................................................ 72

7. PHOTOLITHOGRAPHIC ETCHING ...................................................................................... 73
  7.1. Materials and methods ........................................................................................................ 74
    7.1.1. Sample fabrication ........................................................................................................ 74
    7.1.2. Sample characterization ............................................................................................... 76
  7.2. Results .................................................................................................................................. 76
  7.3. Discussion ............................................................................................................................... 80
    7.3.1. On test results and reaction layers .............................................................................. 80
    7.3.2. On photolithographic etching ..................................................................................... 81
  7.4. Conclusions ............................................................................................................................ 82

8. GENERAL DISCUSSION ......................................................................................................... 83
  8.1. On the need for novel and enhanced titanium metallo-ceramics techniques ..................... 83
  8.2. On metallo-ceramic joints and fractography ...................................................................... 83
  8.3. On future aspects .................................................................................................................. 86

9. CONCLUSIONS ...................................................................................................................... 89

10. TIIVISTELMÄ SUOMEKSI .................................................................................................... 90

REFERENCES ............................................................................................................................. 94
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFAP</td>
<td>area fraction of adherent porcelain</td>
</tr>
<tr>
<td>ALD</td>
<td>atomic layer deposition</td>
</tr>
<tr>
<td>ASM</td>
<td>American Society for Metals</td>
</tr>
<tr>
<td>CAD</td>
<td>computer-aided design</td>
</tr>
<tr>
<td>CAM</td>
<td>computer-aided manufacturing</td>
</tr>
<tr>
<td>CB</td>
<td>conductance band</td>
</tr>
<tr>
<td>cpTi</td>
<td>commercially pure titanium</td>
</tr>
<tr>
<td>CTE</td>
<td>coefficient of thermal expansion</td>
</tr>
<tr>
<td>E_BG</td>
<td>band gap energy</td>
</tr>
<tr>
<td>EDS</td>
<td>energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>FPD</td>
<td>fixed partial denture</td>
</tr>
<tr>
<td>IMC</td>
<td>intermetallic compound</td>
</tr>
<tr>
<td>MPIIID</td>
<td>metal plasma immersion ion implantation and deposition</td>
</tr>
<tr>
<td>ND/YAG</td>
<td>neodymium-doped yttrium aluminum garnet (laser)</td>
</tr>
<tr>
<td>SAM</td>
<td>scanning acoustic microscope</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>TI[O]_x</td>
<td>titanium oxygen solid solution (oxygen atoms in octahedral spaces of titanium lattice, not titanium oxide), see section 4</td>
</tr>
<tr>
<td>TPB</td>
<td>three-point bending</td>
</tr>
<tr>
<td>VB</td>
<td>valence band</td>
</tr>
<tr>
<td>WEDM</td>
<td>wire electric discharge machine</td>
</tr>
<tr>
<td>WDS</td>
<td>wavelength dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
This thesis comprises four intercomplementary parts that introduce new approaches to brittle reaction layers and mechanical compatibility of metallo-ceramic joints created when fusing dental ceramics to titanium.

The first part investigates the effects of TiO$_2$ layer structure and thickness on the joint strength of the titanium-metallo-ceramic system.

Three groups of standard metallo-ceramic samples with different TiO$_2$ layer thickness and crystal structure were tested. The TiO$_2$ layers were produced using atomic layer deposition (ALD). Scanning acoustic microscopy (SAM), three-point bending (TPB), cross-section microscopy, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS) were employed.

Samples with all TiO$_2$ thicknesses displayed good ceramics adhesion to Ti, and uniform TPB results. The fracture mode was independent of oxide layer thickness and structure. Cracking occurred deeper inside titanium, in the oxygen-rich Ti[O]$_x$ solid solution surface layer.

During dental ceramics firing TiO$_2$ layers dissociate and joints become brittle with increased dissolution of oxygen into metallic Ti and consequent reduction in the metal plasticity. To accomplish an ideal metallo-ceramic joint this needs to be resolved.

The second part introduces photoinduced superhydrophilicity of TiO$_2$.

Test samples with ALD deposited anatase TiO$_2$ films were produced. Band gap energy ($E_{bg}$) for the TiO$_2$ layers was estimated from transmittance measurements. Samples were irradiated with UV light ($> E_{bg}$) to induce superhydrophilicity of the surfaces through a cascade leading to increased amount of surface hydroxyl groups. Samples were divided into two groups D and E to study the required irradiation time. Hydrophilicity of the TiO$_2$ surfaces was assessed by sessile drop contact angle measurements.

The reference contact angle prior to UV radiation was $\sim 55^\circ$. Superhydrophilicity (contact angle $\sim 0^\circ$) was achieved within 2 minutes of UV radiation. After initial partial recovery during the first 10 minutes, the contact angle remained below 20’ for 1h. Total recovery was not observed within 24h storage.

Photoinduced ultrahydrophilicity can be used to enhance wettability of titanium surfaces, an important factor in dental ceramics veneering processes.

The third part addresses interlayers designed to restrain oxygen dissolution into Ti during dental ceramics fusing.
The main requirements for an ideal interlayer material are proposed. Based on these criteria and systematic exclusion of possible interlayer materials silver (Ag) interlayers were chosen. Six groups of standard metalloceramic samples were studied. Groups F, J, K and L were Al₂O₃-blasted, Groups G and H were left polished. Thin silver interlayers were produced on Groups G, H, J and K by using the DIARC® plasma coating method and thicker interlayers on Group J by electrochemical baths. Analysis methods were as in the first part.

Good ceramics adhesion to titanium was observed in all test groups save for G and H, which both exhibited several areas of poor contact. SEM/EDS analyses revealed attachment of alumina particles on the Al₂O₃-blasted titanium. Ag covered this contamination in Group L. TPB results were significantly better in Group L samples compared to Group F. Generally, cracking occurred inside titanium in oxygen-rich Ti[O]ₓ solid solution (F, G, H, J, K), locally also between Ti and dental ceramics (K, L). In Group L multiple cracks occurred inside dental ceramics, none inside Ti structure.

Ag interlayers of 5 μm on Al₂O₃-blasted samples can be efficiently used to retard formation of the brittle oxygen-rich Ti[O]ₓ layer, thus enhancing metalloceramic joint integrity. Based on the literature, isolation of alumina blasting particle contamination was also considered beneficial. The most brittle component in metalloceramic joints with 5 μm Ag interlayers was bulk dental ceramics instead of Ti[O]ₓ.

The fourth part investigates the importance of mechanical interlocking and presents a new approach to overcome mechanical problems of brittle reaction layers.

Mechanically polished, Al₂O₃-blasted, and photolithographically etched standard metalloceramic samples, Groups M, N and P, showed no significant TPB test differences. Cracking occurred through Ti[O]ₓ, but in photolithographically etched samples also locally through dental ceramics.

Hence, the significance of mechanical interlocking achieved by conventional surface treatments can be questioned as long as the formation of the brittle layers (mainly oxygen-rich Ti[O]ₓ) cannot be sufficiently controlled. Photolithographically etched pits can be used to cause cracking of dental ceramics instead of the more brittle reaction layers. The current depth and steepness of the pits, however, were insufficient for extensive stress redistribution.

In summary – in contrast to former impressions of thick titanium oxide layers – this thesis clearly demonstrates diffusion of oxygen from sintering atmosphere and SiO₂ to Ti structures during dental ceramics firing and the following formation of brittle Ti[O]ₓ solid solution as the most important factors predisposing joints between Ti and SiO₂-based dental ceramics to low strength. This among other predisposing factors such as residual stresses created by the coefficient of thermal expansion mismatch between dental ceramics and Ti frameworks can be avoided with Ag interlayers.
1. INTRODUCTION

Titanium is a widely used material in prosthetic dentistry. It first became renowned after the pioneering research and good clinical results on titanium dental implant fixtures by P-I Brånemark et al., and has been used in metalloceramic crowns since the 1970s. Recent progress in CAD/CAM processing methods has made wrought titanium solutions possible in addition to ordinary cast titanium applications, increasing titanium’s applicability and use in dental metalloceramics. Current developments in framework production techniques, excellent corrosion resistance and documented biocompatibility have made titanium a reasonable choice compared to considerably more expensive gold and palladium alloys in crown and bridge designing as well as overlay dentures. This brings esthetic and durable fixed prosthetics into the reach of a vast number of new people offering a chance to enhance patients’ quality of life.

The high reactivity of titanium presents a problem in fusing of dental ceramics to titanium structures, however: joints are relatively brittle. There are many factors behind this, including differences in the coefficient of thermal expansion (CTE) between metallic frameworks and ceramics materials; use of too high fusing temperatures or framework casting and subsequent α-case layer formation; and brittle reaction layers formed through diffusion of oxygen and ceramics material into the titanium lattice. While different approaches including low-fusing dental ceramics, surface roughening and various bonding agents have been adapted to enhance mechanical integrity of joints, dissolution of oxygen into metallic titanium during dental ceramics firing, related solid solution strengthening and significantly reduced plasticity of surface layers of metallic titanium remain a practical problem.

Recent publications have stated a concern about the insufficient amount of research of titanium-based metalloceramics [Garbelini et al. 2003, Vásquez et al. 2008]. While adherence problems between titanium and dental ceramics have been considered the main limiting factor in manufacturing titanium-ceramic restorations for decades [Wang et al. 1999], understanding the effects of different surface treatments on the formation of critical reaction layers in titanium-ceramics joints is still defective. Thorough fractographic analyses, i.e. identification of crack initiation, pattern of crack propagation, energetics of the fracture and classification of the phases along the fracture plane have been infrequent [Marshall et al. 2010]. Use of titanium-based metalloceramics, however, is already established in routine dental technology, healthcare practice and patients’ knowledge. Thus it is of the foremost clinical importance and duty to study and solve problems associated with fusing dental ceramics to titanium.
2. REVIEW OF THE LITERATURE

The focus of the study is on brittle reaction layers in joints between dental ceramics and titanium. The first part of the literature overview gives a general introduction to titanium in comparison to other metals in dental metallo-ceramics – such as gold, palladium, their alloys and cobalt chromium – and to clinical performance of titanium-based metallo-ceramics. The second part discusses the most important factors influencing integrity of joints between Ti and dental ceramics. The third part of the review addresses methods designed to increase joint strength are discussed. The last section introduces available methods to study metallo-ceramic joints.

2.1. Titanium in comparison to other metals in dental metallo-ceramics

Expensive conservative noble alloys in fixed prosthodontics have been gradually replaced by more affordable base metal alloys [Yilmaz & Dinçer 1999, Roach 2007, Roberts et al. 2009]. Noble alloys are usually based on gold or palladium and comprise alloys such as Au-Pt-Pd, Au-Pd, Au-Pd-Ag, Pd-Ag, Pd-Cu and Pd-Ga. Base metal alloys consist of nickel- (Ni) and cobalt- (Co) based solutions, both containing chromium (Cr) as their second largest constituent. In addition to high cost, low sag resistance of noble alloys inflicts limitation of applications to crowns and fixed partial dentures (FPDs) with restricted amount of units, and some alloys also display discoloration of dental ceramics. [Roberts et al. 2009] Casting techniques and handling of noble alloys is, however, well known and has been in clinical use and the focus of follow-up for decades. Investigation on fusing of dental ceramics to gold alloys was roughly at the same stage in Finland in the 1970s [Yli-Urpo 1975] as the corresponding study of titanium alloys presently is. Unfortunately, some of the methods subsequently developed for improving on this joint are not applicable to titanium [Kimura et al. 1990].

Also base metal alloys portray several problems. Carpenter and Goodkind [1979] stated, based on their investigations and evaluation of surface texture for roughness, surface area, re-entrant angles and stress concentration of Au-Ag-Pd and Ni-Cr alloys, that in dental ceramics, veneering wetting of metal surfaces of the precious alloy was better than that of the nonprecious alloy. Further disadvantages of base metal alloys are poor biocompatibility, low corrosion resistance, and discoloration of porcelain [Yilmaz & Dinçer 1999]. Nickel-chromium-beryllium alloys can no longer be recommended because of the health concerns associated with beryllium. For patients allergic to nickel, cobalt-chromium alloys have been the most common base-metal alternative. [Roberts et al. 2009]
Titanium provides a competitive alternative both in affordability and biocompatibility. It has many advantages and favorable properties over the other dental alloys and Ti restorations are definitely much cheaper than their gold alloy counterparts [Vásquez et al. 2008]. Titanium is considered to be the most biocompatible metal for dental prostheses [Roberts et al. 2009]. Even with gold (Au), a positive relationship between contact allergy to gold and the amount of dental gold surfaces in oral cavity and dose-related release of gold into blood plasma from dental gold restorations has been suggested [Ahlgren et al. 2002, Ahlgren et al. 2007]. Thus, Ti has been a welcomed material in prosthodontics.

Even though there are not as many or as long follow-up studies with titanium metalloceramics as with traditional noble alloy metalloceramics, the first results of clinical performance look promising [Nilson et al. 1994, Walter et al. 1994, Kaus et al. 1996, Lövgren et al. 1997, Chai et al. 1997, Milleding et al. 1998, Smedberg et al. 1998, Bergman et al. 1999, Walter et al. 1999, Lövgren et al. 2000]. Survival rate varying from 84% to 99% in follow-ups of 1 to 6 years, as well as changes mainly from excellent to acceptable in the California Dental Association (CDA) ratings for surface, color and anatomic form, have been reported [Table 1]. Good margin integrity, high patient acceptance and low incidence of caries have also been stated. Modern individual design of outer surfaces of titanium copings not executed in some of the older studies might further improve the success rates and reduce ceramic material failures by optimizing stress distribution [Nilson et al. 1994, Bergman et al. 1999].

Nilson et al. [1994] compared results from their clinical studies with titanium metalloceramics to previous follow-up studies where survival rates concerning ceramics material defects were 90% with cast palladium (Pd) base alloy FPDs after 3 years and 97-98% in conventional metalloceramic restorations after 10 years. In a 5-year study comparing veneers on titanium and a gold alloy [Walter et al. 1999], the respective intact dental ceramics survival rates of 84% and 98% were reported. No significant difference, however, was found in defects requiring removal of the studied FPDs. A single such case, from metalloceramic joint fracture, was observed with titanium framework. The rarity of such defects, however, suggested clinical suitability of titanium veneers.

In addition to clinical studies, suitability of titanium for long term use has been studied by evaluating the effects of thermal and mechanical cycling on flexural strength of metalloceramic joints [Vásquez et al. 2007, Oyafuso et al. 2008, Vásquez et al. 2009]. Bond strength results are influenced by numerous factors difficult to equalize, yet they can be used for rough comparison between different systems. Oyafuso et al. [2008] compared gold alloy and titanium-based metalloceramic systems, showing on average higher three-point bending test results for the gold alloy systems (55 MPa vs. 32 MPa), regardless of the fatigue conditions imposed. Mechanical and thermomechanical fatigue conditions decreased the test results significantly for both systems. Vásquez et al. [2009] tested three dental ceramics materials designed for titanium and one control group designed for Au-Pd alloy. Shear bond strength results of the titanium-based systems ranged between 42 and 64 MPa, one system.
even exceeding results achieved with Au-Pd alloy (61 MPa). The study also included mechanical and thermal cycling, which had a significant impact on the dental ceramics material systems designed for titanium but not on the reference system designed for Au-Pd. In an earlier study Vásquez et al. [2007] studied the effects of mechanical and thermal cycling on three-point bending test results of three different dental ceramics materials fused to titanium. Control values between 33 MPa and 39 MPa were decreased to 27-28 MPa, significantly for all the tested metalliceramic combinations.

Pang et al. [1995] reported bond strength of dental ceramics fired on cast titanium or fired on machine-milled titanium to be statistically comparable yet also statistically inferior to results achieved with palladium-copper alloy dental ceramics system. The respective mean loads at bond failure in three-point bending test were 8 N, 7 N and 13.5 N, which is still equivalent to bond strength close to 40 MPa for the dental ceramics system used with titanium. The elastic modulus of the cast titanium is not stated in the paper, however, and so the bond strength results are not easily comparable with other studies. Dérand and Herø [1992] reported high bond strength values of 40-50 MPa in a four-point bending setup with titanium-based metalloceramics close to values recorded with palladium alloys veneered with dental ceramics in a previous study by Syverud, Kvam and Herø [1987]. Homann et al. [2006] studied strain energy release rate in four-point bending for Ti metalloceramic test samples and a gold-palladium reference group. One low fusing dental ceramics bonder and two gold materials were also tested with the titanium system. Higher interfacial toughness values were achieved with the two gold bonder materials than with the gold-palladium reference samples. Normal paste bonder performed worst in these tests. Yılmaz and Dinçer [1999] suggested bond compatibility cast titanium-based metalloceramics to be comparable with the Ni-Cr dental ceramics system – even without reporting of special removal of the α-case layer [see section 2.2.3.]. Atsü and Berksun [2000] reported three-point bending test values of three different dental ceramics systems with titanium to range from 33% to 60% of the results achieved with a Ni-Cr control group. All bond strength results were considerably poor. Özcan and Uysal [2005] reported three-point bending test values of SiO2-coated titanium samples with applied dental ceramic systems and titanium to be 47% to 64% of the values achieved in the control group with dental ceramics applied on Ni-Cr.

Even though the most typical failures in clinical tests occur inside dental ceramics, and only rarely in joints between titanium and ceramic material, mechanical tests generally imply inferior bond strength in titanium-based systems compared to noble alloys [Pang et al. 1995, Oyafuso et al. 2008, Vásquez et al. 2009]. According to recent reviews titanium-based metalloceramics would appear to have a promising future in fixed prosthodontics as a biocompatible and less expensive solution, though much work remains in optimizing the dental ceramics fusing methods [Haag & Nilner 2007, Roberts et al. 2009].
## TABLE 1.
**CLINICAL PERFORMANCE OF Ti METALLOCERAMIC SYSTEMS**

<table>
<thead>
<tr>
<th>Study</th>
<th>Survival Rate (single crowns or FPD’s) (%</th>
<th>Follow-up (months)</th>
<th>n (units)</th>
<th>Failure in</th>
<th>Main CDA changes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nilson et al. 1994</td>
<td>96 (single crowns) / intact ceramic veneer</td>
<td>26-30</td>
<td>44</td>
<td>bulk ceramics</td>
<td>excellent to acceptable</td>
</tr>
<tr>
<td>Walter et al. 1994</td>
<td>95 (both) / no need of removal</td>
<td>36</td>
<td>147</td>
<td>----N/A----</td>
<td>----N/A----</td>
</tr>
<tr>
<td></td>
<td>84 (both) / intact ceramic veneer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaus et al. 1996</td>
<td>98 (both) / no need of removal</td>
<td>30</td>
<td>116</td>
<td>both bulk ceramics chipping and veneer loss</td>
<td>no statistically significant</td>
</tr>
<tr>
<td></td>
<td>85 (single crowns) / intact ceramic veneer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>59 (FPD’s) / intact ceramic veneer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lövgren et al. 1997 &amp; 2000</td>
<td>99 (single crowns) / cumulative success rate</td>
<td>60</td>
<td>333</td>
<td>bulk ceramics</td>
<td>excellent to acceptable</td>
</tr>
<tr>
<td></td>
<td>98 (FPD’s) / cumulative success rate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>94 (single crowns) / intact ceramic veneer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>87 (FPD’s) / intact ceramic veneer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chai et al. 1997</td>
<td>99 (single crowns) / no need of removal</td>
<td>12</td>
<td>232</td>
<td>bulk ceramics</td>
<td>no statistically significant</td>
</tr>
<tr>
<td></td>
<td>98 (FPD’s) / no need of removal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>98 (FPD’s) / intact ceramic veneer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Milleding et al. 1998</td>
<td>98 (single crowns) / intact ceramic veneer</td>
<td>24</td>
<td>40</td>
<td>bulk ceramics</td>
<td>excellent to acceptable</td>
</tr>
<tr>
<td>Smedberg et al. 1998</td>
<td>96 (FPD’s) / intact ceramic veneer</td>
<td>24</td>
<td>151</td>
<td>----N/A----</td>
<td>excellent to acceptable</td>
</tr>
<tr>
<td>Bergman et al. 1999</td>
<td>93 (single crowns) / intact ceramic veneer</td>
<td>60-78</td>
<td>44</td>
<td>----N/A----</td>
<td>excellent to acceptable</td>
</tr>
<tr>
<td>Walter et al. 1999</td>
<td>95 (FPD’s) / no need of removal</td>
<td>72</td>
<td>75</td>
<td>both metal-ceramic joint and bulk ceramics</td>
<td>----N/A----</td>
</tr>
<tr>
<td></td>
<td>84 (FPD’s) / intact ceramic veneer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*FPD = fixed partial denture*
2.2. Factors influencing joint integrity

Success of porcelain-fused-to-alloy restorations has traditionally been considered to depend acutely on success of strong bonding between dental ceramics and metal frameworks [Wang et al. 1999]. There are several different factors that influence joints between titanium and dental ceramics. Most of the major complications of joint integrity arise from the dental ceramics fusing processes. Different furnaces, dental ceramics materials and firing programs have been developed in attempt to find the most suitable way to produce an esthetical and functional tooth like ceramic veneer on titanium supporting structure.

Dental ceramics fusing processes consist of consecutive material application and firing steps. Ceramics material is stored as powder to which a lubricant agent is added prior to use. The material is applied onto titanium surfaces with fine instruments such as various sized paintbrushes. Sintering of the applied ceramics is performed in a dental ceramics firing furnace, including first an optional bonder material firing step, then opaque powder firing steps, bulk/dentin material firing steps and a final glaze firing. Recommended parameters of the steps vary between dental ceramics manufacturers. The material and equipment choices affect parameters such as coefficient of thermal expansion (CTE) compatibility between dental ceramics and Ti, and firing temperature, atmosphere and vacuum influencing oxygen dissolution during the firing process, both critical factors to joint integrity between titanium and dental ceramics.

Some of the quintessential problems are solved but some only depressed. The most important factors influencing joint integrity are reviewed in the following section.

2.2.1. Coefficient of thermal expansion (CTE)

Strengthening of ceramics material occurs through one or two mechanisms: by the development of residual compressive stresses within the surface of the ceramics material, and by interruption of crack propagation through the material [Reyes et al. 2001]. The most common way of strengthening ceramics is by introducing residual compressive stresses within the ceramics surface so that tensile stresses must first exceed the applied residual compresion before any net tension will develop and lead to crack initiation and propagation. A common way to achieve the wanted compressive stress on the ceramics surface is through thermal tempering; a rapid cooling of the material surface is performed while the material remains hot and in its molten state. The pull of the slower solidifying and shrinking ceramics core develops net residual compressive stresses within the outer surface.

When objects consisting of titanium and dental ceramics mass go through a glass sintering firing step, a joint forms between the ceramics and titanium. During the cooling process, the component with the greater CTE value will shrink more, causing a residual stress state to the joint even if the metallocceramic restoration is not subjected to any external stress.
If the CTE of the metal coping is greater than that of dental ceramics, the porcelain will be placed under compression along the interface on cooling. Some authors suggest the CTE of dental ceramics and titanium should be equal in behavior, while others suggest a slight mismatch leads to creation of the required residual compressive stresses of dental ceramics to strengthen the complete restoration [Yilmaz & Dinçer 1999, Bieniaš et al. 2009]. Even higher CTE values for dental ceramics than for Ti structure have been encouraged [Dérand and Herø 1992]. This would lead to an unfavorable stress state in joints, however, causing residual tensile stresses. For example, the CTE of a common commercial dental ceramics material designed for titanium copings, DuceratinPlus® (DeguDent, Dentsply International), is advertised to be $9.5 \cdot 10^{-6} \text{ K}^{-1}$ for the first Opaque layer and $8.7 \cdot 10^{-6} \text{ K}^{-1}$ for the bulk Dentine ceramics. The mean CTE of linear expansion for commercially pure titanium (cpTi, ASTM grades 1-4) is $10 \cdot 10^{-6} \text{ K}^{-1}$ between 0-815 ºC and $9.7 \cdot 10^{-6} \text{ K}^{-1}$ between 0-540 ºC [Boyer et al. 1994] ($T_{\text{max}}$ of DuceratinPlus firing protocol is 780 ºC). This will produce a two-stage compression effect; one on the ceramics layer closest to titanium compared to the Dentine ceramics of the bulk ceramics restoration and another between the titanium and the Opaque ceramics perhaps strengthening the ceramics and the joint.

Kimura et al. [1990²] showed how metalloceramic joint of low fusing dental ceramics with CTE greater than that of titanium failed during dental ceramics firing. Kimura et al. also suggested that thermal compatibility of porcelain-metal systems appears more dependent on the opaque ceramics than the body ceramics. Yilmaz and Dinçer [1999] showed a CTE value lower than that for titanium for the tested dental ceramics material at all temperatures. The bond compatibility between this dental ceramics material and titanium was found to be comparable to the conventional NiCr alloy system used in the study. They also suggested that the expansion coefficient mismatch between titanium and the used dental ceramics was above the proposed thermal compatibility and thus thermal compatibility was not observed. This CTE mismatch was later questioned in another study since the values disclosed by manufacturers for the same dental ceramics material were higher and thus the mismatch more appropriate [Garbelini et al. 2003].

Nielsen and Tuccillo [1972] studied a gold-porcelain system. They considered shear strength of the joint to be about 90 MPa and if thermal shear stresses that arise from a CTE mismatch approach or even exceed 90 MPa the joint would be destroyed. They also stated that it is difficult to select the upper temperature of the cooling range, at which the dental ceramics begin to behave as a shear-supporting solid. This temperature can be defined as the lowest temperature of a glass with an internal equilibrium in the distribution of clusters and domains that comprise the intermolecular structure, or when the glass begins to behave as a true shear-stress-supporting solid, instead of stress relaxing viscous glass. Both rate of cooling and degree of stress, however, changed this transition temperature. Nielsen and Tuccillo experimentally determined the temperature below that the used dental ceramics behaved as a rigid solid to be about 590 ºC. Thus a CTE mismatch of $0.23 \cdot 10^{-6} \text{ mm/mm-K}^{-1}$ would be safe, whereas one as high as $1.08 \cdot 10^{-6} \text{ mm/mm-K}^{-1}$ could be very harmful. The calculations were
based on stresses generated during cooling after one firing of opaque dental ceramics. Nielsen and Tuccillo also stated that evidence indicates that upon refiring the interfacial shear stress builds up to higher values due to transition temperature increase.

Besides individual material CTE values, the three dimensional design of the final restorations where metal copings are surrounded from multiple sides by dental ceramics must be accounted for; the net forces should never pull joints open and ceramics portions apart from more shrinking metal cores. The three dimensional shape of a metal ceramic restoration has a significant impact on the stresses that arise from a mismatch of expansion coefficients between metal and dental ceramics as represented already in 1972 [Nielsen & Tuccillo 1972]. Thus the effect of CTE mismatch differs greatly between simple veneers and full coverage crowns. Attention should also be paid in the design of supporting titanium structures and layering technique of ceramics material by dental technicians.

2.2.2. Wetting of titanium surfaces

Proper wetting of metal surfaces during dental ceramics veneering is essential [Carpenter& Goodkind 1979, Reyes et al. 2001]. The key principles for good interface formation can be considered to be creation of a clean surface; generation of a rough surface for interfacial interlocking; good wetting of frameworks by applied materials; adequate flow and adaptation for intimate interaction; and acceptable curing [Marshall et al. 2010] – i.e. sufficient sintering time and temperature, in the case for metalloceramics. Poor wetting prior to dental ceramics sintering may cause development of voids or air pouches in joints, which disrupt the ceramics structures during iterative firing cycles, or render metalloceramic constructions intact when observed visually, but at the same time joints incomplete and weak. Wetting is categorized from liquid contact angle [Figure 1] as non-wetting (>90˚), wetting (<90˚), and complete spreading (~0˚). Although all liquids do wet all solids to some extent, degree of wetting can be considered comparable to degree of adhesion, so that the goal should always be to select conditions that promote spreading [Marshall et al. 2010], as long as no other property crucial to good joint formation is compromised by doing so.
2.2.3. α-case layer

When dental ceramics for titanium were first developed, a problem related to titanium’s phase transformation emerged in the titanium casting processes and dental ceramics sintering processes using high fusing temperatures occupied from gold framework based metalloceramics. Pure titanium has two crystal forms: a close-packed hexagonal α-structure below 882 °C and a body-centered cubic β-structure above it. In the hexagonal structure, there is one octahedral site for each Ti atom. Dissolved oxygen atoms can occupy these octahedral sites, and as oxygen dissolves in titanium, a large amount of energy is released, making even dilute solutions of oxygen thermodynamically very stable. [Könönen & Kivilahti 2001]

The difference in oxygen contents between α- and β-structures at elevated temperatures can be substantial, owing to the hexagonal crystal structure of α-titanium. Increasing the amount of oxygen stabilizes the α-structure, making a larger percentage of the α/β-solution hexagonal. During cooling (e.g. after casting a fixed partial denture framework), the β-titanium will transform back to α-titanium. The α-titanium with high oxygen content formed during elevated temperatures does not convert into low-oxygen content α-titanium, because of the low kinetics, but forms instead the notorious α-case layer on top of underlying α-titanium with low oxygen content, transformed from the β-titanium [Figure 2]. Oxygen in the octahedral sites of the α-case layer expands the crystal lattice and reduces mobility of dislocations in the metal, making the layer harder, less plastic and more brittle than the underlying α-titanium. Consequential detachment of the α-case layer from the underlying titanium even in low stress is a problem – specifically in current conventional titanium casting, as high dental ceramics fusing temperatures exceeding the phase transformation temperature are no longer used. Instead, low-fusing dental ceramics materials with sintering

Figure 1. Schematic representation of contact angle. $\gamma_{xy}$ is the tension between liquid, solid and gas phases, the phases being identified by x & y.
temperatures below 882 °C are presently used, and the firing times are short. Thus, during normal fusing of modern dental ceramics designed for titanium, temperature of the titanium structure surfaces can never exceed the phase transformation temperature. After titanium casting, it is essential to remove the α-case-layer of the titanium frameworks prior to dental ceramics firing. [Könönen & Kivilahti 2001]

There are still many misinterpretations of the composition of the α-case layer in current papers, as it is commonly misreferred to as a thick layer of titanium oxide [Atsü & Berksun 2000, Garbelini et al. 2003, Vásquez et al. 2008]. Some studies even refer to using a dental ceramics material based bonding agent in a bid to circumvent the incompatibility problem between the α-case layer and dental ceramics [Vásquez et al. 2008]. Misunderstandings of this sort in the development, nature and handling of the α-case layer possess a clear threat to the clinical success of titanium metalloceramics. Large cast titanium

**Figure 2.** Section of the binary phase diagram of the Ti-O system illustrating formation of the α / β phase boundary and α-case layer [adapted from Massalski 1996]
structures are progressively being supplanted by CAD/CAM processed frameworks, which fortunately diminishes the amount of $\alpha$-case layer inflicted problems.

2.2.4. Oxygen and titanium oxides

Oxygen has several important roles regarding the integrity of joints between dental ceramics and titanium. As portrayed by the $\alpha$-case layer, abrupt differences of oxygen content below the titanium surface can be detrimental to metalloceramic restorations. Even without a distinct layer caused ultimately by the phase transformation during cooling from casting temperatures or the high sintering temperatures of early dental ceramics, the dissolution of oxygen into the titanium lattice, subsequent occupation of vacant octahedral sites and solid solution strengthening can make oxygen exposed surfaces of metallic frameworks brittle. The focus in most of the earlier and current publications, however, has been on titanium oxide layers rather than on the effects of dissolved oxygen in metallic titanium.

Kimura et al. [1990] used X-ray diffraction analyses to study oxide formation during fusing of dental ceramics to titanium. A heat treatment resembling a single firing cycle of dental ceramics was conducted in an ordinary dental ceramics fusing furnace on titanium samples without any dental ceramics application. A minor vacuum was used with half of the samples during ramping of temperature, and no vacuum was used with the other half. The maximum temperature ($T_{\text{max}}$ ranging between 600 to 1000°C) was held for 60 s prior to a cooling period of several minutes. Vickers hardness measurements and X-ray diffraction analyses were performed. A small peak of TiO$_2$ was observed on titanium samples heat treated at 800 °C and yet larger ones on samples heat treated at 900 °C and 1000 °C. After these measurements, dental ceramics were fired on the heat treated titanium samples. Tension-shear bond measurements were carried out. Titanium oxide detected in the first tests without dental ceramics application was blamed for adhesive failures observed in the tension-shear bond tests at what was stated as the metal-metal oxide interface of the second group of samples. Vickers hardness rose significantly when using a temperature of 1000 °C instead of 900 °C. In a similar study, Adachi et al. [1990] used 750 °C and 1000 °C heat treatments in an attempt to create oxide films and to measure oxide adherence strength. Heating started at 650 °C and the temperature was increased 55 °C/min to 750 °C or to 1000 °C. X-ray diffraction analyses revealed peaks of rutile TiO$_2$ and hexagonal close-packed Ti ($\alpha$-titanium) on samples heated in 1000 °C. No new peaks were detected in samples heated in 750 °C (close to the maximum firing temperature of modern low fusing dental ceramics designed for titanium) compared to unheated samples. The 1000 °C heat treatment reportedly produced oxide films with low oxide adherence strength, approximately 1 μm thick by visual estimate from SEM images.

These two papers published in the early 1990s designating titanium oxide to be the primary reason for poor strength of titanium-ceramics joints have subsequently been widely
2. REVIEW OF THE LITERATURE

referred to [Atsü & Berksun 2000, Suansuwan & Swain 2003, Garbelini et al. 2003, Yamada et al. 2005, Özcan & Uysal 2005, Vásquez et al. 2008]. The two studies, however, regarded neither exceeding the phase transformation temperature of titanium, nor the temperature accelerated dissolution of oxygen into the metallic titanium and the related solid solution strengthening. No conclusive measurement of oxide layer thickness was done [Kimura et al. 1990], or oxide layer thickness evaluation was done based on visual estimates [Adachi et al. 1990]. Thus, no clear evidence was portrayed as to whether cracking truly occurred through the metal-metal oxide interface as claimed. In addition, oxide formation was only studied on titanium samples exposed to dental ceramics sintering temperatures, but without actual application of the SiO$_2$-based dental ceramics, most probably influencing oxygen diffusion from atmosphere inside dental ceramics furnaces [Özcan & Uysal 2005]. Blaming titanium oxide for poor bonding without confirming the existence of a true oxide layer or performing a deeper study of joint interfaces is also a feature of more recent papers [Atsü & Berksun 2000, Garbelini et al. 2003, Özcan & Uysal 2005, Vásquez et al. 2008]. The problems associated with microanalyses of the oxygen-titanium system, solid solutions of Ti and oxygen and effects of actual TiO$_2$ layers and their significance in fusing of dental ceramics to titanium are discussed in later sections of this monograph.

2.2.5. Titanium silicides

Könönen and Kivilahti [1994 & 2001] have presented another brittle reaction layer responsible for the low strength of the titanium-dental ceramics system, the titanium silicide layers. The Ti-Si system comprises one non-stoichiometric (Ti$_5$Si$_3$) and four stoichiometric (TiSi$_2$, Ti$_2$Si, Ti$_5$Si$_4$, Ti$_3$Si) compounds. As dental ceramics fused to titanium are usually based on SiO$_2$ the most important elements reacting in metalloceramic joints are Ti, O and Si. While oxygen atoms can occupy vacant octahedral sites in the solid solution of titanium and oxygen, Si atoms reside in the same substitutional lattice as Ti atoms. The most prominent compound in titanium silicide layer is Ti$_5$Si$_3$(O) which contains 37.0-40.0 at% silicon. Könönen and Kivilahti [1994] have previously presented the Ti-O-Si phase diagram at 750 °C. The isothermal section of the system at 750 °C is depicted in Figure 3 with a predicted diffusion path of descending activity. As atoms cannot intrinsically diffuse in a direction in which their activities will increase, the phase diagram data, together with the related activity diagram, can be used to predict the layer sequence of the joint of titanium and dental ceramics:

$$\text{SiO}_2 \rightarrow \text{Ti}_5\text{Si}_3(\text{O}) \rightarrow \text{Ti}[\text{O}]_x \rightarrow \text{Ti}$$
Silicate glasses formed during the diffusion of Si from dental ceramics to titanium are extremely brittle. Despite the relatively low mobilities of the elements in the titanium silicides, extensively long firing times or iterative firing that might be needed in large multiple unit metalloceramic restorations could create a detectable thick brittle silicide layer, compromising the joint integrity. Using extended firing times at 800 °C, Könönen and Kivilahti demonstrated dual crack propagation through a silicide layer and titanium oxygen solid solution. As reactivity is necessary for chemical bonding, whereas in titanium-ceramic systems, brittle reaction products may impair mechanical compatibility of joints, complexity in fusing of dental ceramics to titanium is obvious. [Könönen & Kivilahti 1994]

Figure 3. Isothermal section of the Ti-O-Si system at 750 °C, near the dental ceramics fusing temperature, with predicted reaction path (dotted line) [adapted from Könönen & Kivilahti 1994 and 2001]
2. Methods to increase joint strength

Several different approaches have been tried in order to enhance joint strength between titanium frameworks and dental ceramics. Out of these, predominately Al$_2$O$_3$-blasting and dental ceramics paste bonders are in routine use. Even these methods need to be controlled and properly executed to attain beneficial results.

2.3.1. Surface roughening

To improve dental ceramics’ adhesion to titanium, the metal framework surfaces are commonly roughened. Aluminum oxide blasting is one method recommended by researchers and ceramics’ manufacturers [Mo et al. 2003, Al Hussaini & Al Wazzan 2005]. Al$_2$O$_3$-blasting has been reported to substantially improve the ceramics bonding, compared to polishing, Si-coating or pre-oxidation, by enabling microscopic interlocking, increasing the joint area and reducing the maximal tensile stresses in the interfacial regions [Carpenter & Goodkind 1979, Könönen & Kivilahti 1994, Mo et al. 2003]. In addition to enhancing mechanical retention, surface irregularities increase wetting of the metal surfaces by dental ceramics [Reyes et al. 2001]. Excessive surface roughening can result in stress concentration at ceramics-alloy interfaces, however, and steep re-entrant angles may not allow complete wetting and therefore result in air entrapment and voids at metalloceramic joints [Carpenter & Goodkind 1979]. Thus, it must be kept in mind that increasing surface roughness does not always lead to increased bond strength [Reyes et al. 2001].

Al$_2$O$_3$-blasting of metal surfaces prior to dental ceramics fusing has also been proposed for use in removal of debris that might cause surface contamination [Carpenter & Goodkind 1979]. Impurities in metalloceramic joints lead to lowering the external stresses that the titanium dental ceramics interfaces can sustain without failure [Dérand & Herø 1992]. Blasting particles themselves have been reported to cause abrasive contamination, however, which can potentially modify the physicochemical interaction capacity of blasted surfaces [Dérand and Herø 1992, Kern & Thompson 1994, Darwell et al. 1995, Papadopoulos et al. 1999, Cai et al. 2001, Bagno & Di Bello 2004]. Excess of Al in joints of titanium alloy and dental ceramics have also been suggested as the reason for reduced bond strength compared to the use of pure titanium [Yamada et. al 2005]. Ultrasonic cleaning of Al$_2$O$_3$-blasted titanium frameworks to remove loose surface particles prior to dental ceramics fusing has been recommended [Kern & Thompson 1994].

Blasting particle sizes between 50-250 μm, pressures of 200-400 kPa and times up to 10 seconds have been studied in surface roughening of cast and wrought Ti surfaces [Dérand & Hero 1992, Papadopoulos et al. 1999, Garbelini et al. 2003, Özcan & Uysal 2004, Vásquez et al. 2008]. No consensus of the best parameters exists, though particle size of 150 μm and blasting pressure of 200 kPa is a frequent combination [Garbelini et al. 2003, Vásquez et al.
Higher surface microhardness, small porosities, lower bond strength and increased particle number and area of contamination were all associated with blasting by the smallest Al₂O₃ particles [Papadopoulos et al. 1999, Dérand & Herø 1992]. Nevertheless, surfaces not receiving airborne-particle abrasion are considered to be prone to an unsatisfactory titanium-ceramic bond [Al Hussaini & Al Wassan 2005].

Titanium surface roughness can also be increased by chemical etching without the adverse effects of surface Al₂O₃ contamination [Reyes et al. 2001, Al Hussaini & Al Wassan 2005, Troia et al. 2008]. Multiple combinations of different acidic or caustic treatments are available, including 10-35 % HCl, 5-10 % HF, 50 % NaOH, 35 % HNO₃, H₂SO₄, H₂O₂ and HF/HNO₃/H₂O (1:1:2) preceded or followed by Al₂O₃-blasting, but not all of them are useful in enhancing bond strength, even if they are successful in increasing surface roughness [Troia et al. 2008, Reyes et al. 2001]. Application of caustic bath combined or non-combined with acidic baths was shown to be beneficial when used with following alumina blasting compared to solely Al₂O₃-blasted samples. Changes in elemental composition of the titanium surfaces were proposed to cause the improvement in test results, even though no compositional analysis of the titanium surfaces was reported [Troia et al. 2008]. The most promising of the acid treatments was HCl, yet some controversy exists [Reyes et al. 2001, Al Hussaini & Al Wassan 2005, Troia et al. 2008]. Since benefits of one and the same treatment cannot be considered reproducible, acid treatments will need much further study before they can be valuable for clinical use.

Some novel surface roughening techniques have also been proposed and tested to investigate their effectiveness [Inan et al. 2006, Kim & Cho 2009]. Laser etching with neodymium-doped yttrium aluminum garnet laser (Nd/YAG) resulted in markedly lower Rₘ values than Al₂O₃-blasting, but no significant difference emerged in shear bond strength test values. Since there was no alumina contamination of the Ti surfaces when using Nd/YAG, the question of possible disadvantages of Al₂O₃ residues to metalloceramic joint integrity is again evident [Kim & Cho 2009]. Surface roughening with spark erosion also produced improved Rₘ-values, yet Al₂O₃-blasted samples showed a tendency of slightly better TPB results. Spark erosion deforms the surface layers of titanium and causes microcracking, residual tensile stresses and other defects possibly detrimental to integrity of the titanium layers in contact with dental ceramics, thus complicating assessment of the effects of surface roughness or use of alumina on joint strength [Inan et al. 2006].

2.3.2. Bonding agents and interlayers

In addition to surface roughness modification, several different interlayer systems have been developed to enhance bond strength of dental ceramics fused to titanium. The most traditional interlayer between bulk dental ceramics material and titanium framework is dental ceramics based bonding agents also known as bonders. Bonding agents can be subdivided into low
viscosity ceramic bonders known as paste bonders, and special bonders containing additional elements like gold, not observed in bulk ceramics portions [Dérand & Herø 1992, Suansuw & Swain 2003, Homann et al. 2006]. Even though bonding agents are considered an essential factor, playing a major role in metalloceramic bonding, and most of the modern commercial dental ceramics systems are provided with a characteristic bonder, the results achieved with bonding agents remain inconsistent [Suansuw & Swain 2003].

Paste bonders of common dental ceramics materials are low fusing dental ceramics with low viscosity at the firing temperature, containing no fillers so that they could readily wet titanium surfaces and prevent diffusion of oxygen from the firing atmosphere to titanium and/or oxide layer formation during the next iterative firing cycles [Gilbert et al. 1994, Suansuw & Swain 2003]. Generally, they are considered beneficial [Atsū & Berksun 2000, Al Hussaini & Al Wassan 2005]. Yet it has been debated whether paste bonders are sufficiently tough to resist crack propagation, or in fact render metalloceramic joints to failure [Suansuw & Swain 2003]. Overly thick bonding agent layers should in any case be avoided. Atsū and Berksun [2000] suggested that bonder thickness of 30-40 μm could be considered an excessive width for an optimal bond.

Out of special bonders, bonding agents containing gold have been of special interest [Dérand & Herø 1992, Suansuw & Swain 2003, Homann et al. 2006]. Suansuw and Swain [2003] found that when using a gold-containing bonder, they could achieve greater critical strain energy release rate values ($G_c$) at crack tips for a specific load or stress than with conventional systems. They suggested that gold particles found in the bonding agent contributed to resisting crack extension through plastic deformation and thus in inflicting a more tortuous path for crack propagation. Also Dérand and Herø [1992] studied effects of a similar bonding agent, yet with opposite results. They observed significantly lower bond strengths in four-point bending tests. Flakes of gold were detected near the Ti surfaces. No trace of bond formation in the vicinity of these particles was observed. Homann et al. [2006] studied strain energy release rates in four-point bending test configuration for titanium metalloceramic test samples and a gold-palladium reference group. Two gold and one dental ceramics bonder material were tested in water and in kerosene that was supposed to serve as an inert environment. Higher interfacial toughness values were achieved with the two gold bonder materials than with the dental ceramics bonder. Reduced interfacial toughness values in water in the dental ceramics bonder group and the reference group were suggested to be related to stress corrosion and thus weakening of the bond strength.

As a noble metal, gold has been considered a good candidate for restraining oxygen diffusion from dental ceramics and firing atmosphere to titanium frameworks in many research hypotheses, and thus has also been researched as an interlayer material [Sadeq et al. 2003, Lee et al. 2004]. Sadeq et al. [2003] used approximately 1 μm of gold sputter coating on Al$_2$O$_3$-blasted titanium surfaces. Results acquired after artificial crack initiation using area fraction of adherent porcelain (AFAP) to evaluate bonding were inconsistent. Lee et al. [2004] studied 300 μm gold paste layers and 1-1.5 μm gold sputtering, alone and in
combination. Significant improvement in AFAP was found in samples with only sputter coating. X-ray diffraction (XRD) analyses revealed formation of rutile TiO$_2$ on uncoated control samples subjected to dental ceramics firing protocol without dental ceramics materials. No protection against fusing atmosphere originated oxygen was provided by a dental ceramics layer. Rutile was also detected on sputter coated samples without dental ceramics application. The authors suggested that given the limitations of XRD it was not possible to determine whether this layer was created through diffusion of oxygen through thin sputtered gold layer or through diffusion of titanium on the surface of gold. The authors did point out that the sputter coated gold layer contained many structural defects that could have provided diffusion paths for elements during dental ceramics firing. Conforming to this, a change in color of sputter coated samples was observed gradually along dental ceramics firing protocol. No change in color was observed on the group with thick gold paste during iterative firing sequences. Intermetallic compounds (IMCs) between gold and titanium were observed. Increased adhesion results were suggested to result mainly from the interfacial chemical bonding. It was stated that gold coatings used in this study were not effective barriers to completely protect titanium from oxygen during the dental ceramics firing but might alter the oxygen dissolution and formation of Ti[O]$_x$ solid solution. Gold intermediate layers have also been studied in metalloceramic systems using palladium as framework material. Okazaki et al. [1998] proposed good chemical bonding between gold and palladium and better bending test results with gold intermediate layers. Problems associated with IMCs and gold as an oxygen diffusion barrier for titanium during elevated temperatures are further discussed in section 6.

Wang and Fung [1997] investigated sputter coated and electroplated chromium as an oxygen diffusion barrier on titanium during dental ceramics firing. Oxidation at 750 °C, 850 °C and 950 °C was analyzed using thermogravimetry. Five groups with varying combination and application time of electroplating and/or sputter coating and one control group were tested. The best effect was achieved with combining introductory sputter coating with electroplating and using the longest application times. No attention was paid to the phase transformation of titanium during the heat treatment, nor was any discussion of the ratio of titanium oxide vs. the amount of oxygen diffused in metallic titanium stated. No tests were done to demonstrate applicability of chromium coatings with common dental ceramics materials. Wang et al. [1998] also studied palladium as an interlayer material using a scanning acoustic microscope (SAM) and four-point bending. Palladium coated samples had fewer interfacial defects and a higher load to failure than other groups. Here the use of chromium produced no differences from the control group.

The SiO$_2$-based interlayers with special application methods other than the normal dental ceramics layering technique used with SiO$_2$ paste bonders have been proposed in addition to different metallic interlayers [Wang et al. 1999, Özcan & Uysal 2005, Bieniaś et al. 2009]. Wang et al. [1999] studied 1 μm thick silicon nitride coatings, implemented through metal plasma immersion ion implantation and deposition (MPIIID), as an oxygen diffusion
barrier. $\text{Si}_3\text{N}_4$ was chosen because it was believed to be corrosion resistant at dental ceramics sintering temperatures and to bond well with Ti as well as dental ceramics. Ti samples coated with $\text{Si}_3\text{Ni}_4$ coating had mean four-point bending load to failure values six times higher than samples without the protective coatings. Cracking in samples with protective coatings occurred inside the dental ceramics and not at the Ti/$\text{Si}_3\text{Ni}_4$ coating or at the $\text{Si}_3\text{Ni}_4$-coating/dental ceramics interface. Coated samples thermocycled without dental ceramics, in simulation of dental ceramics firing process, demonstrated localized oxide formation on top of the Ti in areas of $\text{Si}_3\text{Ni}_4$ coating cracks. Here, nothing protected the framework from the firing atmosphere. Thus, one could expect accelerated oxygen dissolution into titanium lattice in the areas of protective coating cracks and subsequent oxide formation in the surface parts of Ti with oxygen amount exceeding the saturation solubility needed for formation of the first oxide. Özcan and Uysal [2005] used magnetron sputtering to create 500 nm thick $\text{SiO}_2$ coatings on titanium samples before applying dental ceramics, a method resembling the use of common low viscosity bonder ceramics. A well-attached and intact layer of $\text{SiO}_2$ on a titanium surface accomplished without excessive heating prior to the first high temperature cycle of dental ceramics firing can possibly diminish oxygen dissolution from the surrounding atmosphere even better than low viscosity ceramic bonders, thereby improving bond strength. Özcan and Uysal showed up to a 30% increase in bond strength when using $\text{SiO}_2$ coatings. Depending on the manufacturer, bonder ceramics include various amounts of Na, Al, K and Sn as components in contrast to pure $\text{SiO}_2$. According to Özcan and Uysal, these differences of bonder compositions might significantly affect their performance in metalloceramic joints. In a recent study Bieniaś et al. [2009] used a sol gel dipping technique to create 3 $\mu$m $\text{SiO}_2$ and $\text{SiO}_2$-$\text{TiO}_2$ interlayers, achieving significantly improved three-point bending test results. The $\text{SiO}_2$-$\text{TiO}_2$ interlayers proved more efficient than $\text{SiO}_2$-only interlayers. Cracking of joints after three-point bending occurred at the interfaces between the interlayers and dental ceramics material. Good adhesion of the interlayers to titanium remained after three-point bending. Therefore bond strength between sol gel interlayers and titanium was better than the bond strength between dental ceramics and titanium, but the bond strength between the interlayers and dental ceramics was still inferior to the strength of the used dental ceramics. The sol gel technique required two long heating steps; first 30 min at 500 °C and then 30 min at 750 °C [Bieniaś et al. 2009]. It should be noted here that $\text{SiO}_2$ is a source for formation of brittle titanium silicides in long firing cycles that can be detrimental for joints if a thick continuous layer is formed. $\text{SiO}_2$ is in itself one source for oxygen that can diffuse to titanium frameworks during elevated temperatures; thus it cannot be considered as an entirely ideal interlayer material [see sections 2.2.5.; 4.3.4.; section 6].
2.4. Testing joints between dental ceramics and titanium

Various tests have been designed and selected by researchers to evaluate and compare bond strengths of different metalloceramic systems. These tests can be classified according to the nature of stresses created such as shear, tensile, flexural strength, torsion or a combination of the previous. Unfortunately there is no consensus as to which method is the best or the most valid for clinical implications. [Hammad & Talic 1996] Studies concerning dental ceramics bond strength to framework alloys are very difficult because of the inherent myriad of variables that evolve during the fabrication of test samples and within the test designs themselves [Carpenter & Goodkind 1979].

Flexural tests belong to the most common mechanical crack initiating tests used amongst researchers. The most common bending test is the DIN 13 927 / ISO 9693 standard three-point bending test [Könönen & Kivilahti 1990, Boening et al. 1992, Gilbert et al. 1994, Pang et al. 1995, Pröbster et al. 1996, Oshida et al. 1997, Yılmaz & Dinçer 1999, Atsü & Berksun 2000, Reyes et al. 2001, Al Hussaini & Al Wazzan 2005, Özcen & Oysal 2005, Inan et al. 2006, Troia et al. 2008, Bieniaś et al. 2009, Papadopoulos & Spyropoulos 2009]. Various unstandardized four-point bending test setups have also been used [i.a. Carpenter and Goodkind 1979, Wang et al. 1998, Suansuwan and Swain 2003, Yamada et al. 2005, Homann et al. 2006]. Carpenter and Goodkind [1979] stated that four-point bending and similar three-point flexural bend tests are affected by inherent design-induced stress concentration characteristics and that the stress concentration in the tests is nonuniform and varied, causing the test results to be prone to error. Because test results are dependent on the elasticity of the tested alloy, an alloy with a greater modulus of elasticity will also resist bending to a greater extent, producing higher bond strength results. This can complicate comparison of bond strength results of metalloceramic samples with different framework materials. The evident advantages of flexural tests are simplicity and ease of fabrication. When the cpTi frameworks are used, rough comparison of results between different studies can be done.

Various additional crack initiating mechanical tests including pull-through and push-through tests, planar interface shear tests, oblique shear tests, conical interface shear tests, tension tests, bending tests and torsion tests have been presented. Experimental variables in each test set are common and must be recorded well and minimized by means of standardization within the chosen research frame. No single test method can be universally nominated to be the most valid for clinical implications [Carpenter and Goodkind 1979, Hammad & Talic 1996]. Because the stress states generated by different tests are remarkably complex the term bond strength in separate studies can consist of various different subcomponents and be in itself misleading. All bond strength results should thus be considered as results of the specific test used in the given study and best comparable to other results achieved using the same test method in the very same or possibly another similar study.
Thorough evaluation of crack propagation in metal-ceramic failures is always important, even though cohesive failures within dental ceramics have been used as an indication of clinically acceptable bond strength [Hammad & Talic 1996]. Currently this is considered insufficient, and thorough fractography – identification of fracture origin (crack initiation), direction and pattern of crack propagation, energetics of the fracture (single event or fatigue; brittle or ductile), and the phases included along the fracture plane – found rare and one of the future challenges in dental materials research [Marshall et al. 2010]. Studying cracks initiated by bending tests can be much more informative than bond strength results achieved from the actual bending tests. Prevailing means for examining cracked samples is scanning electron microscopy (SEM) and the related specimen preparation methods including cross sectioning, epoxy casting, and sputtering techniques. Cracked specimens can be studied either with or without invasive cross sectioning. When a metalloceramic sample is separated into two individual samples, the fracture surfaces can be examined without excessive invasive methods. Many studies publish images and findings from surfaces of framework alloys, such as evaluations of area fraction of adherent porcelain (AFAP) [Adachi et al. 1990, Sadeq et al. 2003, Lee et al. 2004]. Only the examination of both detached samples will, however, reveal the level of cracking and the adjacent material zones along the fracture plane. This allows the determination of whether poor bonding resulted in cracking in an adhesive manner between the dental ceramics material and alloy frameworks or has the cracking occurred inside the brittle surface layers of titanium in which case traces of Ti can be found on the surfaces of detached dental ceramics parts. Even though the latter is not truly an adhesive failure type, typically only cracking of dental ceramics and coexistent intact joints between dental ceramics and framework alloy are referred to as cohesive cracking. Some studies have shown no correlation between AFAP and the force needed to joint failure [Papazoglu & Brantley 1998]. The benefits of using AFAP alone in evaluation of joint quality can therefore be questioned.

SEM studies can be further extended with X-ray microanalyses [Atsū & Berksun 2000, Suansuwan & Swain 2003, Lee et al. 2004, Vásquez et al. 2008, Vásquez et al. 2009]. Many SEM units are equipped with energy dispersive X-ray spectroscopy (EDS) capability. EDS can be used to evaluate the element compositions of single measurement points, defined as areas of specimen surface or used in line scan mode to study elemental gradients across selected interface or joint. It can be efficiently used to examine interface of Si and Ti. After personal communication with E. Heikinheimo (Chief engineer at Dept. of Materials Science & Engineering, Helsinki University of Technology), however, it is evident that microanalyses have some important limitations in studying brittle reaction layers of titanium-based metalloceramics, especially when using EDS, that are perhaps not emphasized enough in previous research. Low X-ray yield and high absorption of oxygen combined with low current used in energy dispersive X-ray spectroscopy all account for low count rates when analyzing solutions of Ti and O, the most brittle layers of titanium-ceramics joints [Hautaniemi et al. 1992, Könönen & Kivilahti 1994]. Another error source is created by sensitivity to surface

28
contamination of metalloceramic microanalysis samples and low peak to background ratio when analyzing crosssection samples with native TiO$_2$ scales only 3-8 nm thick [Lausmaa 1996, Poilleau et al. 1997, McCafferty & Wightman 1999, Sittig et al. 1999]. Peak overlaps can also predispose to inaccurate interpretation of EDS microanalysis results. Peaks for O-K$_\alpha$ and Ti-L$_\alpha$ are close to each other – 0.523 keV and 0.452 keV respectively – and easily misread. Therefore, evaluating the ratio of Ti and O using only energy dispersive X-ray spectroscopy can not be considered exact or reliable. Wavelength dispersive X-ray spectroscopy (WDS) offers better accuracy due to a higher peak to background ratio and higher spectral resolution (typically EDS resolution is ~150 eV, versus WDS resolution which is ~5 eV) constituting fewer peak overlaps (sharper peaks) and less spectral interferences. Expensive WDS equipment is not as common as EDS equipment and thus is used only in an extremely limited number of existing literature of titanium-ceramics joints studies [Könönen & Kivilahti 1994]. EDS is more than adequate, however, for obtaining quantitative data about elements such as Si, Ti and Al, all important factors at metalloceramic joint interfaces.

Pouilleau et al. [1997] studied structure and composition of passive titanium oxide films with a wide array of other microanalysis and surface analysis methods including x-ray photoelectron spectroscopy (XPS), Rutherford back scattering, X-ray diffraction and atomic force microscopy. Native oxide film of SiC-polished samples, heat treatment generated films (400 °C during 10 min in air), and films generated by anodic oxidation were studied. Even though the study does not discuss dental metalloceramics, it provides good insight into the various methods and study of titanium oxide on titanium samples that are similar to those used in almost all dental titanium metalloceramics studies.

Metalloceramic joints can also be studied before any crack initiation in order to study inherent weaknesses related to poor wetting or cracking during dental ceramics fusing. Design of common DIN 13 927/ISO 9693 [1990 and 1999] metalloceramic three-point bending test samples with dental ceramics of standard dimensions fused on titanium are ideal for non-invasive analyses using a scanning acoustic microscope (SAM). SAM analyses are based on differences in the specific acoustic impedance of studied materials and can efficiently detect interfaces between dense materials such as titanium and voids possibly created in metalloceramic joints. The most pronounced benefit of this method is the possibility for non-destructive evaluation of test samples [Wang et al. 1998]. Resulting data can be used to concentrate further crosssection sample analyses on the most interesting areas. The results of SAM analyses have been shown to correspond well to bending test results [Könönen & Kivilahti 1991, Könönen & Kivilahti 1994, Wang et al. 1998].
3. AIMS OF THE STUDY

This study of modern dental titanium metallo-ceramics demonstrates the significance of brittle reaction layers as the limiting factor for strength of joints between titanium structures and dental ceramics, and presents new, interdisciplinary solutions to increase bond strength.

The main aims are:

I. To investigate the direct effects of crystallinity and thickness of the titanium frameworks’ TiO$_2$ layers on bond strength. The hypothesis is that TiO$_2$ layer thickness prior to dental ceramics fusing is insignificant to the joint brittleness.

II. To introduce special photoinduced wetting properties of TiO$_2$. According to hypothesis, superhydrofilicity of TiO$_2$ surfaces can be achieved within minutes of ultraviolet activation.

III. To restrain oxygen dissolution into the titanium lattice during dental ceramics fusing. According to the hypothesis, Ag interlayers produced on titanium surfaces can suppress diffusion of oxygen into titanium structures and thus prevent formation of excessively thick and brittle oxygen-rich Ti[O]$_x$ layers.

IV. To study stress redistribution in photolithographically etched samples and the importance of mechanical interlocking. According to the hypothesis, preventing the formation of brittle reaction layers is more important than only enhancing the mechanical interlocking. Photolithographic etching increases the joint area and divides mechanical stress between brittle reaction layers and dental ceramics, which should prevent cracking of continuous planar reaction layers.
4. SIGNIFICANCE OF TITANIUM OXIDE LAYERS

A native oxide layer of 3–8 nm [Lausmaa 1996, Poilleau et al. 1997, McCaffery & Wightman 1999, Sittig et al. 1999, Brunette et al. 2001] almost instantaneously forms on metallic titanium at ambient atmosphere. This passivating, corrosion resistant oxide surface can be accredited for much of titanium’s biocompatibility. Titanium oxide has a variety of different stoichiometries from Ti$_3$O to Ti$_2$O, Ti$_3$O$_2$, TiO, Ti$_2$O$_3$, Ti$_3$O$_5$ and, most importantly, TiO$_2$ which is the main constituent of natural surface oxide films [Poilleau et al. 1997]. TiO$_2$ exists in three crystallographic forms (rutile, anatase and brookite), but although a certain degree of short-range order in the nanometer scale is likely to occur, thin surface oxides on bulk titanium are essentially non-crystalline [Kasemo & Lausmaa 1988, Browne & Gregson 1994, Brunette et al. 2001].

The titanium oxide layer is generally considered pernicious for dental metalloceramic systems’ mechanical integrity [Adachi et al. 1990, Kimura et al. 1990$^1$, Hautaniemi et al. 1992, Atsü & Berksun 2000]. Simultaneously, however, research suggests that the cracking of titanium metalloceramics occurs deeper within the bulk metal, inside a solid solution of Ti and oxygen and/or a layer of brittle titanium silicides [Hautaniemi et al. 1992, Könönen & Kivilahti 1994]. To react with mostly SiO$_2$-based dental ceramics during the relatively high temperatures in dental ceramics firing, metallic Ti has to at least partly dissociate its own oxide layer, since the diffusion path of silicon through TiO$_x$ would be against silicon’s increasing activity and thus against the general principles of diffusion [Könönen & Kivilahti 1994, Könönen & Kivilahti 2001]. Thus, in principle the titanium oxide layers also play an important role in chemical bonding and in preventing the formation of unfavorable reaction layers such as thick titanium silicide layers.

In prosthodontics, titanium oxide layers are commonly modified either by electropolishing, anodic oxidation or thermal oxidation [Lausmaa 1996, Poilleau et al. 1997]. These pretreatment methods have not been unproblematic, and the results considering the interfacial bond strength with dental ceramics and titanium have not always been advantageous [Mo et al. 2003]. To avoid disadvantages found in conventional titanium surface treatments affecting the oxide layer composition, the TiO$_2$ layers in this section and later in the study are produced using atomic layer deposition (ALD). The ALD method enables production of extremely controlled and considerably thick TiO$_2$ layers without excessive and long lasting heating of titanium frameworks at high temperatures. This reduces dissolution of oxygen into titanium lattice during oxide layer manufacturing, which could otherwise impair the metal-ceramic bonding [Hautaniemi et al. 1992, Könönen & Kivilahti 1994, Könönen & Kivilahti 2001]. Most importantly, it allows reliable study of the specific influence of titanium oxide layer thickness on dental ceramics bonding.
4. SIGNIFICANCE OF TITANIUM OXIDE LAYERS

ALD is a chemical gas phase thin film deposition method based on separate precursor vapor pulses with self-limiting surface reactions, so that each precursor pulse creates a monomolecular layer of material onto a given substrate. The method was developed by Suntola and co-workers in Finland in the late 1970s, and was first introduced as atomic layer epitaxy [Suntola & Antson 1977, Suntola et al. 1983¹, Suntola et al. 1983²]. The self-limiting nature of film growth enables excellent conformality, uniformity and accurate film thickness control even onto complex 3D surfaces or trenches [Nalva 2002]. Although there are many distinguished studies of TiO₂ thin layers and atomic layer deposition [Aarik et al. 1995, Aarik et al. 1996, Aarik et al. 1997, Sammelselg et al. 1998], no previous studies have applied ALD within dental metallo-ceramics.

The purpose of this section of the study was to investigate the role of the TiO₂ layer properties in critical reaction layer formation and in the joint strength of the titanium-metallo-ceramic system. The hypothesis is that the TiO₂ layer thickness prior to dental ceramics fusing is insignificant to the joint bond strength.

4.1. Materials and methods

4.1.1. Sample fabrication

Titanium test samples, sized 25 mm x (3.0 ± 0.1) mm x (0.50 ± 0.05) mm according to DIN 13 927/ISO 9693 three-point bending test standard [1990 and 1999], were fabricated. A titanium strip was cut from a 1.4 mm thick, commercially pure, grade 1 titanium plate with an ordinary metal cutter and cold rolled to 0.7 mm thickness. From this strip, standard samples were cut with a wire electric discharge machine (WEDM: Charmilles Robofil 400). The WEDM was programmed to leave an excess of 100 μm in width, in addition to the 200 μm in thickness. All samples were then mechanically polished with 1200 grit (Federation of the European Producers of Abrasives, FEPA) wet polishing (Struers LaboPol-21) SiC paper to the standard dimensions mentioned above. After polishing, all the titanium substrates went through a uniform cleaning cycle, including a bath in Slotoclean S20 cleansing liquid containing mild sulfuric acid, an acetone bath and an isopropanol bath, to remove possible polishing debris and grease. Substrate surfaces were dried with compressed air, and smudging of the adhesion surfaces was carefully avoided afterwards.

Three test groups (A, B, C) with varying oxide layer thickness and crystallinity were produced. The TiO₂ and TiO₂-SiO₂ films were deposited by using a flow-type F-120 ALD reactor by ASM Microchemistry at Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology. TiCl₄ and γ-aminopropyltrimethoxysilane (APTMS) were used as metal precursors. H₂O and O₃ were used as oxygen sources for titanium and silicon, respectively. O₃ was used as oxidiser and it was generated from O₂ (99.999 %) in an ozone
generator (Fischer model 502). Nitrogen (>99.999 %, Schmidlin UHPN 3000 N₂ generator) was used as carrier and purging gas.

During the first step of the TiO₂ deposition cycle, TiCl₄ molecules react with the functional –OH groups of the titanium surface. The following purge removes excess, unbound precursors from the chamber before dosing of H₂O. Next, the H₂O molecules react with the Cl-ligands, producing TiO₂ and additional reactive surface –OH sites. This reaction cycle was repeated until the desired film thickness was obtained [Figure 4].

![Reaction cycle repetition diagram](Image)

**Figure 4.** Schematic representation of the ALD reaction cycle

The oxide layers were deposited both onto the titanium samples and the Si(100) and Al₂O₃ reference substrates. The oxide layers of the Group A were 95 nm thick, with a Si/(Si + Ti) ratio of 16% to preserve an amorphous nature in the deposited oxide layers. The reaction temperature was 300 °C. In Groups B (95 nm TiO₂) and C (460 nm TiO₂), the reaction temperature was 350 °C, and no Si was added to the TiCl₄ precursor pulses, thus crystalline films were obtained. Test group specifications are given in Table 2.

Throughout the thesis, the dental ceramics material used in the samples was DuceratinPlus® (DeguDent, Dentsply International) to keep the fundamental test setting invariable and results comparable. The fusing of dental ceramics was carefully done according to manufacturer’s protocol. First, DuceratinPlus® Haftbond® bonding agent was fired on the length of 8.0 (±0.1) mm [DIN 13 927/ISO 9693] in the middle of the TiO₂-coated
samples as a very thin coating, followed by two layers of opaque ceramics and two layers of bulk ceramics. Before each firing, excess ceramics was carefully cleaned from the sides of the titanium samples. The firing was executed in a vacuum of ca 5 kPa (5 \cdot 10^{-2} \text{ atm}) and the maximum temperature during the firing was 780 °C. After polishing the ceramics into a thickness of 1.0 (±0.1) mm [DIN 13 927/ISO 9693] with a dental technician’s grinding stone, a glazing firing was performed at 730 °C. The standard dimensions were controlled by optical microscopy and micrometer.

<table>
<thead>
<tr>
<th>GROUP</th>
<th>N</th>
<th>OXIDE LAYER THICKNESS</th>
<th>CRYSTAL STRUCTURE</th>
<th>DEPOSITION TEMPERATURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7</td>
<td>95 nm</td>
<td>amorphous</td>
<td>300 °C</td>
</tr>
<tr>
<td>B</td>
<td>7</td>
<td>95 nm</td>
<td>anatase</td>
<td>350 °C</td>
</tr>
<tr>
<td>C</td>
<td>7</td>
<td>460 nm</td>
<td>anatase</td>
<td>350 °C</td>
</tr>
</tbody>
</table>

### 4.1.2. Sample characterization

Oxide film thickness was evaluated by using the optical fitting method [Yilammi & Ranta-Aho 1993]. The reflectance and transmittance spectra for thickness analyses were obtained from Si(100) samples in a Hitachi U-2000 double beam spectrophotometer. Crystallinity of the deposited films was determined by X-ray diffraction (XRD) using Cu Ka radiation (Philips MPD 1880). The silicon to titanium ratio was measured by X-ray fluorescence spectroscopy from samples deposited onto Al₂O₃ substrates in a Philips PW 1480 WDS spectrometer using Rh excitation. Data were analyzed with the UniQuant 4.34 program, which is based on fundamental parameters and experimentally determined instrumental sensitivity (Omega Data Systems, Netherlands).

After dental ceramics fusing, the metalloceramic interface was studied using a scanning acoustic microscope (SAM: Hitachi mi-scope hyper). Non-destructive analyses by SAM were performed in immersion with water as a coupling medium, in 25 MHz mode to achieve good resolution for detection of small defects in the joint regions. In preparation, the uncoated sides of the titanium-ceramics samples from each test group were polished with 1200 grit wet SiC paper to remove possible ceramics firing debris. To ensure the correct probing depth, echoes from the metalloceramic interface were compared to data from areas without ceramics application. The acquired data are represented as images in which areas
without excessive reflection at the joint depth, i.e. with good ceramics bonding, appear in shades of blue (dark in grayscale version), and delaminated areas as well as areas without ceramics application appear in shades of yellow and red (lightly colored in grayscale version). To verify the ultrasonic examination results, cross-sectional sample microscopy was done. Details of the SAM methods have been given elsewhere [Könönen & Kivilahti 1991, Wang et al. 1998].

After the aforementioned examinations, the crack-initiation (bond) strength of the titanium-porcelain joints was analyzed by the three-point bending test according to DIN 13 927/ISO 9693 standard. Three-point bending tests were performed on seven randomly selected samples of each three groups with a MTS 858 bending machine (MTS 661.18D-01 with 1kN force sensor, maximal inaccuracy 5 % of the measured force) and a standard bending jig. The specimens were placed ceramics side down on the bending jig, and loaded with a bending piston [Figure 5] by increasing applied force to keep the piston speed constant (1.5 (±0.5) mm/min according to the standards). A disruption in the load deflection curve indicated cracking of specimen. The maximal forces (F<sub>max</sub>) reached before cracking were recorded. The crack-initiation strengths (τ) [DIN 13 927 / ISO 9693] were calculated using the formula τ = k<sub>τ</sub> · F<sub>max</sub> (given in the DIN/ISO standard) where the coefficient k<sub>τ</sub> is a function of the elastic modulus and sample thickness. A curve for the k-values is also given in the standard.

![Three-point bending](image)

**Figure 5.** DIN 13 927/ISO 9693 metallo ceramic test sample and the three-point bending test setup.
The value for the elastic modulus of commercially pure titanium (grade 1) was acquired from the literature [Boyer et al. 1994; see 4.3.3.]. In order to check that the high fusing temperatures used in this study do not alter the value of the modulus – due to increase in Ti grain size – the following measurements were implemented, however. Four titanium strips sized 70 mm x 0.65 mm x 6 mm were cut and polished from the cold rolled titanium plate used in all of the standard specimens. These strips went through the same pretreatments and ceramics firing sequences as the standard specimens, without any ceramics application. The strips were stretched with the MTS 858 unit, increasing the tensile force one Newton per second up to 90 N; the strain was recorded. The elastic modulus (E) was calculated with the formula \( E = F/(A \cdot \varepsilon) \) where \( \varepsilon \) equals strain (\( \Delta l/l \)).

Fracture surfaces and cross-sectional samples of the cracks were analyzed with optical microscopy and scanning electron microscope (SEM: JEOL JSM-6335F) accompanied with energy dispersive X-ray spectroscopy (EDS: ISIS & INCA, Oxford Microanalyzer). Samples randomly selected for the cross-section analyses were embedded into EpoFix resin, ground and mechanically polished perpendicular to the metal/ceramic interface, and sputter coated with chromium.

### 4.2. Results

X-ray diffraction (XRD) analyses of the ALD-manufactured TiO\(_2\)-surfaces confirmed the film crystal structure. Group A samples had an amorphous oxide layer structure, whereas Groups B and C had anatase crystal structure. The film thicknesses of Groups A, B and C were 95 nm, 95 nm, and 460 nm, respectively.

After the dental ceramics application, SAM analyses of the metalloceramic interface showed good adhesion between the ceramics and the underlying titanium in every test group; no large delamination areas could be found. Minor (\( d < 0.15 \) mm) delaminations were observed somewhat more often, the thinner the created TiO\(_2\) layer was. The best results of interfacial adherence were achieved in samples from test Group C of which an example is given in Figure 6, yet no significant difference between the test groups was found. SEM results of test sample cross-sections were congruent with the non-destructive analyses, revealing minimal delamination only.

Three-point bending test results for Groups A, B and C were 31.5 MPa (SD 7.3 MPa), 30.4 MPa (SD 3.6 MPa) and 32.0 MPa (SD 6.7 MPa) respectively. The elastic modulus for titanium, determined as the arithmetic average of the measurements from the four test strips (105.1 GPa, SD 8.8 GPa), yielded a k-value of 4.8 mm\(^{-2}\). The one-way analysis of variance showed no significant difference between the groups with a significance level (\( \alpha \)) of 0.01. During the three-point bending, the entire porcelain part detached from 2, 1 and 2 samples from Groups A, B and C, respectively. On the margins of the titanium side of Group A and B samples, some areas with remaining dental ceramics were found during optical and scanning
electron microscopy. The diameter of the residual porcelain sites was about 30 μm. No residual porcelain was observed on Group C samples. The detached ceramics sides of samples of all the groups were covered with a titanium-colored reaction layer. SEM/EDS analyses showed that this reaction layer contained mostly titanium.

**Figure 6.** The SAM test setup using water as coupling medium. Scanning acoustic microscope image of a sample from Group C. The dark area between the four arrows indicates good bonding without large delamination. Light gray area indicates area without dental ceramics.

4. SIGNIFICANCE OF TITANIUM OXIDE LAYERS
Cross-section analyses of samples with dental ceramics still partly attached showed cracks that had propagated relatively far along the reaction zone, beginning from either end of the ceramics applied on the sample. The cracking mainly occurred 0.8 to 1.2 μm deep in the titanium substrate in all the sample groups. SEM images of Groups A, B, C and EDS line scan analysis graph of one representative sample from Group C are given in Figure 7.

**Figure 7.** Compositional backscattered electron images of cracks in samples from Groups A, B and C. The 0.8 μm to 1.2 μm exfoliated titanium layer (light gray between arrows 1. and 2.) is observed above the main crack (dark area between arrows 2. and 3.). The thickness of the layer is independent of sample group. EDS linescan shows that this layer contains mostly Ti. Opaque ceramics (above arrow 1.) contain Si and small amounts of Sn and Al.  

4. SIGNIFICANCE OF TITANIUM OXIDE LAYERS
4.3. Discussion

4.3.1. On ALD manufactured TiO\textsubscript{2} layers

Atomic layer deposition offers many benefits in studying thin surface layers on metallic samples. Thickness and quality control of ALD fabricated thin layers is accurate and simple. The self-limiting growth process makes deposition rate dependent only on the number of deposition cycles without need for reactant flux homogeneity, and enables uniform film thickness deposition even onto various 3-dimensional objects [Nalva 2002]. In addition, processing temperatures as low as 100 ºC are possible [Aarik et al. 1995], thus avoiding excessive heating inflicting accelerated oxygen dissolution into the bulk metal during thin layer production. All this allows the researcher to concentrate on the effects of the thin surface layer, free of the artifacts of coarser surface processes.

The samples of Groups A and B represent oxide films over eleven times and of Group C over fifty times as thick as the natively formed oxide layers [Lausmaa 1996, Poilleau et al. 1997, McCafferty & Wightman 1999, Sittig et al. 1999] – prior to the effects of dental ceramics firing. Oxide films twice as thick have been previously deposited by ALD [Rosental et al. 1997]. Due to the relative slowness, the most evident limitation of the method, this is often impractical, however. Even though the TiO\textsubscript{2} layers used in this study are not near the maximal stable thickness processable by ALD they can be considered thick compared to the natively formed TiO\textsubscript{2} layers.

TiCl\textsubscript{4} is a very common [Ritala et al. 1993, Kumagai et al. 1995, Aarik et al. 1997, Rosental et al. 1997, Sammelselg et al. 1998, Rosental et al. 1999] but by no means the only possible precursor of titanium for ALD-based production of TiO\textsubscript{2} layers. A wide array of combinations including e.g. TiCl\textsubscript{4}/H\textsubscript{2}O; TiI\textsubscript{4}/H\textsubscript{2}O; TiI\textsubscript{4}/H\textsubscript{2}O\textsubscript{2}; TiI\textsubscript{4}/O\textsubscript{2}; Ti(OMe)\textsubscript{4}/H\textsubscript{2}O; are presented in a recent review [Puurunen 2005].

4.3.2. On scanning acoustic microscopy

Acoustic microscopy has an advantage over other spectroscopy techniques in that it allows non-destructive evaluation of materials [Wang et al. 1998]. It produces reliable results comparable with cross-sectional microscopy [Könönen & Kivilahti 1991, Könönen & Kivilahti 1994], and correlating with results of the four-point bending test [Wang et al. 1998].

The challenge in ultrasonic analyses is to ascertain the acute probing depth. The time based wave pattern depends directly on the specific acoustic impedance of the sample and can be affected by heterogeneity in the specimen composition and density. Probing from the polished titanium side of the metalloceramic DIN/ISO standard specimens is ideal for acoustic microscopy, as the acoustic impedance and thickness of titanium substrate is constant.
in practice and the area without ceramics application gives a good reference of the joint level of the current specimen. Visible defects have previously been found at the metallo-ceramic interface in electrolytically polished titanium samples using congruent SAM methods [Könönen & Kivilahti 1991, Könönen & Kivilahti 1994]. No defects of this magnitude could be found from current test groups, indicating good ceramics adhesion.

4.3.3. On three-point bending testing

If results from different studies are to be comparable, the same standard test methods must be used. The three-point bending test executed according to DIN/ISO standard was chosen for the thesis because of the explicit test instructions and the wide use of the method [Könönen & Kivilahti 1990, Boening et al. 1992, Gilbert et al. 1994, Pang et al. 1995, Pröbster et al. 1996, Oshida et al. 1997, Yilmaz & Dinçer 1999, Atsü & Berksun 2000, Reyes et al. 2001, Al Hussaini & Al Wazzan 2005, Özcan & Oysal 2005, Inan et al. 2006, Troia et al. 2008, Bieniaś et al. 2009, Papadopoulos & Spyropoulos 2009]. In TPB, the actual interfacial strength of the test samples does not consist of plain shear or tensile strength, and the terminology used in literature has been inconsistent. This monograph uses the inaccurate “bond strength” term to indicate the results acquired from the three-point bending test. Bond strength results are commonly reported in literature in either N/mm$^2$ or in MPa (1 MPa = 1 N/mm$^2$).

The coefficient $k_\tau$ used in calculating the bond strength according to the DIN/ISO standard is a function of the titanium substrate thickness and its elastic modulus. The Young’s modulus (E) for titanium is somewhat dependent of the concentration of the alloying element and temperature [Boyer et al. 1994, Kikuchi et al. 2005]. Typical values of E for pure titanium at room temperature lie in the range of 100 to 110 GPa [Boyer et al. 1994], but some dental material reference books give values as high as 120 GPa [Boyer & Gall 1991]. This inconsistency between the E-values given in the literature, the importance of the Young’s modulus for bond strength determination, and the possible effects of ceramics firing sequences rationalize the elastic modulus measurement. Our test results are consistent with the ASM International values [Boyer et al. 1994].

4.3.4. On titanium and oxygen

Several difficulties associated with titanium oxide and dental ceramics bonding have been proposed in the literature. Epitaxial stresses may arise in very thin oxide scales, and the different characteristics of oxide and metallic titanium can generate residual stresses in the joints after ceramics firing, resulting in unsatisfactory joint strength [Hautaniemi et al. 1992]. Previous research [Adachi et al. 1990, Kimura et al. 1990$^1$, Wang & Fung 1997, Yamada et al. 2005] has reported surface oxygen layer thickening during heat treatments resembling
dental ceramics firing in titanium samples with no applied-on SiO$_2$-based dental ceramics. These oxide layers have been associated with the low bond strength results achieved, after the sintering of dental ceramics on the heat treated titanium frameworks. This has led to blaming TiO$_2$ for the low bond strengths in Ti-based metalloceramics in general [Wang et al. 1998, Atsü & Berksun 2000, Garbelini et al. 2003, Özcan & Uysal 2005, Vásquez et al. 2008].

There are some important facts to be remembered when interpreting the aforementioned findings. First, Könönen and Kivilahti have pointed out in their previous study [Könönen & Kivilahti 2001] that although titanium has many stable oxides, it differs distinctly from other strong oxide-formers such as aluminum and magnesium by having a very large potential for dissolving oxygen. Even a relatively low percentage of dissolved oxygen makes the solid solution of titanium brittle. Saturation solubility needed for formation of the first oxide is, however, exceptionally high: 33% at 780ºC [Massalski 1996] [Figure 8], the maximum temperature in the present ceramics firing protocol. Secondly, diffusion of silicon through Ti[O]$_x$ is against silicon’s increasing activity, so that metallic Ti first has to at

**Figure 8.** Binary phase diagram of the Ti-O system. Saturation solubility needed for formation of the first oxide is exceptionally high: 33% at 780ºC. [Massalski 1996.]

4. SIGNIFICANCE OF TITANIUM OXIDE LAYERS
least partly dissociate its own surface oxide layer to enable formation of titanium silicides at the joint interface. Previously portrayed dual crack propagation through a silicide layer (mostly Ti$_5$Si$_3$(O)) and relatively thick titanium oxygen solid solution in titanium metalloceramic samples with dental ceramics already applied and subjected to extended firing times at 800 ºC [Könönen & Kivilahti 1994] shows that the dental ceramics firing process inevitably leads to dissociation – not thickening – of the underlying native titanium oxide layer and to accelerated diffusion of oxygen into titanium lattice. The EDS analyses of the present study also suggest Si diffusion into Ti in the regions closest to dental ceramics.

Color changes in the sample surface observed during the first oxygen firing step support the notion that dissociation of the oxide layer may take place even without the presence of dental ceramics atop it [Figure 9].

Hautaniemi et al. previously investigated titanium ceramics bonding using various firing times, vacuum levels, four-point bending and X-ray photoelectron spectroscopy (XPS) [Hautaniemi et al. 1992]. According to their results, the fractures that were created in the four-point bending tests occurred between metallic titanium and titanium oxide (for the samples with dental ceramics firing time of only few minutes) or in metallic titanium with high oxygen solubility (for the samples of longest ceramics firing time). The more complex or esthetically demanding the clinical metalloceramic restoration, the greater number of firings and the greater heat load involved. Cumulative firing times equal to the longest firing time used in the study by Hautaniemi et al. are thus by no means uncommon. As oxygen dissolution to titanium is highly increased with rising temperature, there exist two main supplies for the increasing amount of oxygen needed. First, the oxygen can be obtained by the

\[ \text{Figure 9: 95 nm anatase samples on firing stand: yellow color created by optical properties of ordered TiO}_2 \text{ layer is disrupted immediately during the first sintering cycle in dental ceramics firing furnace, indicating disruption of the homogeneous TiO}_2 \text{ layer.} \]
reduction of SiO$_2$-based dental ceramics, since the Gibbs free energy of solution of oxygen in titanium is more negative than the Gibbs free energy of formation of SiO$_2$ (per mole O$_2$) [Pajunen & Kivilahti 1992, Könönen & Kivilahti 1994]. This source was also presented by Hautaniemi et al. [1992], as their group found out during XPS measurements that silicon near the ceramics-titanium interface appeared only partly in the oxidized state, whereas further away from the interface it appeared mostly in the oxidized state.

The other source for oxygen is naturally the surrounding atmosphere. Indeed, there are studies on the influence of different firing atmospheres on ceramics bonding [Atsü & Berksun 2000, Sadeq et al. 2003]. Atsü and Berksun [2000] studied the effect of the firing atmosphere on bond strength. They studied three different dental ceramics systems on cast and wire electrical discharge machine worked non-cast titanium. The furnace used in dental ceramics firing was designed to be flushed with 10 pulses of high purity argon gas to minimize the amount of residual oxygen present during firing. The three-point bending test results of half of the tested groups were improved when using protective atmosphere. Unfortunately, no testing was done to measure the amount of residual oxygen in the firing chamber. Sadeq et al. [2003] performed biaxial flexure test and reported higher AFAP values of titanium metallo ceramics fired in argon atmosphere compared to samples fired in minor vacuum of 3-4 kPa.

The current commercial firing recommendation is for a vacuum of ca 5 kPa (5 \( \cdot \)10$^{-2}$ atm). Rotary pumps of older dental furnaces used by dental technicians create a vacuum of roughly 1.3 \( \cdot \)10$^{-3}$ kPa [Wang et al. 1999]. Preventing any significant oxygen dissolution into titanium at above 700 °C, however, requires the vacuum to be of very high level, preferably 10$^{-6}$ kPa or better. Thermodynamically the equilibrium of titanium/oxygen systems, based on Ellinghams diagram, requires approximately 10$^{-110}$ atm to 10$^{-90}$ atm of oxygen partial pressure between 400 °C to 800 °C. It is impossible to achieve this low an oxygen partial pressure by any means imaginable [Lee et al. 2004].

In addition, oxygen released from dissociation of TiO$_2$ layer in the beginning of dental ceramics firing somewhat increases the amount of dissolved oxygen in titanium [Figure 10].

4. SIGNIFICANCE OF TITANIUM OXIDE LAYERS
Figure 10. Formation of thick oxygen-rich Ti[O]$_x$ solid solution during elevated ceramics fusing temperatures.

SiO$_2$ applied in dental ceramics firing processes at the first sintering cycle can possibly markedly reduce diffusion of oxygen from the surrounding atmosphere [Özcan & Uysal 2005]. At the same time, high temperature of dental ceramics firing increases oxygen dissolution deeper into Ti framework. Thus saturation solubility needed for formation of the first oxide is not easily achieved in surface layers of Ti frameworks during normal dental ceramics firing, and oxide thickening is avoided, in contrast to previous reports on the oxide scales of bare heat treated titanium samples [Adachi et al. 1990, Kimura et al. 1990, Wang & Fung 1997, Yamada et al. 2005]. This is also roughly the basis for the use of dental ceramics paste bonders. The high temperature results in extensive dissociation of the native oxide layer, however, and enables faster oxygen dissolution into titanium from SiO$_2$. Oxygen content inside metallic titanium can rise significantly, resulting in thick Ti[O]$_x$ solid solution and a brittle joint between dental ceramics and titanium. It should be evident that this cannot be restrained by paste bonders. The increase in oxygen diffusion kinetics has been left undiscussed in the traditional papers suggesting titanium oxide as the most important factor behind low bond strength results of titanium-based metalloceramics [Adachi et al. 1990, Kimura et al. 1990].

In the experiments of this section (and the thesis work in general), thickness of the oxide layers prior to dental ceramics firing did not significantly contribute to the measured bond strengths. Comparable three-point bending test bond strength results have been achieved
in Al$_2$O$_3$ particle blasted samples without excessively thick TiO$_2$ layers [Al Hussaini & Al Wassan 2005]. The cracking occurred much deeper in Ti substrates than what was the combined thickness of oxide layers artificially manufactured (95-460 nm) and natively formed (can be estimated to be less than 10 nm). Based on the above discussion and thermodynamical considerations, the oxygen-rich Ti[O]$_x$ solid solution zone should be identified as the region of vulnerability, and mechanisms of oxygen dissolution into this zone should be considered the factor most affecting bond strength.

There exists no sharp boundary between the oxygen-rich titanium and the bulk titanium. The crack may propagate at any solid solution depth where the quantity of oxygen diffused into octahedral sites sufficiently affects the solution so that mobility of dislocations over slip planes, i.e. plasticity, no longer occurs. Therefore even a careful analysis of oxygen concentration is insufficient in precisely predicting the crack propagation occurrence depth; at most a zone of probable occurrence could be identified if an oxygen depth profile were available. As previously indicated [see section 2.4.], such depth profiling is a complex undertaking, perhaps best sidestepped in favor of direct measures to limit oxygen propagation.

The relatively low mobilities of the elements in the titanium silicides leave the silicide layer comparatively thinner than the titanium oxygen solid solution [Könönen & Kivilahti 1994]. As no dual crack propagation was observed during the thesis study, the relatively thick TiO$_2$ layers formed prior to dental ceramics application can be considered to have prevented excessive formation of continuous thick titanium silicide layers [see section 2.2.5.]. In the cross-section SEM images of cracked specimens, the two-layered structure of the remaining Ti containing layer on the dental ceramics side is barely visible. EDS line scan data suggests Si diffusion to Ti, and the upper 0.5 μm thick, intact segment of the remaining Ti containing layer closest to dental ceramics can thus be interpreted as a titanium silicide layer [Figure 7; see also 2.2.5]. The diffusion is observed at the limits of the resolution of the EDS method, however. It will further be shown that even a native oxide layer is sufficient in preventing extensive dual crack propagation [see sections 6.2. and 7.2.], albeit again a segment of the remaining Ti containing layer can be seen as a silicide layer (as a darker band in SEM images). The cracking in the native oxide samples occurs identically to that of thick oxide layer samples. Thus the TiO$_2$ layers can be considered benign if not beneficial, and completely doing away with these layers would in any case be a futile prospect.

The results from TiO$_2$ layer application in this section of the study are in accordance with those findings and interpretations in the literature concentrating on the effects of dissolution of oxygen in titanium [Könönen & Kivilahti 1994, Könönen & Kivilahti 2001]. On the other hand, the results contradict the research emphasizing the effects of TiO$_2$ thickness [Wang et al. 1998, Atsü & Berksun 2000, Garbelini et al. 2003, Özcan & Uysal 2005, Vásquez et al. 2008]. Those only appear relevant for certain rather artificial heat treatment sequences [Adachi et al. 1990, Kimura et al. 1990$^1$, Yamada et al. 2005].
The third part of this work [section 6] will tackle the issue of restraining the aforementioned dissolution of oxygen from surrounding atmosphere and SiO$_2$-based ceramics to the bulk titanium.

### 4.4. Conclusions

A thick TiO$_2$ layer on titanium is not as disadvantageous as previously claimed for the mechanical integrity of titanium-ceramic system. Scanning acoustic microscopy revealed good ceramics adhesion to titanium in all the test groups, and no significant connection between bond strength and TiO$_2$ film thickness or crystal structure could be found. The fracture mode was uniform and thus independent of oxide layer thickness. On the other hand, no dual crack propagation could be observed in the test specimens; a uniform oxide layer is expected to sufficiently restrain unwanted thickening of the silicide reaction product layer between SiO$_2$-based ceramics and titanium. The problem of excessive oxide dissolution remains to be solved so that an ideal metal-ceramic bond can be accomplished.
Titanium has several interesting aspects not widely discussed in research associated with dental metallo ceramics. Before further discussing restraining oxygen dissolution during dental ceramics firing, a new aspect to TiO$_2$ is presented. TiO$_2$ possesses two distinct semiconductor photochemistry-based photoinduced features: a better-known photocatalytic phenomenon, which leads to breakdown of organics; and the more recently discovered photoinduced superhydrophilicity [Fujishima et al. 2000, Mills & Lee 2002]. Here, the latter phenomenon is introduced to dental metallo ceramics research.

A semiconductor material such as TiO$_2$ comprises electrons at the valence band (VB) and, at a higher energy state, largely vacant electron energy levels called the conduction band (CB). The energy difference between these two bands is called the bandgap, $E_{BG}$, which is characteristic to each respective semiconductor material. When a semiconductor material is subjected to radiation with ultra-bandgap light, i.e. photons with $h\nu > E_{BG}$, promotion of a VB electron to CB may occur. The subsequent formation and fate of an electron-hole pair ($e^- & h^+$) largely determines the photoactivity of the semiconductor material. [Benedix et al. 2000, Mills & Lee 2002].

Typically in non-photoactive conductors such as metals, electron-hole pairs recombine immediately [Benedix et al. 2000] and produce heat. Recombination is promoted by defects, and amorphous materials usually portray poor photoactivity [Mills & Lee 2002]. If some of the photoexcited electron-hole pairs diffuse to the surface of the semiconductor material, it is possible for them to interact with surface species [Benedix et al. 2000, Mills & Lee 2002]. This is the basis for photosynthesis, photocatalysis and photoinduced superhydrophilicity. In photosynthesis, the Gibbs free energy change for reactions of electron-hole pair and their surrounding environment is positive; in photocatalysis, negative [Mills & Le Hunte 1997]. With TiO$_2$, in the absence of large amounts of adsorbed competing species such as dirt, the surface species participating in reactions with the electron-hole pair are the oxides’ own Ti(VI) and bridging O$^{2-}$ groups. The Ti(III) species are generated via reduction of the Ti(IV) surface species by photogenerated electrons, and oxygen vacancies are generated via oxidation of the bridging O$^{2-}$ groups to oxygen by photogenerated holes [Fujishima et al. 2000, Mills & Lee 2002]. Water molecules can then occupy these oxygen vacancies, producing adsorbed OH groups, which tend to make the surface hydrophilic [Fujishima et al. 2000] [Figure 11]. In addition to this chemically adsorbed H$_2$O a lesser amount of physically adsorbed H$_2$O can also be found, at least in porous oxide films [Yu et al. 2000]. With the increase of chemically adsorbed OH on the surface of TiO$_2$, van der Waals forces and hydrogen bonds interactions between H$_2$O and the hydroxyl groups will be increased and water can easily spread across the surface [Yu et al. 2000]. The process is reversible, as Ti(III) sites are in the dark slowly oxidized back to Ti(IV) by ambient oxygen, hydroxyl groups

5. PHOTOINDUCED SUPERHYDROPHILICITY
reactively desorb, and the oxygen vacancies are filled again by $O^{2-}$ ions, now generated as a consequence of the oxidation reaction. Unlike other semiconductor materials, dual photoinduced phenomena are almost exclusively seen with TiO$_2$ [Fujishima et al. 2000, Mills & Lee 2002].

Photoinduced superhydrophilicity was originally discovered by accident in 1995 [Fujishima et al. 2000]. It has since produced many commercial solutions including non-fogging glass applications and self-cleaning surfaces.

In dental metallocceramics, good wetting of metal surfaces during ceramics veneering is of great importance [Carpenter & Goodkind 1979, Reyes et al. 2001]. It is also considered one of the key principles for good interface formation [Marshall et al. 2010]. Areas that exhibit poor wetting by the first applied ceramics layer or the paste bonder prior to sintering may develop into voids or air pouches, disrupting the ceramics structure during iterative firing cycles; or worse, leaving the finalized metallocceramic product visually intact, but the joint incomplete and failing under stress generated by the occlusal forces. Good examples of this are shown in section 6. Improving wettability of titanium (or more exactly its surface TiO$_2$) might avoid generation of faults endangering integrity of the joints.

There exists a discrepancy in reported time frames needed for achieving good superhydrophilicity (i.e. contact angle near 0˚); results vary from ~30 min to 5 min [Fujishima et al. 2000, Miyachi et al. 2000, Miyachi et al. 2002, Miron et al. 2004]. A corresponding discrepancy exists in assumed duration of superhydrophilicity; it has been proposed to last for as long as from 2 days up to weeks [Sakai et al. 1998, Benedix ym, 2000], or to gradually return close to normal during 12 hours [Miron et al. 2004]. Various parameters of light source and TiO$_2$ are known to have an influence on photoactivity.

The hypothesis is that superhydrophilicity of the TiO$_2$ surface can be achieved within a reasonable time (minutes) of ultraviolet activation, so that it can be of possible benefit in dental ceramics veneering process. The purpose of this section of the study is to investigate the achievable time frame for inducing superhydrophilicity and to present photoactive nature of TiO$_2$ to dental metallocceramics research.
5. PHOTOINDUCED SUPERHYDROPHILICITY

Figure 11. Schematic representation of photoinduced superhydrophilicity.

5.1. Materials and methods

5.1.1. Sample fabrication

TiO$_2$ films 200 nm thick were deposited on 10 (±0.1) mm x 10 (±0.1) mm x 1.0 mm glass samples by using a Beneq TFS 500 ALD reactor at Micronova laboratory in Helsinki University of Technology. Glass was chosen as the test specimen framework material for the actual TiO$_2$ film to facilitate characterization of the deposited oxide, since the framework material has previously been found to have no evident impact on the photoactivity of the film [Vilhunen et al. 2009]. Glass plates were fabricated from ordinary microscopy glass slides using a diamond glass cutter, and mechanical polishing (Struers LaboPol-21) with 1200 grit.
wet polishing SiC paper on the specimen sides. Samples went through ultrasonic and chemical cleaning with aceton, isopropanol and water prior to ALD application.

In the ALD process, TiCl$_4$ and H$_2$O were used as metal and oxygen sources, respectively, and nitrogen as carrier and purging gas. The reaction temperature was 300 ºC. The TiO$_2$ crystal structure was anatase. The TiO$_2$ process parameters were chosen based on a recent study on photoinduced systems [Vilhunen et al. 2009].

### 5.1.2. Photoinduced hydrophilicity characterization

Transmittance of the TiO$_2$ films was measured from 4 randomly chosen samples using the Perkin-Elmer Lambda 900 spectrophotometer to evaluate the optimal wavelength for the UV source. From the acquired transmittance data, absorption coefficient $k_{abs}$ was evaluated according to $k_{abs} = \frac{1}{d} \ln \left( \frac{1}{T} \right)$ where $d$ is the TiO$_2$ film thickness and $T$ the transmittance [Mardare et al. 2000, Wang et al. 2001, Zhang et al. 2009]. Extrapolating the linear parts of experimental curves to $k_{abs} = 0$, one can find approximation of the optical band gap for each curve. The UV source wavelength was chosen to top the approximated $E_{BG}$ and to ensure no unnecessary transmittance.

The contact angle between the TiO$_2$ surface and water prior and after UV radiation was measured using sessile drop method. Regulated drops (2.5 μl) of distilled water were applied onto the sample surface using constant application height and speed with automated equipment and software (KSV Instruments Ltd. CAM 200). Prior to UV radiation, reference contact angle values for each sample were first measured after sample storage in dark for several days. The samples were then irradiated using a 1000 watt Mercury Arc Lamp (Oriel Instruments Model 6287). Radiation wavelength was controlled with a monochromator (Bentham Instruments TMc300) to 312 (±2.5) nm, based on transmittance measurement results. Irradiance on the TiO$_2$ surface was set to 2.5 mW/cm$^2$ and confirmed with pyroelectric measurements (LaserProbe Inc. Power Probe RkP-575, Power Meter Rk-5710).

UV radiation was applied for 10 min on the first two samples (Group D) and for 2 min on second two samples (Group E) at normal room temperature and humidity [Table 3]. After UV exposure, the contact angle measurements were performed with 5 min intervals until 30 min time point, and then at 60 min, 120 min, 180 min and 240 min after the beginning of UV exposure. Samples were stored in the dark between measurements.
5. Photoinduced Superhydrophiliciry

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Oxide layer thickness</th>
<th>Crystal structure</th>
<th>UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>2</td>
<td>200 nm</td>
<td>anatase</td>
<td>10 min</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>200 nm</td>
<td>anatase</td>
<td>2 min</td>
</tr>
</tbody>
</table>

### 5.2. Results

Transmittance values and the UV source wavelength are shown in Figure 12. The absorption coefficient $k_{abs}$ and $E_{BG}$ were approximated from the transmittance results as shown in Figure 13.

The reference contact angle average for all samples was 54.2° (±5.2°). Both Group D and Group E samples displayed superhydrophilicity (contact angle close to 0°, unmeasurable) after UV radiation [Figure 14]. After initial recovery to 10-15° during the first two 5 min intervals, the contact angle remained below 20° for one hour [Figure 15]. Total recovery was slow and not observed during the first 240 min.

![Figure 12. Average transmittance, standard deviations and applied UV wavelength.](image)
Figure 13. Approximation of $E_{BG}$ from measured transmittance data.
Figure 14. Sessile drop measurements before and immediately after UV irradiation.

Figure 15. Average contact angle vs. time after UV irradiation.
5.3. Discussion

5.3.1. On titanium as photoactive material

Photoactivated materials are usually called photocatalysts, owing to the earlier discovery of photocatalysis compared to photoinduced superhydrophilicity. The term photocatalysis is, however, a subject of some debate [Mills, Le Hunte 1997]. It is argued that the idea of a photocatalyzed reaction is fundamentally incorrect, since it implies that light is acting as a catalyst, whereas it rather acts as a reactant, which is consumed in the process. The term is in such widespread use that it is here to stay; it is not meant to, nor should it ever be used to, imply catalysis by light, but rather the “acceleration of a photoreaction by the presence of a catalyst” [Mills, Le Hunte 1997]. The term photoreaction is sometimes elaborated on as a photoinduced or photoactivated reaction, all to the same effect [Mills, Le Hunte 1997].

Traditionally an ideal semiconductor photocatalyst material should be chemically and biologically as inert as possible, photocatalytically active, easy to produce and use, cheap as material and – owing to its common use in self cleaning outdoor surfaces – activated by sunlight [Mills & Lee 2002]. TiO$_2$ does not entirely meet these terms, yet it is one of the most ideal photoactivated materials, since it is highly stable chemically, relatively inexpensive, and the photogenerated holes are highly oxidizing [Fujishima & Zhang 2006]. The two most common crystal structures of TiO$_2$ are rutile and anatase. The mobility of charge carriers is easier in anatase, which makes it electrically the more ideal crystal structure [Ilola et al. 2003]. It can be considered the most photoactive crystal structure of TiO$_2$ [Mills & Lee 2002]. The $E_{BG}$ for anatase is slightly higher than that of rutile (3.2 eV and 3.0 eV correspondingly) [Mogyorósi et al. 2003]. In previous research, a commercial mixture of 75% anatase and 25% rutile called P25 (Degussa Chemical Company, Germany) has been used in various solutions [Blake et al. 1999, Mills & Lee 2002, Balasubramanian et al. 2003]. According to Riley et al. [2005], a TiO$_2$ layer already present on the surface of commercial dental implants may also act as photocatalyst, even though photoinduced superhydrophilicity was not studied. In the thesis study, anatase TiO$_2$ was chosen because of the general conception of its higher photoactivity.

The existence of dual photoinduced phenomena is almost unique for TiO$_2$ [Fujishima et al. 2000, Mills & Lee 2002]. For example WO$_3$ and V$_2$O$_5$ are only active in photoinduced superhydrophilicity [Miyauchi et al. 2002] and SrTiO$_3$ does not become hydrophilic under UV irradiation, even though it has a similar photocatalytic oxidation power to TiO$_2$ [Miyauchi et al. 2000]. In addition to TiO$_2$, on which most of the study of photoinduced superhydrophilicity has concentrated, SnO$_2$ and ZnO also portray both photocatalytic oxidation and photoinduced superhydrophilicity [Miyauchi et al. 2002].
Possibly a more straightforward explanation for photoinduced superhydrophilicity compared to Fujishima et al. [2000] and Mills & Lee [2002] is the one formulated by Miyauchi et al. [2002]: photogenerated holes are trapped at the surface lattice oxygen atoms, causing a dissociation of their bonds with the Ti atoms, followed by the adsorption of water molecules at these sites; or that UV illumination simply causes the dissociation of atomic bonds between oxygen and metal atoms in the topmost surface layers of TiO$_2$ followed by adsorption of water molecules at these defect sites. Thus it is easy to understand that bonding strength between metal ions and oxygen ions is supposedly important for photoinduced superhydrophilicity. Miyachi et al. argue that photoinduced superhydrophilicity can also be due to surface structural changes of different origins, and that multiple kinds of surface oxygen vacancies might be in agreement with increased wettability. They showed that when bombarding TiO$_2$ and WO$_3$ films known to portray photoinduced superhydrophilicity with Ar$^+$ ions for 1 min, the films became highly hydrophilic with a contact angle of 0°. Noticeably, SrTiO$_3$ films exhibited better crystal stability during Ar$^+$ bombardment, and did not portray photoinduced superhydrophilicity. Miyachi et al. also elucidate how the strength of oxidation activities of different metal oxides is roughly explained by the position of valence and conduction bands, while the surface morphology, crystallinity and optical absorption properties also play an important role.

Processing the properties of the TiO$_2$ surface can be used to influence the proportion of photocatalytic character to superhydrophilic character [Fujishima & Zhang 2006]. Breakdown and washing of dirt from the surface increase hydrophilicity, as part of the contaminant compounds tend to change the surface to hydrophobic [Madaeni & Ghaemi 2007]. Even though hydrophilicity is not induced only by the photocatalytic oxidation of organic hydrophobic (dirt) compounds on the surface [Miyauchi et al. 2002], hydrophilicity is considered to increase the photocatalytic activity of TiO$_2$ since most of the OH groups can be adsorbed on the photocatalyst surface due to hydrophilicity [Madaeni & Ghaemi 2007]. Photoinduced hydrophilic conversion and photocatalytic oxidation process may also competitively proceed on the TiO$_2$ surface under UV radiation, though even a slight decrease in the quantum efficiency of photocatalysis can increase quantum efficiency of the hydrophilic conversion drastically [Sakai et al. 2003]. The photoactivity of TiO$_2$ films may be affected by influencing on many possible factors such as film composition, porosity, crystallinity, crystal size, surface area and roughness in attempt to widen the excitation wavelength (i.e. $E_{BG}$) and reduce recombination of electron-hole pairs [Balasubramanian et al. 2003, Fu et al. 2005]. Consequently, there are many attempts to customize photoactivity to wanted levels, such as by use of inorganic and organic doping agents, and these can be found e.g. in extensive reviews [i.a. Carp et al. 2004].
5. PHOTOINDUCED SUPERHYDROPHILICITY

5.3.2. On light source, UV parameters and achieved hydrophilicity

Typical light sources used in previous research and commercial photoactivated solutions are 365 nm blacklight bulbs and low-pressure mercury lamps ($\lambda_{\text{max}} = 254$ nm), which have extremely long lifetimes up to $>14000$ h, and even gallium nitride based semiconductor LEDs have been used [Mills & Lee, 2002]. Doping agents such as Au have been used to widen the absorption spectra so that high pressure sodium bulbs ($\lambda > 400$ nm) could also have been used in addition to UV-B or UV-A wavelengths [Li & Li 2001].

In order for light to induce photoactivity, energy of photons must top the $E_{\text{BG}}$ of the semiconductor surface, 3.2 eV for bulk anatase. Light wavelength should thus be typically less than 385-388 nm [Maness et al. 1999, Benedix et al. 2000]. The $E_{\text{BG}}$ for artificially created TiO$_2$ surfaces, however, can be considerably higher, e.g. 3.66 eV or 3.75 eV corresponding to wavelengths of 338 nm and 330 nm, depending on the oxide properties [Mogyorósi et al. 2003]. Thus the optical properties of the TiO$_2$ surface designated for use must be properly characterized to select optimal parameters for the light source.

The transmittance measurements in this section proved to be sufficient for estimating efficient wavelength for photoinduced superhydrophilicity. In the transparency region, scattering of light influences the optical absorption spectrum calculated from transmission spectrum. At shorter wavelengths, however, the fundamental absorption evidently dominates the scattering losses. Therefore, some information about the optical band gap can be obtained from the transmission spectra [Aarik et al. 1997, Mardare et al. 2000] and the simplified relation $k_{\text{abs}} = d^{-1} \ln (1/T)$ [Zhang et al. 2009, Mardare et al. 2000, Wang et al. 2002] can be used to evaluate the absorption coefficient from the measured transmittance. The results achieved in this thesis are close to the values of pure anatase and rutile. The 3.15 eV values obtained by Mardare et al. [2000] were considered to represent a mixed structure of rutile and anatase. It is possible that the TiO$_2$ structure used in the thesis also contained some rutile components. It must be kept in mind that the obtained band gap value is, however, only an approximation.

Sakai et al. [2003] stated that the hydrophilic conversion rate strongly depends on the wavelength of the light source. The onset wavelength for hydrophilic conversion is almost consistent with that for absorbance spectrum, and the conversion rate increases as absorbance increases. Previously Miron et al. [2004] achieved superhydrophilicity using a broad spectrum light source covering transmittance change from maximum to minimum, and Vilhunen et al. [2009] used TiO$_2$ films – similar to those used in the thesis – with light wavelengths well over band gap energies (85% of the radiation in the range of 250-260 nm) to successively induce photocatalysis. In comparison, the narrow width of the spectrum used in this thesis ensured complete supra band gap energy of the employed radiation as well as minimal transmittance, and gave more accurate information about the irradiance participating in the photoinduced phenomena. This information will markedly simplify future selection of radiation sources in comparable photoinduction experiments.
The level of irradiance used here can be considered sufficient for inducing superhydrophilicity, but a radiation source of optimal parameters could meet the needs at lower power. Miron et al. [2004] reported that 1 mW/cm² UV radiation was sufficient to induce surface superhydrophilicity in 5 min on amorphous TiO₂ surface with a short range, anatase-like atom ordering. The irradiance of 2.5 mW/cm² used in the thesis systematically resulted in superhydrophilicity and the spreading of the water droplet on the anatase TiO₂ in only 2 minutes (Group E). Increase in irradiance does not, however, necessary shorten the time, as Sakai et al. [1998] reported superhydrophilicity only after 10 min when using 40 mW/cm² Hg-Xe lamp (though the contact angle was already markedly reduced in the first measurement point at 5 min). Sakai et al. [2003] stated that, based on the comparison of the hydrophilic conversion rate with the rate for the reverse process or relaxation, the critical contact angle (the lowest value of the contact angle under UV irradiation) is obtained when the reconstruction of the surface hydroxyl groups and their relaxation process are equilibrated under UV irradiation, and that domination of the recombination of photogenerated electron-hole pairs limits the hydrophilic conversion rate under high UV intensity [Sakai et al. 2003].

Optimation of UV intensity and wavelength of the light needs further study, since they directly affect the inducing of superhydrophilicity. Even though it has been proposed that it can take over 20-30 min to achieve superhydrophilicity [Fujishima et al. 2000, Miyachi et al. 2000, Miyachi et al. 2002] it is obvious that if the E_BG of the oxide can be evaluated and a sufficiently optimal wavelength and intensity of the radiation chosen, superhydrophilicity can be induced in reasonable time (minutes) and lasts long enough to be practical for dental technicians use during the metalloceramics manufacturing step. Measurements of this sort are not easily performed alongside dental technicians’ daily work or with equipment commonly found in dental laboratories. Thus adjustable or wide spectrum light sources are needed, and general guidelines for the irradiance and wavelength needed for photoinduced superhydrophilicity on different titanium oxide structures must be provided by the basic research. The light source used in the current study was ideal for research use owing to its high controllability, and it proved efficient in promoting photoinduced hydrophilicity.

Relaxation to normal was recorded as featuring a sharp initial rise in contact angle during the first half an hour, followed by a more gradual rise. The results roughly agree with Miron et al. [2004] and Sakai et al. [2003], who further discuss the subject and the variables involved in the exact nature of the relaxation process. If necessary, the relaxation period can possibly be hastened with the use of ultrasonic treatment, and reinduced again with a new UV exposure [Sakai et al. 1998].

5.3.3. On Ti wetting with dental ceramics

Though wetting is essential for achieving good bonding [Carpenter& Goodkind 1979, Reyes et al. 2001, Marshall et al. 2010], restraining excessive oxygen diffusion into the titanium
lattice during dental ceramics firing must be considered the first priority for mechanical integrity of titanium-ceramic systems in modern dental metalloceramics. No pronounced wetting problems were detected in the SAM investigations of the previous section of the thesis. In the next section, however, evident drastic consequences of poor contact between dental ceramics and metal structure are shown. It is thus essential to further study the wetting properties of titanium-ceramic systems – different dental ceramic materials, Ti frameworks (CAD/CAM manufactured vs. cast, different alloys) and their native oxide layers – after the dissolution of oxygen can be controlled or constrained.

This section illustrates how Ti and especially TiO$_2$ possess several notable characteristics that remain novel and unfamiliar to dental metalloceramics research even though titanium has already been used for quite some time in clinical practice.

5.4. Conclusions

Photoinduced superhydrophilicity is an easy and effective method to increase wetting of TiO$_2$-covered titanium surfaces into extreme hydrophilicity. This can possibly be used to circumvent the emergence of detrimental flaws – voids and air pouches – in joints between titanium and dental ceramics, thus improving joint integrity and success of metalloceramic restorations. Photoactivity of surface TiO$_2$ in CAD/CAM manufactured titanium frameworks after normal processes prior to dental veneering needs further research.
6. SILVER INTERLAYERS

The most brittle component in the joints of common dental ceramics and Ti is the oxygen-rich solid solution Ti[O]_x in the surface layer of titanium frameworks, as stated earlier. The plasticity of Ti[O]_x is significantly reduced through the diffusion of oxygen into titanium. Resultant stresses caused by iterative dental ceramics firing cycles and thermal expansion mismatch of the two materials burden the metalloceramic structures. Also, the brittle reaction products such as titanium silicides and possible contamination debris such as aluminum from Al_2O_3 blasting particles might further weaken the joints. Even though several different methods to improve joint strength have been tried out, only a few account for all of the aforementioned factors.

A vacuum produced by conventional dental furnaces is not even close to sufficient in order to prevent dissolution of the firing atmosphere originated oxygen into titanium [Wang et al. 1999, Lee et al. 2004]. Using high vacuum fusing furnaces or a protective gas environment can perhaps reduce the oxygen dissolution, yet such furnaces are relatively expensive and rare. More economical ceramics bonding agents have been designed to efficiently wet and cover the application area of titanium, thus sealing the firing atmosphere after the first firing sequence. Results of their efficacy in this particular function are not well documented, however, and the SiO_2 will serve as an excellent oxygen source in itself [Pajunen & Kivilahti 1992, Könönen & Kivilahti 1994]. Thus, use of an oxygen diffusion barrier material other than SiO_2 based ceramics bonder would seem reasonable.

The ideal interlayer material must fulfill several requirements. It must be biocompatible and suitable for oral environment, act as a barrier to diffusion of oxygen, be strongly adherent to Ti structures, and be capable of establishing a strong bond to dental ceramics [Wang et al. 1999, Könönen & Kivilahti 2001]. Even though strong bonding requires chemical bonding, the interlayer must not produce excess reaction products with Ti or dental ceramics, and/or must sufficiently reduce reactions between Ti and Si to avoid excess formation of brittle titanium silicides [Könönen & Kivilahti 2001]. The interlayer must possess plastic deformability, so that it can attenuate residual stresses afflicting the joints [Könönen & Kivilahti 2001]. Sealing of the blasting particle contamination from dental ceramics contact can be considered beneficial [Carpenter& Goodkind 1979, Dérand & Herø 1992, Kern & Thompson 1994, Darwell et al. 1995, Papadopoulos et al. 1999, Cai et al. 2001, Bagno & Di Bello 2004, Yamada et. al 2005]. Finally, the interlayer material needs to be applicable on titanium with practical methods. After application, it should also maintain its original properties as much as possible [Könönen & Kivilahti 2001].

Metallic interlayers of a noble metal familiar as dental biomaterial could fulfill many of these criteria. Metallic materials offer important inherent capability to withstand plastic deformation and thus residual stresses inflicted during dental ceramics fusing, e.g. due to
differences in CTE of dental ceramics and titanium frameworks can be attenuated to maintain integrity of metal-ceramic joints. The following interlayer metal alternatives were considered based on criteria for suitability as an oxygen diffusion barrier: Ag, Au, Pd, Pt, Co and Cr. Cobalt and chromium were discarded owing to their inferior mechanical properties. Out of the four remaining possibilities, Ag was chosen on the basis of higher reactivity of Au, Pd and Pt with Ti, so that fast formation of thick brittle reaction layers between the interlayer material and Ti could be avoided, and the interlayers would remain sufficiently plastic to reduce residual stresses. Also, Ag has only two intermetallic compounds (IMCs) with Ti, TiAg and Ti$_2$Ag, less than for example Au. A more thorough comparison on the thermodynamics of different interlayer metals will be published later by Könönen, Saloniemi, Varpavaara and Kivilahti.

The purpose of the present investigation is to propose an interlayer material that best meets the aforementioned criteria, and to compare mechanical compatibility of this new system with one commercial titanium-ceramic system using the three-point bending test. According to the hypothesis, Ag interlayers produced on titanium surfaces can suppress diffusion of oxygen into titanium and thus prevent formation of excessively thick and brittle oxygen-rich Ti[O]$_x$ layers.

6.1. Materials and methods

6.1.1. Sample fabrication

DIN 13 927/ISO 9693 standard titanium test samples were fabricated, mechanically polished with 1200 grit wet polishing SiC paper, and chemically cleaned in the aforementioned manner [see section 4.1.1.].

Five test groups with varying Ag interlayer thickness and surface roughness and one control group were produced. Each group contained eight samples. Samples in Groups F, J, K and L were blasted with Al$_2$O$_3$ particles (Q-dent High-Grade Corundum) for a few seconds with 250 kPa pressure from the distance of 3 cm. The particle size used was 110 μm as recommended by the ceramics manufacturer. The blasting direction was angled to the titanium surface to avoid excessive alumina attachment. After resting for 10 to 15 minutes, the samples were cleaned with a steam cleaner (Emmevi VAP 6) before veneering, again according to recommendation of the ceramics manufacturer. Samples in Group G and H were left polished. Group F samples served as a control group and had no Ag coating. The Ag coatings were prepared on Ti substrates of Groups G, H, J, K and L by DIARC-Technology Inc. using the DIARC® plasma coating method. Coatings were deposited in a vacuum at a temperature below 100 °C and were between 50-200 nm thick. On this Ag layer a thicker Ag layer up to 5 μm was constructed on Group L samples using electrochemical baths containing
80.5% silver cyanide, potassium cyanide, distilled water, sulphuric acid and nitric acid (Silver Glo 3K, Rohm and Haas Electronic Materials). The current density range was 0-7.0 A/dm$^3$ and the operating temperature was 21-29 °C. Test group specifications are given in Table 4.

The fusing of dental ceramics was carefully done according to manufacturer’s protocol and the DIN/ISO standards as described in section 4.1.1..

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Ti surface</th>
<th>Ag layer thickness</th>
<th>Deposition method</th>
</tr>
</thead>
<tbody>
<tr>
<td>F 8</td>
<td></td>
<td>Al$_2$O$_3$-blasted</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>G 8</td>
<td></td>
<td>1200 grit SiC-polished</td>
<td>50 nm</td>
<td>DIARC®</td>
</tr>
<tr>
<td>H 8</td>
<td></td>
<td>1200 grit SiC-polished</td>
<td>200 nm</td>
<td>DIARC®</td>
</tr>
<tr>
<td>J 8</td>
<td></td>
<td>Al$_2$O$_3$-blasted</td>
<td>50 nm</td>
<td>DIARC®</td>
</tr>
<tr>
<td>K 8</td>
<td></td>
<td>Al$_2$O$_3$-blasted</td>
<td>200 nm</td>
<td>DIARC®</td>
</tr>
<tr>
<td>L 8</td>
<td></td>
<td>Al$_2$O$_3$-blasted</td>
<td>5 μm</td>
<td>DIARC® + electroplating</td>
</tr>
</tbody>
</table>

6.1.2. Sample characterization

Additional Ti samples with surface treatments of Groups F-L were analyzed with SEM and EDS prior to dental ceramics fusing. After dental ceramics firing the metalloceramic interfaces were studied using a scanning acoustic microscope, as detailed in section 4.1.2.. To verify the ultrasonic examination results, cross-sectional sample microscopy was done.

After the aforementioned examinations, the crack-initiation (bond) strengths of the metalloceramic samples were analyzed by the DIN 13 927/ISO 9693 standard three-point bending tests, again as described in section 4.1.2.. Fracture surfaces and cross-sectional samples of the cracks were analyzed with optical microscopy, SEM and EDS.
6. SILVER INTERLAYERS

6.2. Results

Before dental ceramics firing, SEM studies of samples in different groups showed a distinct difference in surface topography as shown in Figure 17. No significant difference was, however, detected between 50 nm and 200 nm coated samples. Sharp edges and corners are smoothened especially in Group L samples. The EDS element maps also show that alumina residues from Al₂O₃-blasting are completely insulated from contact to dental ceramics [Figure 18].

One sample in Group G and one in Group H were destroyed during dental ceramics firing owing to air filled delaminations in the joint. SAM analyses of metalloceramic interfaces in visually intact samples revealed clear areas of delamination and/or inadequate bonding in polished samples of Groups G and H. The areas varied from roughly spherical small areas 0.1 mm in diameter to large delaminated areas of almost 1 mm² as shown in Figure 19. The green areas represent areas with poor contact between titanium and dental ceramics or areas of titanium with no applied dental ceramics. No large delaminations could be found in samples of Groups F, J, K or L. SEM results confirmed these results.

The three-point bending test results of Groups F, G, H, J, K and L were 37.8 MPa (SD 2.4 MPa), 33.3 MPa (SD 6.1 MPa), 31.0 MPa (SD 6.0 MPa), 37.8 MPa (SD 6.2 MPa), 41.2 MPa (SD 7.2 MPa) and 48.2 MPa (SD 2.7 MPa). The corresponding average displacement in μm that the samples lasted before cracking was 95.6 μm (SD 10.3 μm), 91.1 μm (SD 17.7 μm), 83.6 μm (SD 11.8 μm), 105.9 μm (SD 11.3 μm), 122.5 μm (SD 35.8 μm) and 150.0 μm (SD 20.3 μm) in Groups F, G, H, J, K and L. The three-point bending test results are shown in Table 5 and Table 6. One-way analysis of variance showed a significant difference between the TPB results of control Group F and Group L (significance level α = 0.01, p = 1.27⋅10⁻⁶) indicating a better joint strength in samples with ca. 5 μm Ag interlayer. No significant difference emerged between the other groups compared and the control group.

In Groups F, H and J cracking caused by three-point bending occurred 1.4 to 2.5 μm deep from titanium surface inside Ti[O]ₓ solid solution. In samples of Group G and H cracking between titanium and dental ceramics could be seen locally. In these areas a brittle solid solution could be observed on the surface of the titanium structure as shown in cross-section sample [Figure 20]. No continuous Ag layers were visible between dental ceramics and titanium in samples of Groups G, H, J and K. Cracking of Group L samples did not occur inside the brittle surface layers of the titanium structure, but multiple fracture lines can be observed inside dental ceramics. A clear layer of Ag between titanium and dental ceramics, and Ti diffusion through this layer – making adequate chemical bonding to dental ceramics possible – can be observed [Figure 21]. The Ag layers remain unbroken, but the thickness is uneven, between 4 to 10 μm, and locally only less than 1 μm.
Table 5 and Table 6. TPB results of Groups F, G, H, J, K and L. Significantly better results were achieved in Group L.
6. SILVER INTERLAYERS

Figure 17. Different surface topography is observed in SEM micrographs prior to dental ceramics firing. Sharp edges and corners observed in solely Al₂O₃-blasted samples are smoothened by an applied silver interlayer.
Figure 18. Top: compositional backscattered electron image of alumina residues (dark) on Al₂O₃-blasted Ti (light grey). Bottom left: EDS element map of Al₂O₃-blasted sample of Group F prior to dental ceramics veneering, indicating Al in red and Ti in green. Bottom right: EDS element map of Al₂O₃-blasted Ti surface with Ag interlayer in a Group L sample with the same color scale and no dental ceramics. Alumina contamination is efficiently insulated from possible interactions with dental ceramics.
Figure 19. SAM images of samples from Groups F, G, H, J, K and L after dental ceramics firing. Blue areas indicate good bonding between Ti and dental ceramics. Green areas represent Ti without applied dental ceramics (ends of the standard samples) as well as delamination and/or inadequate bonding. Samples in Groups F, J, K and L were found flawless. In Groups G and H (polished samples with 50 nm or 200 nm Ag interlayers) several samples exhibited delaminated areas.
Figure 20. Compositional backscattered electron images of samples from Groups F, H, K and L after TPB. Cracking inside Ti[O]₂ in samples of Groups F, H and K and multiple cracks inside dental ceramics in Group L can be observed. In Group H cracking between dental ceramics and titanium also occurred locally. A brittle solid solution is observable on the surface of Ti in these areas. No continuous lightly colored Ag interlayer is observed in Groups H or K, whereas a clear unbroken layer of Ag between titanium and dental ceramics is found in Group L samples. No significant differences were found between samples in Group G and Group H, or between Group J and K.
Figure 21. An EDS line scan of a cross-section sample from Group H after TPB. The line scan shows two cracks (*) inside the SiO$_2$-based dental ceramics and Ti diffusion through the Ag interlayer. Al and Sn are components of the dental ceramics material.

6.3. Discussion

An interlayer between the dental ceramics material and titanium structure was designed for the needs of dental metallo-ceramics to efficiently contribute to joint integrity and to suppress the formation of a brittle oxygen-rich Ti[O]$_x$ solid solution in the surface layers of Ti during dental ceramics fusing. Several different interlayer materials for improving joint strength and restraining oxygen diffusion to titanium lattice have been previously introduced [Dérand & Herø 1992, Gilbert et al. 1994, Wang & Fung 1997, Okazaki et al. 1998, Wang et al. 1999, Atsü & Berksun 2000, Sadeq et al. 2003, Lee et al. 2004, Suansuwon & Swain 2003, Özcan & Uysal 2005, Homann et al. 2006, Bieniaś et al. 2009]. After a systematic preliminary exclusion of possible materials, Ag interlayers were chosen for this study.
6.3.1. On the biocompatibility of Ag

The biocompatibility of Ag in dental solutions has been discussed recently in various papers. Despite Ag being a noble metal, it has been proposed to be more cytotoxic to osteoblasts and gingival fibroblasts than Au or Pd [Cortizo et al. 2004, Locci et al. 2000, Grill et al. 2000]. Experimental titanium-silver casting alloys (Ti 75% wt, Ag 25% wt) are concluded, however, to impose minimal risks associated with cytotoxicity [Wang & Li 1998], and transient exposure to an acidic oral environment does not significantly increase elemental release from Ag containing alloys [Wataha et al. 1998]. Longer exposure can cause some limited release [Wataha & Lockwood 1998]. The two intermetallic compounds produced in the Ti-Ag joint, TiAg and Ti$_2$Ag, are highly stable. Generally alloys presenting higher amounts of noble elements, including Ag, are more biocompatible [Grill et al. 2000]. Ag has been used in present clinical solutions in alloys with gold and palladium such as Au-Pd-Ag, Pd-Ag, Pd-Ag-Au [Roberts et al. 2009].

6.3.2. On oxygen dissolution

The Ag interlayers served as excellent oxygen diffusion barriers in Group L samples. No indications of brittle oxygen-rich Ti[$\text{O}_x$] layers were observed and the cracking occurred inside less brittle dental ceramics material. Joints between the silver interlayers and titanium structures remained intact showing excellent strength, as did many parts of joints between the interlayers and dental ceramics.

6.3.3. On plastic deformation and bond strength results

The mobility of dislocations generates the characteristic capacity of plasticity in metals. The high plasticity of silver is ideal for its use as an interlayer material, e.g. enabling relief of residual stresses formed due to mismatches in the CTE of dental ceramics and framework metal. The silver interlayers maintained plasticity even after reacting with Ti that diffused through the entire thickness of the interlayers, whereas brittle and faster forming IMCs in Au-Ti systems have been considered disadvantageous to joint strength [Könönen & Kivilahti 2001]. In a yet unpublished study of Könönen, Saloniemi, Varpavaara and Kivilahti compared Al$_2$O$_3$-blasted cpTi samples applied with only Duceratin® (Ducera, Dental-Gesellschaft, Germany); Duceratin® with first applied designated Haftbond® (Ducera, Dental-Gesellschaft, Germany) bonding material; or with electrochemically composed Ag layers of up to 10 μm thickness. The 1200 grit SiC polished cpTi samples with the aforementioned Ag layers were also studied. Congruent to the study of this monograph with thinner Ag layers, the Al$_2$O$_3$-blasted samples treated with Ag-plating performed best in three-point bending tests, resulting
in crack initiation (bond) strength values 51.1% higher than the values of solely Al₂O₃-blasted samples without use of any bonding agent. In the samples without Ag-plating, load curves recorded during the three-point bending tests showed a very sharp dropping at the bond failure loads compared to the Ag-plated samples where corresponding curves showed more plasticity at failure load levels [Figure 22]. In the curves of Al₂O₃-blasted samples with Ag interlayers, multiple sharp peaks represent multiple cracks inside the dental ceramics material in contrast to only one sharp drop in samples without Ag-plating, representing cracking of continuous planar layers of brittle Ti[O]ₓ. These observations strengthened micrograph findings concerning the mode of joint failure and were congruent to findings of the study in this monograph. The percentual increase achieved with the 5 μm Ag interlayers was also larger in mean displacement and better withstood prior cracking than in bond strength results [Table 5 and Table 6]. This can be explained by the very same plasticity of the Ag interlayers.

**Figure 22.** Sharp dropping at the joint failure load is observed in samples without Ag interlayers (groups 1 and 2). TPB results with Ag interlayers are better even without Al₂O₃-blasting and the cracking represents more elasticity (group 4). Multiple sharp peaks representing multiple cracks inside dental ceramics can be observed in samples both Al₂O₃-blasted and Ag-plated (group 3) [unpublished data of Könönen, Saloniemi, Varpavaara and Kivilahti]
Özcan and Uysal [2005] stated that it must be remembered that results achieved with oxygen diffusion barriers can vary substantially with different dental ceramics. There is no indication that Ag would perform worse as a diffusion barrier with any other dental ceramics material. Bonding between the interlayers and dental ceramics can, however, be dependant on the ceramics material composition. Even though bonding between the interlayers and other SiO$_2$-based ceramics material can be presupposed as similar, it needs further research. Ti diffusion through the interlayers and IMCs formed between Ti and Ag have a critical role in chemical bonding to SiO$_2$ based dental ceramics. In this test, the three-point bending test performance was considered to be limited by the strength of the chosen dental ceramics material.

Previous results achieved with SiO$_2$-TiO$_2$ coatings [Bieniaś et al. 2009] represented good bonding to cpTi and the Ti6Al4V alloy and had markedly better success in the three-point bending tests compared to uncoated cpTi or Ti6Al4V structures. Three-point bending test results were 25.2% better when the SiO$_2$-TiO$_2$ coatings were used with cpTi and 27.8% better when used with Ti6Al4V compared to uncoated samples. The Ag interlayers improved the three-point bending test results 27.5% [Table 5]. Cracks in SiO$_2$-TiO$_2$ coated samples, however, occurred between the coating and dental ceramics, whereas in Ag-coated samples the cracking predominantly occurred inside dental ceramics material, proving markedly better bonding between the interlayer material and dental ceramics. Thus, the three-point bending test results were limited by the strength of dental ceramics material and not by the bonding between the interlayers and dental ceramics.

Ag interlayers do not rule out one of the oxygen sources responsible for Ti[O]$_x$ solid solution formation at elevated temperatures, the native TiO$_2$ formed on surfaces of every Ti sample in ambient atmosphere. This layer, 3-8 nm thick [Lausmaa 1991, Poilleau et al. 1997, McCafferty & Wightman 1999, Sittig et al. 1999], dissociates during dental ceramics firing and is alone too insignificant a source for oxygen to create a brittle solid solution layer thick or oxygen-rich enough to compromise joint integrity as seen in the three-point bending test cross-sectional samples.

### 6.3.4. On applicability and blasting particle contamination

Several different methods have been demonstrated for the application of intermediate layers between dental ceramics and titanium, including metal pastes [Lee et al. 2004], sputter coating [Wang & Fung 1997, Sadeq et al. 2003, Lee & al. 2004, Özcan & Uysal 2005], electroplating [Wang & Fung 1997], sol gel technique [Bieniaś et al. 2009] and even MPIIID [Wang et al. 1999]. In this study, the DIARC® plasma coating method proved insufficient for creating Ag layers thick and continuous enough to function as oxygen diffusion barriers. It demonstrated no harmful effects prior to electrochemical deposition of thicker Ag layers. No significant benefits of using the method were detected when used together with
electrochemical deposition, however, as joint integrity between Ag and Ti remained excellent even in samples with direct electrochemical silver plating (unpublished data of Könönen, Saloniemi, Varpavaara and Kivilahti). Electrochemical baths can be easily adopted into dental technicians’ equipment. Easier chemical silver baths can possibly be produced in the future.

Surface topography of samples with thick Ag interlayer differed from the topography of solely Al₂O₃-blasted surfaces. Sharp edges and corners were smoothened, which might beneficially limit the amount of stress concentration and crack initiation points. Surface topography and material differences also contributed to surface wetting properties. No problem of dental ceramics bonder material wetting was detected in SAM examinations or SEM micrographs of cross-section samples with thick Ag layers, however. Application of dental ceramics material on surface roughened samples with an electrochemically deposited silver interlayer felt as easy as applying dental ceramics on solely Al₂O₃-blasted samples (author’s first-hand opinion).

Electrochemically produced silver layers also removed two variants from the interface next to dental ceramics. Aluminum contamination detected after Al₂O₃-blasting and possibly unfavourable for joint integrity [Carpenter & Goodkind 1979, Dérand & Hørø 1992, Kern & Thompson 1994, Darwell et al. 1995, Papadopoulos et al. 1999, Cai et al. 2001, Bagno & Di Bello 2004, Yamada et al. 2005] was effectively insulated from contact to dental ceramics. Excessive reactions between Si and Ti and following thick titanium silicide layer production were also forestalled.

6.4. Conclusions

Crack-initiation (bond) strengths of Al₂O₃-blasted samples with a 5 μm Ag interlayer were considerably higher than corresponding strengths of samples that were only Al₂O₃-blasted. The samples with the 5 μm Ag interlayers withstood larger displacement during bending.

The cracking of samples conventionally Al₂O₃-blasted or with thin plasma coated Ag layers occurred inside brittle oxygen-rich metallic titanium (Ti[O]ₓ). Cracking of samples with the 5 μm Ag interlayers occurred inside dental ceramics material; Ti/Ag joints remained intact as well as many parts of joints between the silver interlayers and dental ceramics.

Plasma coated Ag layers without consequent electrochemical plating were not beneficial in increasing bond strength. Voids and their related poor dental ceramics bonding were observed at joint interfaces between plasma coated polished titanium and dental ceramics.

The Ag interlayers can be efficiently used to retard dissolution of oxygen into titanium, preventing the formation of oxygen-rich Ti[O]ₓ solid solution in the surface layers of supporting titanium structures, thereby enhancing joint integrity between titanium and dental ceramics.
It is generally believed that the surface texture of titanium greatly influences the mechanical integrity of metal-ceramic systems [Lee 2004] and is therefore of great concern to prosthodontics in determining the durability of the interface between a metallic framework and the dental ceramics applied on it. To improve bond strength between dental ceramics and titanium, roughening of the metal surface by aluminum oxide blasting is commonly recommended [Mo et al. 2003, Al Hussaini & Al Wazzan 2005]. Roughening increases the joint area, mechanical retention and wetting, and reduces maximal tensile stresses in the interfacial regions [Carpenter & Goodkind 1979, Könönen & Kivilahti 1994, Reyes et al. 2001, Mo et al. 2003, Al Hussaini & Al Wazzan 2005].

According to findings of the thesis and other research [Hautaniemi et al. 1992, Könönen & Kivilahti 1994, Könönen & Kivilahti 2001], however, cracking in the Ti/SiO₂-based metalloceramics does not occur inside the dental ceramics or between the ceramics and titanium, but inside the brittle reaction layers formed during diffusion of oxygen and – in long firing processes – ceramics material to titanium framework. Excessive roughening should also be avoided, as too rough a surface texture can result in stress concentration at the joint interface and re-entrant angles too steep to allow complete wetting [Carpenter & Goodkind 1979]. Thus solely increasing surface roughness does not always lead to an increase in bond strength [Reyes et al. 2001]. Blasting particles also reportedly cause abrasive contamination, which can potentially modify the physicochemical interaction capacity of blasted surfaces [Dérand and Herø 1992, Kern & Thompson 1994, Darwell et al. 1995, Papadopoulos et al. 1999, Cai et al. 2001, Bagno & Di Bello 2004]. Generally, impurities in the joint lead to lowering the external stresses that the titanium dental ceramics interface can sustain without failure [Dérand & Herø 1992].

To overcome the mechanical problems of the brittle reaction layers, an approach of larger scale compared to Al₂O₃-blasting is introduced in this study. Uniform titanium surface indentations were formed using photolithographic etching to locally redistribute the mechanical stress between the brittle layers and dental ceramics, and to prevent crack propagation in continuous planar reaction layers. Much like conventional surface roughening methods, photolithographic etching also increases the joint area.

The purpose of this section was to investigate dental metalloceramic fusing, titanium surface roughening, and to present a new approach to overcome the mechanical problems of the brittle reaction layers. According to the hypothesis, based on the preceding results of this study, the degree of mechanical interlocking does not have as great an effect on bond strength as the degree of brittle reaction layer formation, because cracking occurs below the interlocking level. Sections 4 and 6 suggested a difference in bond strength between polished and roughened samples; this is further investigated in this section, eliminating various
interfering variables relating e.g. to the firing processes. To further study the hypothesis, the section also introduces a nonconventional method of improving mechanical interlocking; increasing the joint area and dividing the mechanical stress between brittle reaction layers and dental ceramics should prevent cracking of continuous planar reaction layers.

7.1. Materials and methods

7.1.1. Sample fabrication

Metal-ceramic samples were fabricated according to the DIN 13 927/ISO 9693 standard specifications and went through a chemical cleaning cycle [see section 4.1.1.]. After these preparations, three distinct surface treatments were applied to the titanium samples. One group was left polished (Group M); one was blasted with 110 μm Al₂O₃ particles (Group N); and one was etched with the modified titanium macroetch acid [Petzow 1999] blended for this experiment (Group P) [Table 7].

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>7</td>
<td>Polished</td>
</tr>
<tr>
<td>N</td>
<td>7</td>
<td>Al₂O₃-blasted</td>
</tr>
<tr>
<td>P</td>
<td>7</td>
<td>Photolithographically etched</td>
</tr>
</tbody>
</table>

Samples randomly chosen for etching (Group P) were dehumidified at 120 °C for 20 minutes in a convection furnace (Heraus UT6). A commercial 4500-series AZ positive tone photopolymer (Clariant GmbH) was used as an etching mask on the polished titanium samples. After cooling on a ceramic stand, the AZ photoresist was spin-coated on the samples. The samples rested for 5 minutes to assure planarity and were then baked on a hot plate to evaporate excess solvent and to densify the photoresist film. The baking consisted of three phases, starting with five minutes at 70 °C, followed by a ramping period of five

74
minutes to 110 °C, and a final phase of three minutes at 110 °C. The samples rested again for 60 min on plastic surfaces to avoid overly rapid cooling.

The AZ photopolymer protects the coated area during the etching procedure. A regular pattern of disks (d = 75 μm, 75 μm apart from each other) was exposed through a polymer film contact mask on the AZ resist on the titanium samples as illustrated in Figure 23A, to produce an etching mask for manufacturing anchoring pits in the titanium, outlined in Figure 23B. After exposure, the samples were developed to remove the exposed photoresist. The backsides of the samples were protected with the AZ resist against uncontrolled etching, and the samples were postbaked on a hotplate. The transfer and developing times were controlled by optical microscopy. Disturbances could be readily spotted, and all the coated and developed samples were practically identical.

An HF:HNO\textsubscript{3}:H\textsubscript{2}O (3:4:5, HF 10%, HNO\textsubscript{3} 69%) acid was used as the etchant, mostly because of its high etching speed and reliability. Photoresist remaining after the etching procedure was removed with acetone. The etching results were controlled by optical, stereo and SE microscopy. Prior to ceramics application, the etched samples were cleaned with the same cleaning procedure as previously outlined [see section 4.1.1.].

The ceramics application procedure was executed in the same manner as in previous parts of the thesis [see section 4.1.1.], and identically for all three types of samples as instructed by the manufacturer. 14 SiC-polished, 12 Al\textsubscript{2}O\textsubscript{3}-blasted, and 12 photolithographically etched samples were chosen for ceramics firing.
7.1.2. Sample characterization

The average roughnesses of the three differently modified titanium surfaces were measured by contact profilometry (Sloan Dektak 3) before dental ceramics firing. After ceramics firing all the test samples were screened for voids with a Fein Focus (FXS-160.24) X-ray microscope. Ceramics wetting on the titanium surface was studied by cross-section sample microscopy. Samples randomly selected for the cross-section analyses were embedded into EpoFix resin, ground and mechanically polished perpendicular to the metal-ceramic interface, and sputter coated with chromium. Finally, the bond strength of the titanium-ceramics fusing was measured by three-point bending (TPB) to compare the adhesion of dental ceramics in mechanically polished, Al₂O₃-blasted and photolithographically etched titanium samples. For every test group, seven randomly selected samples remaining from the previous tests were used. Fracture surfaces and cross-sectional samples of cracks were analyzed with optical microscopy and SEM/EDS.

7.2. Results

Profilometry of the three differently modified titanium surfaces showed that the roughnesses of the titanium surfaces displayed tenfold differences. The Rₐ-values were 0.19 μm, 1.1 μm, and 20 μm (depth of the pits) on average for Groups M, N and P. The profilometry of the etched samples also showed some poorly etched areas with a pit depth of 10 μm or less. These poorly etched pits were narrower and had a considerably rougher bottom than the properly etched ones.

The notable difference in the surface roughness was also observed in the SEM images. Further SEM/EDS analyses revealed occasional attachment of alumina particles ca 15 μm in diameter on Al₂O₃-blasted Ti surfaces (Group N).

Of the 38 samples studied with X-ray microscopy, five – 1 SiC-polished, 1 Al₂O₃-blasted, 3 etched – had radiolucent areas indicating voids in the upper parts of ceramics. These findings were confirmed by stereomicroscopy.

Optical microscopy of the cross-sectional samples revealed that the ceramics wetting of all surface types was excellent. In some etched samples, though, small individual regions were found where ceramics in the pit structures had debonded. This debonding of pits had occurred directly at the ceramics-titanium interface with no visible delaminated reaction layer. No cracks prior to the TPB were found.

TPB results of seven randomly selected samples of each group were 32.6 MPa (SD 7.5 MPa), 32.3 MPa (SD 6.9 MPa) and 32.5 MPa (SD 6.8 MPa) for Groups M, N and P, respectively. The one-way analysis of variance showed no significant difference between the test groups with a significance level (α) of 0.01.
The entire bulk ceramics detached from one sample in every test group. Optical microscopy and SEM/EDS analyses of the detached ceramics showed a reaction layer containing titanium and small amounts of Al covering the adhesion surface of the ceramics. The crack had propagated through this layer or between it and the rest of the metallic titanium sample. Both the polished and Al₂O₃-blasted titanium surfaces were devoid of ceramics. Alumina particles from Al₂O₃-blasting were still observed, on both the titanium and ceramics sides, as can be seen from Figure 24. In the etched sample, some pits remained filled with ceramics, indicating different crack propagation [Figure 25].

Cross-sections of the rest of the samples showed cracks that had propagated relatively far along the brittle reaction layer, recognized earlier as oxygen-rich Ti[O]ₓ solid solution, beginning from either end of the sample, from the corner of applied dental ceramics [Figure 26]. In polished and Al₂O₃-blasted samples, the cracking had left a layer of about 3 μm on the ceramics surface as seen in Figures 27 and 28. The distributions of Ti, Al, Sn and Si are given in Figure 29. In the etched samples this layer was somewhat thinner. No detached titanium-containing layer was detected in the pits debonded prior to the three-point bending.
Figure 25. SEI and compositional backscattered electron images of dental ceramics posts remaining in titanium anchoring pits after the three-point bending test.

Figure 26. Crack initiation in the corner of applied dental ceramics where the applied dental ceramics starts to spread on the Ti surface. Cracking occurs through oxygen-rich Ti[O]x along the joint if the dissolution of oxygen from SiO₂ and firing atmosphere to Ti is not restrained. A slightly darker layer closest to dental ceramics in the Ti layer remaining on dental ceramics can be seen, and interpreted as a titanium silicide layer [see 2.2.5 and 4.3.4].
Figure 27. Optical image of crack (dark line) in the upper layers of Al₂O₃-blasted titanium (light gray).

Figure 28. Compositional backscattered electron image of the metalloceramic interface of an Al₂O₃-blasted sample. 2-5 μm continuous, exfoliated titanium layer (light gray, below arrow 3) is observed above the main crack (dark area). Two layers of opaque ceramics are seen between arrows 1,2 and 3.
Figure 29. EDS line scan of the fracture. The line scan shows two Sn containing layers between arrows 1, 2 and 3 in Figure 28 – the opaque ceramics – and a 5 µm layer containing mainly Ti before the main crack.

7.3. Discussion

7.3.1. On test results and reaction layers

All of the three sample groups passed the DIN/ISO TPB standard recommendations of 25 MPa bond strength. Uniform TPB results have previously been achieved with airborne-particle abrasion followed by application of a bonding agent [Al Hussainni & Al Wassan 2005]. No statistically significant difference in bond strength was detected between the test groups in the TPB tests. The lack of significant difference between the groups is understandable as the cracking occurred deep inside the brittle Ti[O]x solid solution in all the test groups, except for the areas of ceramics retention locally in the etched samples. Thus, the mechanical interlocking at the joints achieved by different surface treatments did not have as important a role as the mechanical properties of the reaction layers. This is not completely surprising, as the mere achieving of a rough surface has been found to have ambivalent effects; the specific methods of roughening play a role in the degree of bond strength increase.
achieved [see 2.3.1]. In this case at least, brittle reaction layers consistently demonstrated a crucial role that was independent of the surface roughness.

Nevertheless, the difference in results between sections 4 and 6 supports the fundamental importance of surface roughening. Here one has to take into account the effects of random variation in e.g. handicraft and conditions in manufacturing the samples, as a considerable time passed between the experiments of these two sections. Since section 7 minimized such variables and failed to demonstrate a difference in bond strength, one again has to question whether various previous studies on the effect of roughening are fully cross-comparable.

After the fusing of dental ceramics, some debonded pits without a visible delaminated reaction layer were found. These pits were originally filled with ceramics, because the negative of the pit form could be identified in the debonded material. Previous Duceratin Dentine® has shown good thermal stability after repeated firing [Isgrò et al. 2005], hence minor thermal variation after the application should also have no adverse effect on bond strength [Tróa et al. 2003]. Multiple firing cycles, the explicit geometry of the samples, thermal contraction difference between metal and ceramics [Yilmaz & Dinçer 1999], the glass transition temperature of ceramics, and the elastic constants of the materials used, however, could all have effected residual stresses debonding these areas [Könönen & Kivilahti 2001]. According to the findings in the present study, the actual cracking of the Ti[O]ₓ occurs during bending, not during the high temperature fusing.

7.3.2. On photolithographic etching

Some previous studies have applied photolithographic surface microfabrication in cell experiments [Brunette 1986, Hallgren et al. 2001, Lu et al. 2005, Zhao et al. 2006, Troia et al. 2008]. Although various etching techniques have been tried to enhance dental ceramics bonding [Reyes et al. 2001, Gilbert et al. 1994, Al Hussaini & Al Wazzan 2005], to our knowledge there are no studies published concerning photolithographic methods in prosthodontics.

The three-point bending produces a complex stress state at the metallo ceramic joint owing to the presence of pit structures as well as to different mechanical properties of titanium and dental ceramics. Between the pits, the maximum tensile stress component acting nearly perpendicular to the planar reaction layer surface opens the crack tip and facilitates cracking. At vertical walls of the pits, the crack opening effect of this stress component is reduced. Consequently cracking along the direction of the joint surface is impeded and the crack is more likely to cut ceramic posts inside the pit structures. Compared to Al₂O₃-blasting or polishing, the photolithographic etching created more retention sites in which dental ceramics was found after the cracking.
The three-point bending, however, also creates another tensile stress component large enough for cracks to propagate along the curved reaction layer of the pits in multiple locations. Therefore, in most cases the cracking of the ceramic posts instead of the more brittle reaction layers was not achieved. To improve the interfacial stress distribution, steeper pit structures could be better, further reducing the effects of the stress component normal to the planar reaction layer and thereby forcing the crack more readily to the ceramics. Using the current etching protocol, this proved complicated. The openings in the photoresist mask cannot be made much smaller, and as the etchant propagates equally in all directions, deeper pits would also get wider. Longer etching time inflicts delamination of the AZ mask, causing overetching of the titanium surface around the pit structure. This would compromise the crack directing capability of the surface treatment. The best option could be to use pressurized etching methods in generating deeper but not much wider anchoring structures. Etching via a negative mask, i.e. creating controlled titanium rods or spikes instead of indentations, could also give all the wanted stress directing benefits. Small titanium anchors would also have a considerably greater shear, tensile and compressive strength than ceramics anchors [White et al. 1996].

7.4. Conclusions

The results confirm that the strength of modern dental metallo-ceramic joints is limited by the strength of mechanically brittle reaction layers formed during the fusing of dental ceramics. Photolithographically etched pits can be used to redistribute the crack producing stress, causing cracking of dental ceramics instead of the more brittle reaction layers. The current depth and steepness of the pits, however, was insufficient for extensive stress redistribution. Mechanical interlocking achieved by conventional surface treatments was also found to be less than crucial in light of the prevalence of reaction layer cracking.
8. GENERAL DISCUSSION

8.1. On the need for novel and enhanced titanium metalloceramics techniques

Dental prosthetics is expensive, both to patients and health care organizations. From an epidemiologic viewpoint, however, one can assume an increasing need for prosthetic therapy [Jokstad 2002]. Treatment need on the population level is to a large extent reflected by the fact that there is an increasingly larger proportion of elders today who retain their teeth, owing to a considerable improvement in oral health, in addition to improved general knowledge of the benefits of adequate oral care [Jokstad 2002]. Increased need leads to increased costs. Expenses in Department of Oral and Maxillofacial diseases of Helsinki University Central Hospital used in implants and prostheses increased by 32% from 2008 to 2009 alone [Helsinki University Central Hospital data]. The significant increase in the price of gold in the 1970s prompted development of less expensive dental alloys [Al Hussaini & Al Wassan 2005]. Replacing the high cost noble alloys has been one of the reasons behind the development of titanium-based systems [Yilmaz & Dinçer 1999, Roach 2007, Roberts et al. 2009]. Even though metalloceramic methods have their own solid place in large multiple-unit restorations [Vásquez et al. 2008], one always has to consider other treatment options such as all-ceramic restorations and fiber reinforced composite constructions when establishing the most suitable care for the patient. These are outside the focus of this study, however.

Novel CAD/CAM solutions suitable for multiple-unit framework design have experienced a rapid increase in sale rates. For example, the sale of CAD/CAM produced units by one example dental company increased in Scandinavian countries by over 150% from 2008 to 2009 [Straumann Nordic sales data]. As titanium would appear to have a promising future in fixed prosthodontics as a biocompatible and less expensive solution [Haag & Nilner 2007, Roberts et al. 2009], the resolving of fundamental problems, such as oxygen dissolution into titanium during dental ceramics fusing, is essential. Simple additional methods easily adaptable into dental technicians’ laboratories, such as silver interlayers, are thus more than welcome.

8.2. On metalloceramic joints and fractography

The thesis work concentrated on four aspects of Ti-metalloceramic joints and the fusing of dental ceramics: TiO₂ layers, wetting, oxygen dissolution into titanium lattice, and mechanical interlocking. The methodology and results of the four principal research approaches of this thesis have been discussed in detail in the respective sections.
Consistent with the hypothesis, the TiO$_2$ layer thickness prior to dental ceramics fusing was insignificant to the joint brittleness – contrary to general belief – and no significant difference was found in TPB results. Titanium oxide layers have been considered detrimental to joint integrity based on research on Ti samples without applied dental ceramics and in heat treatments exceeding phase transformation temperature [Adachi et al. 1990, Kimura et al. 1990$^1$], and later widely referenced to when blaming titanium oxides for poor bonding without confirming the existence of a true oxide layer or performing a deeper study of the joint interface [Atsü & Berksun 2000, Garbelini et al. 2003, Özcın & Uysal 2005, Vásquez et al. 2008]. TiO$_2$ layers, however, dissociate during long firing protocols with applied SiO$_2$-based dental ceramics [Könönen & Kivilahti 1994]. Instead, during dental ceramics firing, oxygen acquired from the firing atmosphere (before insulation by the first dental ceramics layers), SiO$_2$-based dental ceramics (during the rest of the firing process), and dissociating TiO$_2$ (an insignificant amount to joint integrity on its own) [Hautaniemi et al. 1992, Pajunen & Kivilahti 1992, Könönen & Kivilahti 1994, Atsü & Berksun 2000, Könönen & Kivilahti 2000, Özcın & Uysal 2005] diffuses into vacant octahedral sites of the Ti lattice. This reduces titanium plasticity and makes the surface of the Ti structure brittle. It is this solid solution of titanium and oxygen that limits mechanical strength of the joint. High firing temperatures further increase oxygen diffusion kinetics – a subject left undiscussed in the traditional papers suggesting titanium oxide as the most important factor behind low bond strength [Adachi et al. 1990, Kimura et al. 1990$^1$]. As the vacuum in dental furnaces cannot be sufficient for inhibiting oxygen from diffusing to Ti [Wang et al. 1999, Lee et al. 2004], and dental ceramics material remains another excellent oxygen source [Pajunen & Kivilahti 1992, Könönen & Kivilahti 1994], methods limiting interstitial oxygen diffusion into Ti are needed in order to achieve an ideal joint.

Good wetting is also needed for good interface formation and is of great importance in dental metalloceramics during ceramics veneering [Carpenter & Goodkind 1979, Reyes et al. 2001, Marshall et al. 2010]. When good wetting is achieved, low fusing dental ceramics paste bonders can cover the Ti surface during the first firing cycle, and provide insulation against the firing atmosphere [Suansuwan & Swain 2003], a more rapid source of oxygen compared to SiO$_2$. Consistent with the hypothesis, extreme hydrophilicity of TiO$_2$ was achieved with only a few minutes of suitable UV activation. The timeline presented by Miron et al. [2004] was supported, and even slightly faster results were achieved. With current dental ceramics, however, wetting is a lesser problem for joint integrity than the oxygen dissolution during dental ceramics firing.

Suppression of oxygen dissolution and the consequent formation of excessively thick and brittle oxygen-rich Ti[O]$_x$ was shown possible with Ag interlayers, congruent with the hypothesis, leaving dental ceramics as the most brittle part of the metalloceramic joint. Even though several different interlayer materials for improving joint strength by restraining oxygen diffusion have been tested [Dérand & Herø 1992, Gilbert et al. 1994, Wang & Fung 1997, Okazaki et al. 1998, Wang et al. 1999, Atsü & Berksun 2000, Sadeq et al. 2003, Lee et
al. 2004, Suansuwan & Swain 2003, Özcan & Uysal 2005, Homann et al. 2006, Bieniaś et al. 2009], and some guidelines for ideal interlayer are given [Wang et al. 1999], no consistent plan for ideal interlayer material selection prior to this thesis has been portrayed. In addition to serving as oxygen diffusion barrier, it is suggested that plasticity of the Ag layers is also beneficial in reducing stresses from the CTE mismatch of Ti and dental ceramics, well-known to be detrimental to the joint [Könönen & Kivilahti 1994]. Also, aluminum contamination detected after Al₂O₃ blasting and possibly unfavorable for joint integrity [Carpenter & Goodkind 1979, Dérand & Herø 1992, Kern & Thompson 1994, Darwell et al. 1995, Papadopoulos et al. 1999, Cai et al. 2001, Bagno & Di Bello 2004, Yamada et al. 2005] was effectively insulated from contact to dental ceramics.

Increasing surface roughness of the metal framework is generally believed beneficial in dental metalloceramics, as it increases joint area, mechanical retention and wetting, and reduces maximal tensile stresses in the interfacial regions [Carpenter & Goodkind 1979, Könönen & Kivilahti 1994, Reyes et al. 2001, Mo et al. 2003, Al Hussaini & Al Wazzan 2005]. In titanium-based metalloceramics, however, the most brittle part of the joints is not the very interface between the dental ceramics and titanium, but the brittle oxygen-rich Ti[O]ₓ solid solution. Photolithographically etched pits succeeded locally in preventing cracking of continuous planar reaction layers, and cracking occurred through dental ceramics instead of Ti[O]ₓ, in accordance to the hypothesis. Stress redistribution, however, was achieved in only some pit structures and no significant difference in TPB results was seen. Perhaps with steeper pit formations, a more uniform effect could have been achieved, resulting in improved results in bond strength. Results from samples with Ag interlayers clearly show that cracking of dental ceramics only occurs when the entire joint withstands a larger stress. Results achieved in this section, in conjunction with results from earlier sections, clearly state that the role of mechanical interlocking achieved by conventional surface treatments can be questioned as long as the formation of the brittle reaction layers, most importantly oxygen-rich Ti[O]ₓ, cannot be controlled sufficiently well.

The thesis work provided also information on fractography – identification of crack initiation, pattern of crack propagation, energetics of the fracture and classification of the phases along the fracture plane – longed for in dental materials research [Marshall et al. 2010]. Cracking occurred in a similar manner in both Al₂O₃-blasted and polished samples, and in samples with native or artificially thickened TiO₂ layer. Crack initiation could be identified at the corner of the dental ceramics portion, where the tensile stress in the three-point bending test has the highest value. Cracking was considered to have proceeded as a single event brittle crack over the midline of the sample, or in few samples completely removing the ceramics portion, as can be observed in the sharp single disruption of the load-deflection curve in TPB test. The optical microscopy, cross-sectional and SEM/EDS studies after specimen bending clearly authenticate a cohesive nature of cracking through the near-interface parts of titanium but far deeper than the normal titanium oxide layer thickness. On the basis of thermodynamics the brittle reaction zone was considered to be the solid solution
of titanium and oxygen, where oxygen atoms in the octahedral spacings of Ti restrained the metallic plasticity. Könönen and Kivilahti have reported similar cracking in a previous study [Könönen & Kivilahti 1994].

Different cracking was observed in samples with 5μm Ag interlayers. Cracking occurred inside dental ceramics material, with multiple brittle cracks along the joint, and significantly better TPB results were achieved. In a yet unpublished study of Könönen, Saloniemi, Varpavaara and Kivilahti samples without Ag-plating presented load-deflection curves recorded during TPB similar to the ones in this thesis, representing very sharp dropping at bond failure load, owing to cracking of the continuous planar layer of brittle Ti[O]$_x$ solid solution. The Ag-plated samples showed more plasticity at the failure load level, and multiple sharp peaks representing multiple cracks inside the dental ceramics material. These observations are congruent to findings in this monograph.

In photolithographically etched samples, stress distribution between dental ceramics and brittle reaction layers was attempted with a different, more mechanical approach. Single crack propagation through brittle Ti[O]$_x$ was forestalled, but only in some of the pit formations, where cracking through dental ceramics occurred. Therefore no significant difference in TPB results was achieved.

Restraining the formation of brittle oxygen-rich Ti[O]$_x$ can be considered of the foremost importance in achieving ideal strength of the joints between dental ceramics and titanium frameworks.

8.3. On future aspects

This thesis portrayed five major factors influencing joint integrity: compatibility of the CTE values, the wetting of titanium surfaces, the α-case layer, the influence of titanium oxides and oxygen, and titanium silicides.

Compatibility between the coefficient of thermal expansion of titanium and that of dental ceramics is extremely important [Nielsen & Tuccillo 1972, Kimura et al. 1990, Dérand and Herø 1992, Yilmaz & Dinçer 1999, Garbelini et al. 2003, Bieniaś et al. 2009]. Some debate is appropriate as to whether the compressive stress should be on the side of brittle dental ceramics, or the side of the even more brittle Ti[O]$_x$ solid solution. The temperature at which modern dental ceramics begin to behave as a shear-supporting solid during cooling should also be estimated [Nielsen & Tuccillo 1972]. With the use of plastically deforming Ag interlayers, however, the mismatch in the CTE between dental ceramics and Ti was considered insignificant, so further research in this sector is not so highly topical.

Wetting of titanium surfaces with dental ceramics is also of great importance [Carpenter & Goodkind 1979, Reyes et al. 2001, Marshall et al. 2010], however, no extreme problems with the current dental ceramics material used in the thesis were detected. Comparison between different materials should, however, be carried out in the future. The
The important of wetting is even more pronounced, if oxygen diffusion barrier interlayers are not used. Wetting of the Ag interlayers was found adequate in samples Al₂O₃-blasted prior to interlayer deposition. Wetting in polished samples, however, was found inconsistent. To obtain the best results with Ag interlayers, wetting of the interlayer material with dental ceramics must be carefully studied further. Perhaps even thin TiO₂ films with the capacity of photoinduced superhydrophilicity can be applied on top of interlayer material in the most vulnerable areas of large metalloceramics restorations to ensure perfect wetting. The mechanical strength of nanometer scale TiO₂ films compared to dental ceramics needs further research.

The risks involved in titanium casting and the α-case layer should be well known by now [Könönen & Kilivalhti 2001]. It has been misreferred to as a thick layer of titanium oxide [Atsü & Berksun 2000, Garbelini et al. 2003, Vásquez et al. 2008], however, and some recent studies even refer to using a dental ceramics material based bonding agent in a bid to circumvent the incompatibility problem between the α-case layer and dental ceramics [Vásquez et al. 2008]. Misunderstandings of this sort possess a clear threat to the clinical success of titanium metalloceramics. Substituting the manufacturing of large cast titanium structures with the more modern CAD/CAM processed frameworks fortunately diminishes the amount of α-case layer inflicted problems.

The formation of Ti[O]ₓ solid solution needs further research. Even though it can be sufficiently restrained by the use of Ag interlayers, a deeper knowledge in Ti[O]ₓ formation kinetics and critical oxygen concentration for mechanical integrity will assist in interlayer development. Due to the limitations of EDS microanalyses [see section 2.4.] in previous research [Suansuwan & Swain 2003, Atsü & Berksun 2000, Lee et al. 2004, Vásquez et al. 2008, Vásquez et al. 2009], further WDS studies are required to supplement the previous studies [Könönen & Kivilahti 1994].

Thick titanium silicide layers [Könönen & Kivilahti 1994, Könönen & Kivilahti 2001] present a problem mostly after highly extended firing times, and their formation is also restrained by Ag interlayers.

In addition to these five approaches, future research on effects of surface microstructure and larger scale shape of underlying titanium framework on stress concentration to dental ceramics is welcome. If results from different studies are to be comparable, the same standard test methods must be used. The three-point bending test executed according to the DIN/ISO standard was chosen for this monograph because of the explicit test instructions and the wide use of the method [Könönen & Kivilahti 1990, Boening et al. 1992, Gilbert et al. 1994, Pang et al. 1995, Pröbster et al. 1996, Oshida et al. 1997, Yilmaz & Dinçer 1999, Atsü & Berksun 2000, Reyes et al. 2001, Al Hussaini & Al Wazzan 2005, Özcan & Oysal 2005, İnan et al. 2006, Troia et al. 2008, Biensiaś et al. 2009, Papadopoulos & Spyropoulos 2009]. In TPB, the actual interfacial strength of the test samples does not consist of plain shear or tensile strength, and the terminology used in literature has been rather inconsistent. This monograph uses the inaccurate “bond strength” term to indicate
the results acquired from the three-point bending test. In addition to TPB, mechanical tests better resembling clinical stress need to be developed.

Although crack initiating mechanical laboratory tests and the following microanalyses and evaluation of crack propagation give many important insights into the weak and brittle elements in fusing of dental ceramics to titanium, more clinical follow up studies are needed. The oral environment is able to induce physico-chemical alterations in the dental materials [Vásquez et al. 2009], and cyclic longterm mechanical and thermal stress might decrease bond strength of titanium metallo ceramics [Oyafuso et al. 2008, Vásquez et al. 2008, Vásquez et al. 2009]. More research should therefore be done on the effects of clinical wear on the joint reaction layers, on clinical fractography, and on the expected longevity of the final restorations.
9. CONCLUSIONS

The thesis is composed of four intercomplementary parts introducing new approaches to brittle reaction layers and mechanical compatibility of metalloceramic joints created by the fusing of dental ceramics to titanium. The following conclusions are stated:

I. The thickness of the TiO$_2$ layer on titanium prior dental ceramics sintering is insignificant for mechanical integrity of titanium-ceramic system. Instead, during dental ceramics firing the TiO$_2$ layer dissociates, interstitial diffusion of oxygen into metallic titanium is increased, and the joint is made brittle by the resulting reduction in plasticity of the metal structure surface.

II. Photoinduced superhydrophilicity was achieved within 2 minutes consuming as little time and effort as Al$_2$O$_3$-blasting. It can be used to enhance wettability of titanium surfaces, an important factor in dental ceramics veneering processes.

III. Plastically deforming Ag interlayers can be used to restrain oxygen diffusion into the Ti lattice and prevent formation of excessively brittle oxygen-rich Ti[O]$_x$ solid solution, thus giving significantly better bond strength results compared to only conventionally blasting titanium frameworks with Al$_2$O$_3$. The most brittle component of the joints with Ag interlayers was the bulk dental ceramics instead of Ti[O]$_x$.

IV. Photolithographic etching can be used to cause cracking of dental ceramics instead of the more brittle reaction layers – only locally, however, as it was used in this study. The significance of mechanical interlocking achieved by conventional surface treatments can be questioned as long as the formation of the brittle layers (mainly oxygen-rich Ti[O]$_x$) cannot be sufficiently controlled.

In summary, in contrast to former impressions of thick titanium oxide layers, this thesis study clearly points out diffusion of oxygen from sintering atmosphere and SiO$_2$ to Ti structures during dental ceramics firing and the following formation of brittle oxygen-rich Ti[O]$_x$ solid solution as the most important factors predisposing joints between Ti and SiO$_2$-based dental ceramics to low strength. This among other predisposing factors such as residual stresses created by the coefficient of thermal expansion mismatch between dental ceramics and Ti frameworks can be avoided with the use of Ag interlayers.
10. TIIVISTELMÄ SUOMEKSI


Väitöskirjan kirjallisuuskatsauksessa käsitellään hammaskeraamien ja titaanin välisen liitosten menestyksen kannalta olennaisia tekijöitä, kuten lämpölaajenemiskertoimien yhteensopivuutta, pinnan kostutusta, faasitransitiolämpötilan ylittämisestä aiheutuvaa hauraan reaktiokerroksen muodostumista (nk. "α-case layer"), happea, sekä titaanin ja piin välisiä reaktiotoiteja. Lisäksi esitellään liitosten parantamiseksi kehitettyjä menetelmiä, vertaillaan titaanimetallokeramia ja muita metallokeramiamuotoja sekä liitosten tutkimukseen soveltuvia menetelmiä.

Väitöskirjatyö lähestyy titaanin ja SiO₂-pohjaisten hammaskeraamien liitosongelmia neljästä lähtökohdasta ja hypoteesista:

I. **Titaanipinnan TiO₂-kerros.** Hypoteesin mukaan polttoprosesseja edeltävällä TiO₂-kerroksen paksuudella ei ole merkitystä liitoksen kestävyyteen.

II. **Titaanipinnan kostetus.** Hypoteesin mukaan TiO₂-pinnasta saadaan voimakkaan hydrofiilinen vain minuuttien ultraviolettialistuksella.
III. Hapen diffuusio titaanihilaan keraamipolttoprosessien aikana. Hypoteesin mukaan titaanirakenteen pinnalle valmistettavan hopeavälikerroksen avulla voidaan tehokkaasti ehkäistä polttoprosessien aikaista hapen liukenemista titaaniin ja tästä seuraavaa titaanin pinnan haurastumista.

IV. Mekaanisen rasituksen jakautuminen liitosalueella. Hypoteesin mukaan hauraiden reaktiokerrosten muodostumisen ehkäisy on tärkeämpää kuin mekaaninen retention aikaansaaminen pinnan karhennuksella. Fotolitografista etsausmenetelmää käytämällä voidaan välttää yhtäjaksoisten tasomaisten reaktiokerrosten haurasmurtuma rasituksen kohdistuessa paikoitellut Ti päälle sintrattuun hammaskeraamiin.

Titaanin pinnalle muodostuu normaaliympäristössä välittömästi mutamien nanometrien paksuinen ns. natiivioksidikerros, joka koostuu pääosin amorfisesta TiO₂:sta. Vaikka titaanin erinomainen biokompatibiliteetti ja korroosionkestävyys ovat ensisijaisesti juuri tämän oksidikerroksen ansiota, titaaniosaiden vaikutuksia metallokeramaisten liitosten muodostumisessa on perinteisesti pidetty erittäin hallituttua perustuen osin käytännön metallokeramiasta poikkeavissa olosuhteissa saatuihin testituloksiin. Vallalla on vielä myös harhalululoja ja väärinkäisyyksiä faasitransitiolämpötilan ylittämisä seurauksena, jälkeen jäähtymisen aikana titaanin pinnalle muodostuvasta, erittäin runsaasta happea sisältävästä "α-case layer"sta, jota on värin perusteinaan muun muassa paksuakset titaaniosaiden diversiteetti. Väitöskirjan ensimmäisessä osion kokeellisessa ja kirjallisessa osassa esitetään kuitenkin työn hypoteesia vastaavasti, kuinka normaaleissa keraamien polttoprosesseissa paksu TiO₂-kerros dissosioituu, hapen diffuusiokinetiikka hopeataan kohonnettaan lampötilan seurauksena, ja uunin sisäilmasta, SiO₂:sta ja dissosioituneesta oksidikerroksesta lähtöisin oleva happi diffundoituu siihen titaanin sisälle, rajoittaen titaanitukirakenteen ylimpien osien plastisuutta; sitä enemmän mitä korkeampi on titaanin liuvenneen hapen pitoisuus eli Ti[O]₃-3-pistetaivutustestisteissä eikä keraamipolttajoja edeltävien TiO₂-kerrosten paksuudella havaittu merkittävää vaikutusta liitoksen kestoon liitosten murtuessa rasitustesteissä järjestelmällisesti syvemmällä titaanitukirakenteen sisältä, Ti[O]-kiinteäluoskerroksessa. Koska hammaskeraamien polttoprosesseissa käytettävien uunien alipaineepumput eivät riitä estämään hapen diffuusiota ympäristöstä titaanii, vaaditaan hapen diffuusiota rajoittavia menetelmiä pinnan haurastumisen ehkäisemiseksi.

Hyvän liitoksen aikaansaamiseksi vaaditaan hyvää pinnan kostutusta, mikä on myös muun muassa mikromekaanisen retention kannalta ensiarvoisen tärkeää kerrostettaessa keraamin materiaali metallipinnoille. Hyvä pinnan kostutus mahdollistaa keraamiliitosaineiden, bonderien, tehokkaan leviämnien peittämään Ti pintaa heti ensimmäisessä keraamipolttoprosessissa rajoittaen polttoympäristöstä lähtöisin olevan hapen pääsyä liitosalueelle. Hypoteesia vastaavasti monografian toisen osion kokeellisessa osiossa
osoitetaan, kuinka TiO$_2$-pinnan superhydrofiilisyys voidaan aikaansaada fotoindusoidusti vain muutamissa minuuteissa. Nykyisiä keraamimateriaaleja käytettäessä titaanipinnan kostuvuus on kuitenkin vähäisempi ongelma verrattuna hapen diffusioon polttoprosessien aikana. Vaikka polttouunin sisältämä ilma on ensisijainen ja tehokkain hapenlähteen, myös SiO$_2$-pohjaiset keraamit toimivat erinomaisena hapenlähteenä kohonneissa polttolämpötiloissa, minkä vuoksi borondierainen käyttö ei voi täysin estää hapen pääsyä titaanin.

Tutkimuksen kolmannessa osiossa osoitetaan, kuinka hopeavälikerroksilla voidaan ehkäistä hapen diffundoituminen polttoprosessien aikana titaanitukirakenteissa. Käsittelemällä pinta Ag-välikerroksin Al$_2$O$_3$-puhalluksen jälkeen saavutettiin tilastollisesti merkittävästi parempi tulos 3-pistetaivutustesteissä ($p = 1.27\cdot10^{-6}$) verrattuna pelkkään pinnan karhentamiseen Al$_2$O$_3$-puhalluksella. Hopeakerroksia käytettäessä liitoksen haurain osa oli poikkeavasti itse hammaskeraami, missä havaittiin lukuisia erillisiä haurausmurtumia titaanitukirangan säilyessä ehjänä. Vaikka lukuisia eri välikerroksia on tutkittu aiemmin liitoslujuuden parantamiseksi ja hapen diffusion ehkäisemiseksi ja joitakin vaatimuksia ideaalisille välikerroksille on esitetty, ei yhtenäistä suunnitelmallista vaalinta parhaimman mahdollisen välikerrosmateriaalin löytämisele ennen tätä väitöskirjaa julkaisusta. Diffuusioeristeenä toimimisen lisäksi Ag-kerrosten plastisuus on suotuisaa keraamin ja titaanin lämpölaajenemiskertoimien eroista johtuvaan jäännösrasitusten laukaisemisessa. Näiden toistuvissa polttoprosesseissa ja jäähtymisissä syntyvien jännitysten haitallisuus liitoksen mekaaniselle kestolle on hyvin tunnettu. Myös pinnan karhennuksessa käytettävästä Al$_2$O$_3$-partikkeleista syntyvien mahdollisesti haitallisten titaanipinnen viirasainejärien eristyminen keraamikontaktista hopeakerrosten ansioista osoitettiin.

Tyypillisesti metallipinnan karhentamisen on uskottu parantavan liitoksen laatua liitospinta-alaa, mekaanista retentiota ja kostutusta lisäämällä, sekä liitokseen kohdistuvaa jännitystä vähentämällä. Titaanimetallokeramiassa liitoksen heikoin kohta ei kuitenkaan ole varsinainen rajapinta keraamimateriaalin ja titaanin välillä vaan runsashappinen Ti[O]$_{1-x}$-kiinteäliuos titaanin. Tutkimuksen neljännessä osiossa mikroelektroniikkateknologian tarpeisiin kehitetty fotolitografista etsautekniikka soveltaen titaanipintaan muodostetaan säännönmukaisia syvennyksiä syvennystä vasten materiaalin rasituksen jakautumista liitousrajapinnassa hammaskeraamin ja hauraiden reaktiokerrosten välillä sekä ehkäisemään murtuman etenemistä yhtenäisissä, tasomaisissa reaktiokerroksissa parantaen täten liitoksen kestävyyttä. Kolmipistetaivutustestitekniikan monikomponenttisen, kompleksin rasitusvirran metallokeramiassa liitokseen litografisesti tuotettujen syvennysten sekä titaanin ja hammaskeraamin omia rasituksissa syvennysta vähemmän, ennen titaanipinnaa muodostettua, rasituksen jakautumista liitosrajapinnassa keraamikoska, sekä titaanin ja hammaskeraamin ominaisuuksissa, hyvin tunnettu. Syvennysten välissä maksimaalinen vetojännityskomponentti vaikuttaa lähes kohtisuoraan reaktiokerrosta varten avaten murtuman kärkeä ja helpottaan murtumaa etenemistä. Pystysuorilla syvennysten seinämillä tämän jännityskomponenttin vaikutus on vähäisimmillään; murtuman eteneminen hauraiden reaktiokerrosten suunnassa vaikeutuu ja murtuma todennäköisemmin etenee titaanirungon pinnaa suuntaan leikaten läpi syvennysvaiheessa olevan vähemmän hauraan hammaskeraamin. Koska hammaskeraamin
murtuminen Ti[O]-kiinteäliuoksen sijasta saavutettiin kokeellisessa osassa vain osassa syvennyksiä, ei 3-pistetaivutustestissä havaittu merkittäviä eroja kontrolliryhmään verrattuna. Mahdollisesti säännönmukaisesti syvempiä ja jyrkempiä syvennyksiä tuottamalla voitaisiin saada merkittävä parannus myös rasitustestesteissä; Ag-välikerroksilla tehdyt testit osoittavat selvästi, että hammaskeraami murtuu vain koko liitoksen kestäessä tavanoamaista merkittävästi suurempia voimia. Neljänneen tutkimusosion tulokset osoittavat myös selkeästi, kuinka perinteisten pinnan karhennusmenetelmien avulla saatavan mekaanisen lukittumisen merkitys liitoslujuudelle on vähäinen, ellei hauraiden reaktiokerrosten – erityisesti runsaasti happea sisältävän Ti[O]-kiinteäliuoksen – muodostumista saada kontrolloitua.


REFERENCES


REFERENCES


Petzow G. Metallographic Etching, 2nd edition: 139-144. 1999. ASM International. USA.


Massalski T. Binary Alloy Phase Diagrams. 1996. ASM International. USA.


REFERENCES


