The system Y-TZP and its porcelain

The interface and firing influences of the porcelain on the “chipping”

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Abstract

Objectives

All-ceramic dental prosthetic materials are in high demand for their aesthetic and biocompatible properties. There is, however, a number of critical clinical problems both in terms of the aesthetic properties and “chipping” fracture of veneering porcelains, especially for porcelain-zirconia restorations. The former area has received minimal attention while the latter has resulted in various structural designs and cooling procedure considerations reduce such behaviour.

This thesis initially addresses the importance of firing of veneering porcelain on its subsequent aesthetic and mechanical properties. The problem of “chipping” of porcelain zirconia frameworks is initially investigated by considering the metastability of the tetragonal phase of yttria tetragonal zirconia polycrystalline (Y-TZP) ceramics during the preparation of porcelain-zirconia restorations. One specific problematic area is the interface between the porcelain and the Y-TZP framework and whether the associated veneering procedures and reactions result in a phase transformation of the zirconia and lead to weakening of interface bonding. The role of temperature gradients during fast and slow cooling for conventional and anatomical zirconia framework designs are compared as well as their influence on residual stress within the porcelain.
Abstract

Methods
The effect of firing on mechanical, thermal expansion and solubility of porcelains were examined on the ISO 6872:2008 standards.

Dry and moist veneering porcelain powders were built up on the zirconia framework. High-resolution SEM observations of the zirconia at the porcelain zirconia interface were made to identify the zirconia microstructure. XRD$^2$ micro diffraction measurements were carried out on the interface area to generate locally resolved zirconia phase information.

The temperature gradients between the inner and outer surfaces of crowns were measured with thermocouples during two different cooling methods with uniform and anatomical frameworks. Direct observation of the residual stresses for the uniform framework crown following fast and slow cooling was made with an optical polarimeter.

Results
For sintering of veneering porcelains the key outcomes were the critical role of the maximum temperature, firing time, vacuum and pre-drying of the porcelain on the physical properties and also for differences of the shade of a dental restoration. The importance of sintering time and temperature were critical for the resultant properties, most noticeably translucency (value) and strength.

Under moist firing conditions the phase composition of zirconia grains at the interface revealed both monoclinic and tetragonal structure. These observations
indicate that destabilisation of the tetragonal phase of zirconia can occur at the interface during the veneering.

Temperature gradients generated during cooling showed that slow cooling decreases the temperature differences between the inner and outer surfaces of the restorations. For fast cooling, temperature differences of more than 140°C at temperatures above the glass transition temperature were recorded. Optical polarimeter observations indicated much lower stresses within the porcelain layer upon slow cooling of the crown. Rapidly cooled crowns resulted in higher stresses within the cusp area, which is the area where “chipping” is most frequently observed.

Conclusions

- A simple firing temperature-time matrix readily enables the optimisation of the aesthetic and physical properties of veneer porcelains.

- The porcelain veneering process, especially with a wet veneer during firing, results in a localized tetragonal to monoclinic structural transformation at the surface of the zirconia framework of all-ceramic dental restorations.

- Slow cooling of the porcelain during the final veneering step on porcelain-zirconia restorations reduces the temperature gradients and residual stresses within the porcelain layer, which represent one of the possible causes for “chipping”.
Publications

Publications and scientific meeting presentations arising from this research/project

*International Journal publications:*


*National (German) Journal Publications:*


*Posters:*

- Benetti P, Tholey M, Thiel N, Kelly JR. Influence of cooling-rate on residual stresses in veneered zirconia structures. San Diego, IADR 2011


**International Meetings Oral Presentations**

• Tholey MJ, Thiel N, Swain MV. Veneering of Y-TZP frameworks with successful result. Bruxelles Belgium, Dental Technician meeting 2010

• Tholey MJ, Thiel N, Swain MV. Facts of veneering of Y-TZP frameworks. Amsterdam, Nederland, Dental Technician meeting 2010

• Tholey MJ, Thiel N, Swain MV. Facts of veneering of Y-TZP frameworks. Nottingham, United Kingdom, Dental Technician meeting 2010

• Tholey MJ, Thiel N, Swain MV. Veneer Porcelain. Stockholm, Sweden, European Ceramic Society (ECerS) 2011


**National Meetings Oral Presentations:**

• Tholey MJ, Thiel N, Swain MV. Verblenden von ZrO2-Gerüsten ohne Risiko. Ludwigsburg, Klassik trifft Moderne, Germany, 2010

• Tholey MJ, Thiel N, Swain MV. Y-TZP Gerüste richtig verblenden. Hamburg, Germany. 2010
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I wish I can dedicate this thesis to my whole family, and thank them with all my heart for their love, care and patience.

**My PhD is dedicated to**…

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…to Frida, our lovely daughter. She was during all the time just the sunshine of my life.

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# Table of Contents

Abstract ....................................................................................................................... I  
Objectives .................................................................................................................. I  
Methods .................................................................................................................... II  
Results ...................................................................................................................... II  
Conclusions ............................................................................................................... III  
Publications ............................................................................................................... IV  
International Meetings Oral Presentations ............................................................... V  
Acknowledgement ..................................................................................................... VI  
My PhD is dedicated to............................................................................................. VIII  
Table of Contents ..................................................................................................... X  
Abbreviations ......................................................................................................... XII  

CHAPTER I ................................................................................................................ 1  
1. Introduction ......................................................................................................... 1  
   1.1 Aspects .............................................................................................................. 1  
   1.2 Statement of the problem .............................................................................. 3  
   1.3 Aims of the study .......................................................................................... 5  
   1.4 Presentation of the study .............................................................................. 6  

Chapter II.................................................................................................................. 9  
2. Literature review ................................................................................................. 9  
   2.1 All-ceramics as a restorative material ............................................................ 9  
   2.2 Veneering porcelain ...................................................................................... 12  
   2.3 Zirconia as a framework material .................................................................. 15  
   2.4 Brief overview on the bonding mechanism of porcelain to frameworks ........ 25  
      2.4.1 Bonding behaviour of PFM (“Porcelain Fused to Metal")....................... 27  
      2.4.2 Bonding behaviour of PFZ (“Porcelain Fused to Zirconia")................... 31  
   2.5 Clinical outcomes ......................................................................................... 33  
      2.5.1 Clinical success of porcelain fused to metal (PFM) ............................... 33  
      2.5.2 Clinical success of porcelain fused to alumina (PFA) ............................ 35  
      2.5.3 Clinical success porcelain fused to zirconia (PFZ)................................. 37  
      2.5.4 Comparison on clinical success of PFM and PFZ................................. 43
Table of Contents

2.6. Veneering porcelain fracture (“Chipping”) ............................................................... 47
2.7. The future of zirconia-based dental restorations ..................................................... 55
2.8. Conclusion ............................................................................................................... 58

Chapter III ................................................................................................................. 60
3. Materials, Methods and Theoretical basis ............................................................ 60
   3.1 Firing of the sample for the determination of the properties .................................. 60
      3.1.1 Pre-Test ................................................................................................................. 60
      3.1.2 Test according to ISO 6872 ............................................................................. 62
      3.1.3 Shade determination ........................................................................................ 65
   3.2 SEM observations of the interface .......................................................................... 67
      3.2.1 Firing of the samples ............................................................................................. 67
      3.2.2 Preparation of the samples .............................................................................. 69
      3.2.3 Observation of the samples ............................................................................. 69
      3.2.4 Brief introduction in the FE-SEM technology ................................................... 70
   3.3 XRD²-Diffraction observation of the interface .......................................................... 73
      3.3.1 Firing of the samples ............................................................................................. 73
      3.3.2 Preparation of the samples .............................................................................. 75
      3.3.3 Observation of the samples ............................................................................. 75
   3.4 Thermal gradients observations of the interface ..................................................... 79
      3.4.1 Crown/sample model ............................................................................................. 79
      3.4.2 Thermal measurement configuration ............................................................... 81
      3.4.3 Polarimeter method .......................................................................................... 83

CHAPTER IV ............................................................................................................ 87
4. Critical role of firing temperature on the physical properties of dental porcelains 87
   4.1 Introduction .................................................................................................................. 87
   4.2 Materials and methods ................................................................................................. 91
      4.2.1 Pre-Test ............................................................................................................... 91
      4.2.2 Test according to ISO 6872:2008(E) ................................................................ 91
      4.2.3 Shade determination ........................................................................................ 92
   4.3 Results ......................................................................................................................... 92
   4.4 Discussion .................................................................................................................... 95
   4.5 Conclusions ................................................................................................................ 102

CHAPTER V ........................................................................................................... 103
5. SEM observations of the Interface between Y-TZP and its veneering material 103
# Table of Contents

5.1 Introduction ................................................................................................................ 103
5.2 Materials and Methods ............................................................................................... 106
5.3 Results ....................................................................................................................... 107
5.4 Discussion .................................................................................................................. 114
5.6 Conclusion ................................................................................................................. 120

CHAPTER VI .......................................................................................................... 121
6.  XRD$^2$ Micro-Diffraction Analysis of the Interface between Y-TZP and Veneering Porcelain: Role of Application Methods .............................................................. 121
   6.1 Introduction ................................................................................................................ 121
   6.2 Materials and Methods ............................................................................................... 124
   6.3 Results ....................................................................................................................... 126
   6.4 Discussion .................................................................................................................. 133
   6.5 Conclusions ................................................................................................................ 138

CHAPTER VII ......................................................................................................... 139
7.  Thermal gradients and residual stresses in veneered Y-TZP frameworks........... 139
   7.1 Introduction................................................................................................................ 139
   7.2 Materials and Methods .......................................................................................... 142
      7.2.1 Crown/sample model ..................................................................................... 142
      7.2.2 Thermal measurement configuration ............................................................. 142
      7.2.3 Polarimeter method ........................................................................................ 142
   7.3 Results .................................................................................................................. 143
   7.4 Discussion ............................................................................................................. 150
   7.5 Conclusions ........................................................................................................... 157

CHAPTER VIII ........................................................................................................ 159
8. Conclusions and Implications .......................................................................... 159
   8.1 Brief Summary ........................................................................................................... 159
   8.2 Conclusion ................................................................................................................. 160
   8.3 Recommendations ..................................................................................................... 163

References ............................................................................................................. 164
Tables .................................................................................................................... 181
Figures ................................................................................................................... 183
## Abbreviations

*(alphabetical order)*

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>∆E</td>
<td>Colour Difference</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
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<tr>
<td>CAD</td>
<td>Computer Aided Design</td>
</tr>
<tr>
<td>CAM</td>
<td>Computer Aided Manufacturing</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of Thermal Expansion</td>
</tr>
<tr>
<td>DKV</td>
<td>Deutsche Kranken Versicherung (German Insurance Company)</td>
</tr>
<tr>
<td>FEA</td>
<td>Finite Element Analysis</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field Emission - Scanning Electronic Microscope</td>
</tr>
<tr>
<td>FPD</td>
<td>Fixed Partial Dentures</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>GADDs</td>
<td>General Area Diffraction Detection System</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric Acid</td>
</tr>
<tr>
<td>HIP</td>
<td>Hot Isostatic Pressing</td>
</tr>
<tr>
<td>ISO</td>
<td>International Standard Organisation</td>
</tr>
<tr>
<td>K&lt;sub&gt;IC&lt;/sub&gt;</td>
<td>Fracture Toughness</td>
</tr>
<tr>
<td>LTD</td>
<td>Low Temperature Degradation</td>
</tr>
<tr>
<td>PFM</td>
<td>Porcelain Fused Metal</td>
</tr>
<tr>
<td>PFZ</td>
<td>Porcelain Fused Zirconia</td>
</tr>
<tr>
<td>SAV</td>
<td>Small Area View</td>
</tr>
<tr>
<td>SBR</td>
<td>Stress Bire-Fringence</td>
</tr>
<tr>
<td>T&lt;sub&gt;G&lt;/sub&gt;</td>
<td>Glass (liquid) Transition Temperature</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>-------------</td>
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<tr>
<td>T&lt;sub&gt;M&lt;/sub&gt;</td>
<td>Melting Temperature (freezing point or crystallization point)</td>
</tr>
<tr>
<td>T&lt;sub&gt;S&lt;/sub&gt;</td>
<td>Softening Temperature</td>
</tr>
<tr>
<td>XRD&lt;sup&gt;2&lt;/sup&gt;</td>
<td>2-dimensional X-Ray Diffraction</td>
</tr>
<tr>
<td>Y-TZP</td>
<td>Yttria Tetragonal Zirconia Polycrystalline</td>
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CHAPTER I

1. Introduction

1.1 Aspects

The word ceramic derived from the Greek word “keramos”, which literally means “burnt stuff” but which has come to mean more specifically a material produced by burning or firing. The first crowns made from pure ceramic were used clinically in 1885 for single anterior crowns. The motive was their better aesthetic and natural look compared to pure metal [1]. However, ceramic materials can only withstand limited tension without fracturing and are susceptible to stress corrosion fatigue fracture. In addition the wide-spread use of all ceramic crowns in dentistry was limited for decades by their brittleness caused by the ceramic covalent atomic bonding [2].

A great milestone in the veneering technology was laid with the development of porcelain firing furnaces with vacuum possibility in 1949 [3]. Despite this significant improvement, however, the decisive breakthrough in metal ceramic was not to be achieved until 13 years later by Weinstein. In 1962 he filed a patent in the USA for a ceramic capable of being veneered to metal [4; 5]. Almost at the same time, in 1962, the first metal-ceramic system to be developed in Europe was brought onto the dental market by the German companies VITA Zahnfabrik and Degussa Dental [6].
Since that time, gold- and non-precious metal-alloys such as for instance cobalt-chromium have retained a position in dentistry as reliable and well-established clinical materials for dental restoration [7]. Metal-ceramic systems are very widely used clinically and are part of every education system for dental technology around the world. These facts along with their extensive clinical success indicate their worldwide acceptance and widespread use since their launch in 1962. Metal-based or porcelain fused to metal systems are known as very reproducible in terms of handling issues.

When fabricating metal–ceramic restorations, the metal framework makes it difficult to imitate natural aesthetics, especially in situations with limited space for the reconstruction. Another problem associated with a metal framework is the possible bluish and greyish appearance of the surrounding soft tissues, which was partly solved by the development of a reduced framework design in the anterior area and shoulder porcelain [8].

Nevertheless, the demand for a better aesthetic, more biocompatible and more natural crown appearance has increased considerably in dentistry in the last decade. This demand lead to the development of a number of different framework materials made entirely of ceramics. The reason was their aesthetic capability and biocompatibility [9].

The market for the use of zirconia-based all-ceramic crowns and more complex dental restorations has been growing rapidly. Zirconia-based restorations have experienced only a few years of basic science of research and laboratory
development, which results also in just a few years of clinical observation. To date, the research results are promising except for a major concern, namely “chipping” [1]. Today’s porcelain for metal frameworks resulted from the development over 5 decades.

This development has allowed compensation for all different metallic colours, gold and non-precious alloys, of the framework and allows resulting in acceptable aesthetic results. Still, to realize the highest possible aesthetic all-ceramic restorations are clearly superior [11]. The reasons are the naturally appearance of the soft red gingival tissue and the greater light transmission of all-ceramic systems for example [11].

However, significantly more clinical observation and research is needed for all-ceramic restorations regarding the development of a better understanding of the factors that contribute to the concern regarding “chipping” and overall reliability.

1.2 Statement of the problem

All-ceramic dental restorations have become more popular over the past decade and the demand is still growing [12]. The advances of the CAD/CAM technology have accelerated the demand for these materials combined with opportunities for faster growth for dental restorations prepared in this manner. Furthermore the introduction of yttria-partially stabilized zirconia (Y-TZP) as a framework material and the ability to machine this material has resulted in a rapid uptake in the market. This material has very attractive properties for dental applications, as mentioned these include the
Over the past few years there have been increasing clinical reports of failure of all-ceramic restorations with zirconia framework with a much higher frequency than porcelain fused to metal crowns and bridges [12; 14; 15]. There have been numerous papers trying to determine the cause of this problem [10; 16]. It is even more noticeable that some dental laboratories have fewer problems with zirconia based dental restorations than others even when using the same framework zirconia materials and the same porcelains.

The cracking or “chipping” seems to extend only through the porcelain. One example of such a failure in a porcelain-zirconia crown is shown in Fig. 1. This figure presents a crack on the mesio buccal cusp of a first molar within the porcelain. This crack is extending after its initialisation into the veneering porcelain leading to a “chipped” fracture.

The consequence of “chipping” has become a major issue and severely retarded the potential demand for zirconia-based all-ceramic restorations and with many clinicians and technicians lead to a renewal in demand for the “old” metal-ceramic system but with cheaper non-precious metals as framework materials.

This “old” technology with non-precious alloys has now, as a result of the incidence of chipping, over 60% of the market share in Germany. For instance CoCr-based
framework material had only 25% share some 10 years ago, but demand is still rising on the German market.

Fig. 1: "Chipping" fracture at the mesio-buccal cusp on a first molar (Magnification: 44x)

One reason for the return to the “old” approach is the price for a dental restoration, which is still lower with non-precious frameworks; the other reason seems to be the significant number of “chipping” failures.

The present thesis investigates some parameters that appear to be critically related to the “chipping” problem and explores solutions to this problem.

1.3 Aims of the study

The aims of this study are summarized as follows:
To determine the influence of ceramic processing on some mechanical and physical properties of the veneering porcelain.

To explore the interface of the porcelain-zirconia dental restoration by SEM high resolution imaging.

To investigate the phase changes of zirconia crystal structure including the nucleation and growth processes during veneering with a novel approach using XRD$^2$ diffraction.

To study and identify residual stresses within the porcelain layer on a zirconia coping by using thermocouples and optical polarimeter methods.

1.4 Presentation of the study

The present study consists of seven chapters.

The historical background of all-ceramic dental restorations is presented in Chapter II. In this review the developments of veneered framework materials from metal alloys up to all-ceramic frameworks is considered and the clinical results of all of these materials are summarised in this chapter. Furthermore a critical summary of zirconia as a framework material is included and a comparison of porcelain fused to metal and porcelain-zirconia restorations is presented. Some images will illustrate the problem and outcomes of the clinical observations, clarifying the reasons for the research.

Chapter III clarifies the various materials, methods and underlying theoretical basis that are used in the following studies. The sample preparation procedure together with the involved porcelains is explained. The description of the FE-SEM, XRD$^2$
diffraction and the polarimeter method for the investigations of the ceramic interface and thermal stress behaviour in the porcelain layer are also included.

Chapter IV summarizes the influences of the firing conditions on the veneering porcelain and forms a basis for the following chapters. All mechanical and various property-testing methods of the ISO standards for veneering porcelain are included. In addition, the influences of the firing conditions on the shade of a dental restoration are included.

In Chapter V, a thorough investigation on the interface of zirconia-based restoration is presented. High-resolution SEM observations are included that enable details of the surface grains of Y-TZP in contact with the veneering porcelain to be investigated. It is concluded that different firing processes with the presence of water in the porcelain influence the phase stability of the zirconia surface.

Chapter VI develops further on the results and observations presented in Chapter V. A new approach using high resolution XRD²-diffractometry is used to identify the influence of moisture on the phase stability of the zirconia grains during the firing process.

In Chapter VII the origin of “chipping” of porcelain fused to zirconia restorations will be considered. The effect of different cooling regimes on the temperature gradients within the porcelain-zirconia crowns will be characterised using thermocouples. In addition the resultant residual stresses in the veneering porcelain layer will be
measured using an optical polarimeter method. This study will show the influence of fast versus slow cooling on the resulting stress in the porcelain layer.

The conclusions arrived at from this thesis are addressed in Chapter VIII. The results and outcomes of all the previous chapters are summarized and this section provides some ideas for further investigations in this area. It will present an approach as to how a dental technician and his dentist can successfully provide their patients dental zirconia-based restorations with the same or better reliability as porcelain fused to metal restorations.
2. Literature review

2.1. All-ceramics as a restorative material

Although routine use of all-ceramics in dentistry is a relatively new phenomenon, the desire for a durable and aesthetic oral restorative material is ancient. Most cultures through the centuries have acknowledged teeth as an essential facial structure associated with health, youth, beauty and dignity [17].

Teeth have routinely been designated with an equally powerful role in cultures where dentitions were purposely mutilated as inspired by narcissism, fashion and religious beliefs [17]. Therefore, it has been almost worldwide that unexpected loss of tooth structure and, mainly missing anterior teeth, create physical and functional problems and often psychological and social consequences as well.

Although dental technology existed in Etruria as early as 700 BC and during the first century BC in the Roman Empire, it remained virtually undeveloped until the eighteenth century. Materials for artificial teeth and dentures till the 18th century were human or animal teeth, ivory, and finally porcelain [17; 18].

As an example, John Greenwood carved teeth from hippopotamus ivory for a complete denture he fabricated for George Washington [18; 19]. After decades of effort, in approximately 1774, a Parisian apothecary Alexis Duchateau, with
assistance of a Parisian dentist Nicholas Dubois de Chemant, made the first successful porcelain dentures replacing ivory prostheses [19].

While not using feldspathic porcelains, Pierre Fauchard described the enamelling of metal denture bases in 1723 in his essential text “Le Chirurgien Dentiste” [20]. Fauchard appreciated the potential of porcelain and initiating research with this material to imitate teeth [20].

Improvements in translucency and colour of dental porcelains were realized through developments that ranged from the formulations of Wildman in 1838 up to vacuum firing in 1949 [20].

By combining burnished platinum foil as a substructure with the high, controlled heat of a gas furnace, Land was capable of introducing the first fused pure feldspathic porcelain inlays and crowns in 1886 [20]. This all-porcelain crown system, despite its aesthetic advantages, failed to gain widespread popularity until the introduction of alumina as a reinforcing phase in dental porcelain [17].

In the 1950s with the addition of leucite to porcelain formulations allowed fusion to metal alloys to form dental restorations. Metal-ceramic systems dominated dental ceramics research during the past 50 years that resulted in improved alloys, porcelain metal bonding, and porcelains.

The introduction during the 1980s of all-ceramic crown systems as Cerestore (Coors Biomedical, USA), VITA-blocs (VITA Zahnfabrik, Germany), castable glass-ceramic
crown system (Dicor, Dentsply, USA) and pressable systems (IPS Empress e.g. by Ivoclar-Vivadent, Lichtenstein) gave the possibility for single tooth restorations.

Towards the end of the 1980s a novel advanced ceramic system renewed interest in all-ceramic prostheses. In-Ceram (originally Infiltration Ceramic, since 2004 renamed into Innovative Ceramic) ceramic, introduced in 1989 by VITA Zahnfabrik, Germany, consists of two three-dimensionally interpenetrating phases, alumina (aluminium oxide) and a lanthanum alumina-silicate with small amounts of sodium and calcium glass. In the original In-Ceram ceramic process, the compacted alumina particles are partially sintered together to form necks between touching particles. This porous, partially sintered alumina is infiltrated with a low-viscosity glass to yield a ceramic coping of high density and strength. It was the first available framework material for up to 3-unit all-ceramic bridges.

With the introduction, in 1998, of the IPS Empress 2 by Ivoclar Vivadent, Lichtenstein, a pressable lithium disilicate glass-ceramic system was available as an all-ceramic alternative for up to 3-unit bridges in the anterior area was available. Another product released in the 1990s, Procera alumina (Noble Biocare, Switzerland), a densely sintered alumina product, became a successful alternative for single tooth restorations.

The above mentioned all-ceramic framework materials are not the main focus of this evaluation. This review is focussed on the advanced ceramic restoration situation of today, where it seems only zirconia and metal alloys are considered appropriate framework coping products for all kinds of dental restorations.
Only a short discussion into the clinical results of In-Ceram Alumina and the densely sintered Procera Alumina all-ceramics will be included to enable a comparison of zirconia-based dental restorations with another veneered ceramic framework material. The reason for this compilation is to provide a focus in this study as how the porcelain works with its framework material in comparison with zirconia-based all-ceramic systems. All other all-ceramic systems were important for the all-ceramic history and development but are not the primary object of this thesis.

2.2. Veneering porcelain

Veneering porcelain is available for all different types of framework materials. This part of the review gives a short overview about this material. The essential of traditional ceramics is that they are composed of a weak, opaque and porous material, namely kaolin (hydrated aluminosilicate, \(\text{Al}_2\text{O}_3*2\text{SiO}_2*2\text{H}_2\text{O}\)) that is unsuitable for dental applications. The blending of this with other minerals such as silica and feldspar produces the desired translucency and extra strength required for dental restorations. Material containing these additional important ingredients has been given the name of porcelain [1]

Porcelain can be produced in nearly every shade and colour. Therefore it is not surprising, that dentistry has turned to porcelain for the production of artificial teeth, crowns, bridges and veneers.

In the description of the US Patent 3,052,982 by Weinstein (1962), the first written article about this type of porcelain to veneer a metal alloy, the porcelain is mainly a mixture of a glass matrix with a coefficient of thermal expansion (CTE) of about \(8*10^{-6}\)
and a crystalline phase of tetragonal leucite (K\text{*}Al\text{*}Si\text{2}O\text{6}) with a CTE of 20*10^{-6} K^{-1} creating the CTE value recommended for each framework material. That means the traditional dental porcelain has the following components [21] with approximately the resulting proportion as presented in Table 1.

### Table 1: Average composition of dental porcelain [22]

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>63.2%</td>
</tr>
<tr>
<td>Aluminium Oxide (Al2O3)</td>
<td>17.5%</td>
</tr>
<tr>
<td>Boric Oxide (B2O3)</td>
<td>1.0%</td>
</tr>
<tr>
<td>Potash (K2O)</td>
<td>11.7%</td>
</tr>
<tr>
<td>Soda (Na2O)</td>
<td>5.7%</td>
</tr>
<tr>
<td>Calcium Oxide (CaO)</td>
<td>0.8%</td>
</tr>
</tbody>
</table>

Dental porcelain is therefore a mixture of clay, also known as kaolin, with silica (quartz), bound together by a flux or binder such as feldspar, which is a mixture of potassium and sodium aluminosilicates, K\text{2}O\text{*}Al\text{2}O\text{3}\text{*}6SiO\text{2} and Na\text{2}O\text{*}Al\text{2}O\text{3}\text{*}6SiO\text{2} as illustrated in Fig. 2. Feldspar is the lowest fusing component and it is this, which melts and flows during firing, uniting the other components in a solid mass [21].
The powders supplied to dental technicians are not just combinations of the various ingredients. During manufacture the ingredients are mixed together (with pigments for the colour and/or compounds for fluorescence) and fused to a frit, which is broken ground into fine powder ready to use [24].

As typical examples for different types of porcelain used for zirconia frameworks Fig. 3 presents SEM (scanning electron microscope) pictures with etched surfaces of VITA VM9 (VITA Zahnfabrik, Germany), Cercon Ceram Kiss (DeguDent, Germany), Vintage Zr (Shofu, Japan) and HeraCeram Zirconia (Haereus, Germany). Each sample has been etched for 20 sec. with a HF-content etch-gel (VITA Zahnfabrik, Germany) to reveal the microstructure. Etched leucite particles (a crystal phase of the feldspar) are the major porcelain content, which is dissolved by the HF etch in between the glass matrix of the samples. These SEM images show the presence of leucite crystals lying in a glass matrix similar as described in Weinstein patent (1962). The content of the leucite crystals depends on the different CTE and the different chemical compositions of the porcelains.
The main focus of chapter IV will be on porcelain and the influences of the firing on its properties.

### 2.3. Zirconia as a framework material

This section is dedicated to zirconia, an all-ceramic framework material. Metal alloys, used as framework material, have numerous basic scientific and clinical studies [25] and are widely observed and do not need further explanation. In contrast, the
comparatively new framework material zirconia, which is also in the major focus of this study, has relatively limited studies in the dental area.

Zirconia holds an exclusive place amongst all other oxide ceramics as (e.g. alumina and spinel) due to its excellent mechanical properties as a framework material. This situation results from the significant amount of research work that has been done since the detection of the transformation toughening abilities of zirconia in the mid-1970s [26].

At ambient pressure pure zirconia can assume three different crystallographic forms depending on its temperature. At room temperature and upon heating up to 1170°C, the symmetry crystal is monoclinic as presented in Fig. 4 on the left. The structure is tetragonal (Fig. 4 in the middle) between 1170°C and 2370°C and cubic above 2370°C and up to the melting point [27; 28], as shown in Fig. 4 on the right hand side.

The transformation from the tetragonal (t) to the monoclinic (m) phase upon cooling is associated by a substantial increase in volume (~ 4.5%), sufficient to lead to
catastrophic failure [25]. This transformation is reversible and begins at \( \sim 950^\circ C \) during the cooling [25]. Stabilizing pure zirconia with oxides such as CaO, MgO, \( Y_2O_3 \) or CeO\(_2\) allows the retention of the tetragonal structure even at room temperature and consequently the chance for stress-induced \( t \rightarrow m \) transformation. This leads to noticeable higher fracture toughness [25; 26; 29; 30].

As a result of this toughening mechanism the introduction of zirconia-based dental materials has generated significant attention in the dental community. The mechanical properties of zirconia are the highest ever reported for any dental oxide ceramic framework material. This allows the realization of posterior fixed partial dentures and a reduction in framework thickness especially in the occlusal area. These capabilities are very attractive in dentistry; mainly especially aesthetics and strength are dominating required properties [25].

However, due to the metastability of tetragonal zirconia, stress-generating surface treatments such as grinding or sandblasting are also capable to trigger the \( t \rightarrow m \) transformation with the associated volume increase. This leads to surface compressive stresses, which increases the flexural strength but also the susceptibility to aging [31].

Fig. 5 presents the \( t \rightarrow m \) transformation zone and toughness increase (\( \Delta K_c \)) development with crack extension on a zirconia surface by Evans [32]. The stress-induced transformations can cause significant toughening include martensitic transformations.
At the simplest level, transformation toughening can be regarded as a process dominated by a volume increase. A residual compressive stress is created within the transformation zone, which stops the crack prolongation. Evans examined a steady state zone of uniform width over the crack surfaces. For the stationary crack, when the long-range strain field of the transformed particles is purely dilatational the mean stress dictates the shape of the transformation zone, which then has the shape shown in Fig. 5 [32]. Another feature is that the toughening increment is related to the volume fraction of transformed tetragonal phase, $V_f$, and also the width, $h$, of the transformed zone. In addition Evans showed that toughening only developed with crack extension where the transformation zone shields the crack tip from the applied stresses.
The low temperature degradation (LTD) of zirconia is also a well-documented phenomenon, intensified particularly by the presence of water [33 - 39].

The consequences of this aging process are multiple, including surface degradation with grain pull-out and micro cracking as well as strength degradation. Although LTD has been shown to be indirectly associated with a series of femoral head prostheses failures in 2001 and despite a well-established definition of the conditions for which LTD is susceptible to occur, there seem to be no clear relationship between LTD and failures by using zirconia for dental restorations [39; 40].
Fig. 6 presents the process of the LTD in the schematic of Chevalier [39]. Water or - in the oral system- saliva leads the surface grains of the zirconia to undergo a $t\rightarrow m$ transformation process associated with a volume increase at ambient or oral cavity temperatures. The volume increase associated with a grain transforming at the surface generates locally high stresses that result in grain boundary cracking and in the presence of moisture the zirconia grains below the surface will also succumb to transformation. The on-going process results in a transformed zone combined with an ageing process.

*Fig. 6: Low Temperature Degradation of the tetragonal to the monoclinic phase of zirconia (After Chevalier [39])*
Although many types of zirconia systems are available [40; 41], only two are really used to date in dentistry as a framework material. These are VITA In-Ceram Zirkonia, a glass-infiltrated zirconia-toughened alumina, which is available from VITA Zahnfabrik, Germany, and not an object of this research and, for the dental market the most important; yttrium partially stabilized tetragonal zirconia polycrystals (Y-TZP), which is the focus of this study. The biomedical grade zirconia usually contains three mol-% Yttria (Y₂O₃) as a stabilizer and is named 3Y-TZP [42].

3Y-TZP is available for nearly every dental restoration possibility as crowns and bridges. The restorations are processed either by soft machining of pre-sintered blanks followed by a sintering step to full density at high temperature or by hard machining of fully sintered blocks. Soft-milling systems are produced by many companies e.g. Lava by 3M/ESPE, Germany, and Nobel Procera zirconia by Nobel Biocare, Switzerland, whereas the hard milling of hot isostatic press-(=HIP)-ed zirconia as e.g. DC-Zirkon by DCS, Switzerland. Supporters of soft milling claim that hard milling may introduce micro cracks in the framework during the milling process, which could lead to fractures [43]. Hard milling supporters claim a greater fit because no shrinkage during a sintering step is involved in their process [43].

The mechanical properties of Y-TZP strongly depend on its grain size and porosity [40; 44; 45]. Above a critical grain size the Y-TZP is less stable and more likely to spontaneous t→m transformation whereas smaller grain sizes are associated with a lower transformation rate [46]. Moreover, below a certain grain size (~0.2μm), the transformation is not possible, leading to reduced fracture toughness [47].
Consequently, the sintering conditions have a strong impact on both stability and mechanical properties of the final product as they dictate the grain size as presented in Fig. 7 by Piconi [42]. Higher sintering temperatures and longer sintering times lead to larger grain sizes [45; 48; 49].

![Fig. 7: Grain size of zirconia depending on the sintering temperatures as reported by Piconi [42]](image)

Presently Y-TZP materials for soft machining of dental restorations are produced with final sintering temperatures varying between 1350°C and 1600°C depending on the manufacturer. This fairly wide range of sintering temperatures is therefore likely to have an influence on the grain size as presented in Fig. 8 and later on the phase stability of Y-TZP for dental applications.
Chapter II

A: sintered at 1350°C

B: sintered at 1450°C

C: sintered at 1500°C

D: sintered at 1600°C

Fig. 8: Differently sintered 3Y-TZP resulting in different grain sizes. All images are at 50.00 KX

The phase diagram, established by Scott (Fig. 9), suggests that 3Y-TZP contains some amount of cubic zirconia [48]. Chevalier et al. demonstrated that the presence of cubic zirconia is not desirable in Y-TZP for biomedical applications and is caused by uneven distribution of the yttrium stabilizer ions. In accordance with the phase diagram (Fig. 9) and the sintering conditions used the cubic grains are enriched in yttrium while the surrounding tetragonal grains have reduced yttrium and therefore they are less stable [49], leading to a more metastable material and, consequently, more $t \rightarrow m$ transformation.
Most dental manufacturers of sintered Y-TZP structures do not recommend grinding or sandblasting to avoid the $t \rightarrow m$ transformation and also the formation of surface defects, which could shorten the long-term mechanical properties by causing microcracks.

In contrast, restorations produced by hard machining of fully sintered Y-TZP blocks have been shown to contain a significant amount of monoclinic zirconia caused by their milling process [50]. This is frequently, as described above, associated with surface micro-cracking, greater sensitivity to low temperature degradation and lower reliability [51].
Although high strength might appear as a beneficial property for dental applications, long-term performance and reliability should also be considered.

Several authors have reported that annealing at 900°C for 1h induces the reverse transformation from monoclinic to tetragonal after, for instance, grinding [52; 53]. The compressive stresses at the surface relax and the strength decreases with this process. But the transformation reversibility should not be understood as providing mechanism for healing of the previously introduced flaws [52].

The mentioned mechanical properties are well above those of all other available dental ceramics, with a flexural strength in the 800–1000 MPa range [54]. Nevertheless, in vitro studies support the use of zirconia materials for all-ceramic dental restorations because of their high flexural strength and fracture toughness [50].

However, early clinical results show that there are two main drawbacks for zirconia restorations compared to metal-ceramics. The first is a high incidence of porcelain fracture, manifesting clinically as “chipping”, and the other is an ageing problem that has been identified to occur in zirconia in the presence of water or saliva [25].

2.4. Brief overview on the bonding mechanism of porcelain to frameworks

Regarding the interface observation, which will be part of the following chapters, it seems important to appreciate what is currently known and what are the differences to the classic metal-ceramic system.
The challenges for bonding systems arise because of the completely different chemical composition and structure of the two materials. There is the veneering porcelain and on the other side the (gold or non-precious) metal-alloys or oxide ceramic frameworks.

Framework materials such as zirconia or metal alloys remain crystalline whereas the porcelain cools down as an amorphous material, which means that there is no long-range order in the structure. Another issue is their different cooling behaviour.

Not only is the amorphous system indicating the difference between the long range atomic coordination these two materials, but also when porcelain is cooling down, the thermal contraction curve has at specific temperatures, a $T_S$ and $T_G$ while the crystalline material has only a $T_M$. It means that during the cooling procedure the crystalline materials will either make a step at the $T_M$ (the melting-temperature), indicating crystallization, combined with the loss of direct volume, whereas for porcelain it remains amorphous with fluid like properties till the $T_S$, the softening temperature, and when it reaches the glass-temperature ($T_G$) it freezes and becomes an elastic non-crystalline structure [21; 24; 55].

A critical aspect for the construction of bonded materials at elevated temperatures is the thermal expansion mismatch when both materials cool to below the $T_S$ temperature in the case when one material is amorphous. The thermal expansion mismatch, which is a consequence of the interatomic forces between atoms in the different structures, must be compensated for the framework and veneering
porcelain. If a framework contracts more than the bonded porcelain, residual stress is developed in the bonded assembly upon cooling to room temperature [56].

It is also well known that metal has good thermal conductivity and dissipates heat quickly so that it can be cooled more quickly, while porcelain has poor thermal conductivity and cools more slowly [21; 55]. Here is also the first important difference between the zirconia versus metallic framework materials, namely zirconia is also a poor thermal conductor as is porcelain [29].

In addition, if the difference in temperature and in the thermal expansion between the framework and porcelain is significantly large when the veneering porcelain has reached its $T_G$, the resulting stress in the porcelain is higher than with a lower temperature difference and thermal expansion [24].

2.4.1. Bonding behaviour of PFM (“Porcelain Fused to Metal”)

The bonding to metallic frameworks has been widely observed in contrast to zirconia frameworks [27]. This section shall focus on the current knowledge of behaviour of metal-porcelain systems.

Fig. 10 [21] presents a summary of issues involved in metal-ceramic systems that the industry wants to avoid. This schematic identifies the different chemical- (see 2.4.1.1), mechanical- (see 2.4.1.2) and thermal- (see 2.4.1.3) issues that may occur during fabrication although various solutions have been found so that it is possible to build reliable metal-ceramic crowns and bridges.
Since the late 1950s when PFM restorations were introduced to dentistry [21], the nature of the metal-ceramic bond has been the target of much research. There have been developments in many aspects of material preparation, composition and application together with new test methods to evaluate this interface. For the metal-ceramic bonding system, shear and flexural bond strength tests have mostly been employed in countless research reports [21; 24].

Bond strength is defined as the strength of the bond developed between substrates, in this case the metal and the porcelain after the porcelain is fused to the metallic framework. There are many different types of measuring procedures for the bond strength such as shear, tensile, 3-point-bending, and 4-point-bending and so on. When the porcelain unites with the alloy, the values of the (shear) bond strength are in the range of 25 to 55 MPa, depending on the porcelain, alloy, and the preparation used [24].
The factors that contribute to a strong bond between metal framework and porcelain are following considered [21; 24; 57].

2.4.1.1. Chemical
Non-precious metals as an alloy component produce metallic oxides at the surface of the framework, which enables a chemical bond to develop with the porcelain. To create a reliable bond an oxide layer needs to be uniform both in thickness and composition. An alloy that forms too much surface oxide after oxidation can lead to lower bond strengths. Therefore, it is important to remove some of the oxide layer thickness by blasting the alloy with Al₂O₃ particles following oxidation. An oxidation/reaction layer is developed at the interface on metals during ceramic firing [21; 24; 57].

2.4.1.2. Mechanical
Reliable mechanical bonding is very important for good clinical performance of metal-ceramic restorations. Removing casting oxides as well as properly sandblasting the alloy with 100 - 250 µm aluminium oxide particles has become the standard approach to create such a reliable mechanical bond. Fig. 11 shows an example of microstructure that results in a reliable mechanical bond for PFM restorations, where the opaque porcelain material has flowed into the created undercuts on the sandblasted surface of the metal alloy. The roughness of the opaque/metal interface in Fig. 11 is a consequence of the grit blasting.
Sandblasting with alumina particles develops considerable surface roughness with many undercuts in which the porcelain can mechanically key into [21; 57].

2.4.1.3. Coefficients of thermal expansion (CTE)

CTE compatibility between the porcelain and underlying framework is necessary to achieve a reliable bond. After producing a homogenous oxide layer and sandblasting, if the CTE of the alloy is not compatible with the CTE of the porcelain it will generate significant stresses that may disrupt the bond [21; 24] either fracturing or debonding the porcelain.

As porcelains are weaker under tensile stresses, it is recommended that upon cooling they develop slight compression and not tension [21; 24]. This is achieved
only if the alloy contracts a bit more than the porcelain during cooling. As a result of
many investigations it is advantageously preferred to have the CTE of the porcelain
slightly lower (approximately 10%) than that of the metal framework to ensure
surface compressive stresses develop during cooling [57; 58].

2.4.2. Bonding behaviour of PFZ (“Porcelain Fused to Zirconia”)
The compatibility of porcelain and zirconia is not easy to characterize. All
manufacturers seem to be using standard dilatometer measurements of coefficients
of expansion and thermal shock behaviour testing of fired crowns during their
product development as they are typical done for PFM systems [59]. An additional
problem is that there is, according to the ISO standards, no approved test method
available to determine of the bond strength of Y-TZP to porcelain.

Yet, as for metal-ceramic systems; different chemical-, mechanical- and thermal
aspects are involved in all-ceramic systems, which influence the fabrication and
functional reliability of dental zirconia-based restorations.

Most manufacturers provide veneering porcelains having a slightly lower CTE (up to
15% as with Triceram by Dentaurum, Germany) than the zirconia. This approach is
the same used for most metal-ceramic systems [21]. Therefore, if a compatibility
issue is occurring with Y-TZP it is most likely not due to a simple thermal expansion
coefficient mismatch between the materials.

All manufacturers of porcelains for dental Y-TZP ceramics provide “liner” or “bonder”
materials, presumably to increase porcelain bonding as well as to provide some
chroma and fluorescence for reducing the consequence of the high value and high refractive index of zirconia.

Although “bonding” to zirconia seems not to appear as an issue for clinical behaviour. Delamination, which is identified clinically as the complete loss of porcelain with resultant exposure of the framework, can only be confirmed after a microscopic examination as Ohlmann [59] argued. This is impossible if the restoration remains in situ, and therefore fractures that have been classified as delamination may in fact be “chipping” fractures [59].

Kappert [12] declared that only cohesive fractures occur in the porcelain layer and no debonding from the zirconia could be found in his observations, which agrees with Ohlmann [59]. The bonding of porcelain to the zirconia framework seems to be better than the response of the porcelain itself against occlusal forces [12].

Perhaps the reason for the including of liners is only to help assure perfect wetting of the framework surface, creating a more chromatic shine or have chemical adjustments to reduce possible interactions with the Y-TZP. This seems to be the fact, as some manufacturers argue that wetting and bonding to the surface can only be reached by a so-called wash-firing of the dentine porcelain mass in the appropriate colour. This means to apply a thin wash of dentin porcelain, typically 50 \( \mu \text{m} \) thick and firing it at 50–80°C higher than subsequent veneering porcelain.

Kappert [12] claimed also that the chemical bonding of zirconia-based restorations is similar to the metal-based situation. He stated that Y-TZP is a metal-oxide, which
enables a chemical bond to develop with the porcelain layer. He mentioned that it is also not proven for metal-based restorations so that this suggestion can also be done for zirconia based restorations [12].

This subject regarding the interface of zirconia frameworks to porcelain will be further present in chapters V and VI.

2.5. Clinical outcomes

The reliability of different restorative systems in the clinic is based upon the percentage of crowns remaining after placement for different time periods or survival data. Comparing results from the literature is challenging because of different ceramic materials, reporting of complications, study conditions, and evaluation times.

This clinical results section gives an overview of the problems and concerns on the dental market with the use of zirconia as a framework for dental restorations. Another issue concerns the failures of both products used for PFM and PFZ. A short discussion to other all-ceramic systems, such as In-Ceram and Procera Alumina, will be given for a further understanding of the problems and results occurring with zirconia-based prosthesis.

2.5.1. Clinical success of porcelain fused to metal (PFM)

For 50 years, since 1962 [21], PFM restorations have been the main type of aesthetic indirect restorations used in dentistry.
A German private insurance company, the DKV (Deutsche Kranken Versicherung), in the year 2000, gave the University of Cologne, Germany, under the leadership of Professor Kerschbaum the job to investigate how many metal-based dental restorations are still in function. His observation was not to see the numbers of failures or fractures of the restorations; it was mainly a simple counting of crowns and bridges with an examination of how many units for a period of up to 25 years are still in the oral environment. He did it without considering a functional consequence, so that even chipped fractures have been counted as survival. At least 4363 crowns and 1664 bridges were calculated.

The results are now the so-called German “gold” standard and the basis that some insurance companies in Germany work with. That means that at least 95% of the
crown and bridge restorations have to be still in function after 5 years’ time and it can be expected that even after 25 years a third of the restorations will still be in use as Fig. 12 presents.

Table 2: Different studies on PFM survival results

<table>
<thead>
<tr>
<th>Study</th>
<th>Crowns</th>
<th>Years</th>
<th>Failures</th>
<th>5 years survival [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reitemeier [61]</td>
<td>190</td>
<td>7</td>
<td>7</td>
<td>97.3</td>
</tr>
<tr>
<td>de Backer [62]</td>
<td>1037</td>
<td>10</td>
<td>116</td>
<td>94.6</td>
</tr>
<tr>
<td>Marklund [63]</td>
<td>42</td>
<td>5</td>
<td>3</td>
<td>92.4</td>
</tr>
<tr>
<td>Walton [64]</td>
<td>347</td>
<td>7</td>
<td>12</td>
<td>97.1</td>
</tr>
<tr>
<td>Jokstad [65]</td>
<td>43</td>
<td>10</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2 offers other clinical results on PFM restorations with mainly the same result given in the long-term study of Kerschbaum. Over 90% success overall seems to be not an issue for PFM restorations for 10 years after placement and this with either non-precious or high gold-based metal alloys.

Only lower survival proportions are reported for porcelain fused to titanium, which is not the object of this compilation. But this high success rate is the goal that all following framework materials such as for instance zirconia have to reach if they want to be as successful as PFM restorations are.

2.5.2. Clinical success of porcelain fused to alumina (PFA)

The optical results achieved with In-Ceram Alumina framework materials were the first option for dental crowns and bridgeworks to look like natural tooth substance. However, due to their low mechanical stability and brittleness these materials were only suitable for 3-unit bridges [66]. In-Ceram Zirkonia, a glass infiltrated ceria stabilized zirconia reinforced alumina product, could provide patient cases for posterior area 3-unit bridges whereas the most common In-Ceram material, In-Ceram Alumina, is only suitable for the anterior area as a bridgework material [67].
All studies together provided data on the survival rate of a total of 6006 crowns after 4.9 years. 430 crowns were reported to be lost. This means interpreted into a 5-year survival for all-ceramic crowns with In-Ceram Alumina framework a clinical success of 93.3%, which is comparable with the results of PFM restorations [67], presented in 2.5.1.

Posterior crowns showed a higher failure rate compared with anterior crowns. The most frequent biological complication was 2.1% loss of pulp vitality per year. The second most common biological complication was dental caries with 0.2%, 0% due to periodontitis and 0.4% due to tooth fracture. For metal–ceramic crowns, these statistics were slightly higher with 0.7% for caries, 0.6% for periodontitis, and 0.9% for tooth fracture [67].

Caries, periodontics and tooth fracture have comparable results for PFM and In-Ceram all-ceramic restorations so that it imply that PFZ restorations will function similarly.

The most frequent technical failure, 85%, of all failures of In-Ceram crowns were framework fractures [67], which is not observed at such a high number in all other framework materials, including metal and zirconia.

For ceramic “chipping”, the main focus of this thesis, the complication was that in one study over 5-years the rate a “chipping” of veneered In-Ceram framework material was 3.7% and for PFM restorations 5.7%, respectively [67].
A study using 99.9% high purity aluminum oxide Procera Alumina (Nobel Biocare, Switzerland) investigated 100 single tooth restorations on 58 patient cases. Of the 97 crowns remaining in the study after 5 years, only 3 crowns had experienced a fracture through the veneering porcelain and the aluminium oxide coping material [68]. Only two additional crowns were replaced as a result of fractures through the veneering porcelain, also known as “Chipping”-fractures. One crown was replaced as a result of recurrent caries. All remaining crowns were ranked as either excellent or acceptable for surface/colour, anatomic form, and marginal integrity [68].

All these results indicate the alumina-based all-ceramic systems work almost perfectly, with even higher clinical success than metal-ceramic systems. “Chipping” does not seem to be an issue for alumina-based restorations. The reports on such kind of failure are very low compared to other framework materials.

Another interesting and unique point is that In-Ceram all-ceramic and densely sintered alumina systems have minimal CTE mismatch between the porcelain and the framework material and this is not leading to higher fracture rates.

2.5.3. Clinical success porcelain fused to zirconia (PFZ)
Zirconia-based restorations are developing as an alternative to PFM restorations. It is notable that most of the studies involve multi-unit and especially posterior prostheses. This also signals some comfort regarding the performance of this material for the restoration of single anterior teeth; reflecting the clinical finding that many less strong or less tough all-ceramic systems are found to have 90% or even
higher survival rates at 5–6 years [66]. It is also interesting that there has been little reporting of any failure from early results [70; 71].

Framework fracture appears to be quite unusual in all studies to date (except the inlay retained fixed posterior denture study of Ohlmann [59]) even with the majority of studies being multi-unit replacing molars. The fractures that have occurred mostly involve connectors of multi-units (≥4) or second molar abutments.

Problems with the porcelain veneer seem to present in most studies (Table 3). In the published reports of different systems, up to 54% developed cracking with minor loss of material after only 1–2 years of observation [70]. Further not as yet published studies may well identify porcelain cracking being the major problem as mentioned in private discussion at universities.

This clearly identifies that the difficulties are clearly material related. The statement in one published study of two representative systems was 8 and 50% occurrence of porcelain “chipping” [71]. It also shows that maybe other non-materials factors such as thickness ratios or framework design play a role in porcelain cracking.

“Chipping” during function can signal the presence or development of stresses associated with the zirconia–porcelain interface. Since the basis of such stresses does not appear to be related to thermal expansion/contraction mismatches, perhaps surface changes of the zirconia are involved [72].
Table 3 shows an overview of clinical observations. This excerpt is chosen as an example of numerous clinical observations with zirconia frameworks.

Table 3: List of clinical studies with PFZ restorations

<table>
<thead>
<tr>
<th>Study</th>
<th>Period [years]</th>
<th>Units</th>
<th>Samples</th>
<th>Framework fracture [no.]</th>
<th>“Chipping” fracture [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tinschert [73]</td>
<td>3</td>
<td>3-10</td>
<td>65</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>Sailer [67]</td>
<td>5</td>
<td>3–5</td>
<td>33</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>Beuer [74]</td>
<td>2</td>
<td>3</td>
<td>21</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Raigroski [75]</td>
<td>2.5</td>
<td>3</td>
<td>20</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>Pospiech [76]</td>
<td>2</td>
<td>3</td>
<td>38</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>Ortrop [77]</td>
<td>3</td>
<td>1</td>
<td>204</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Zembic [78]</td>
<td>3</td>
<td>Implant</td>
<td>18</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ohlmann [59]</td>
<td>1</td>
<td>IRFPD</td>
<td>30</td>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td>Molin [79]</td>
<td>5</td>
<td>3</td>
<td>19</td>
<td>0</td>
<td>36</td>
</tr>
<tr>
<td>Larsson [80]</td>
<td>1</td>
<td>2-5</td>
<td>13</td>
<td>0</td>
<td>54</td>
</tr>
</tbody>
</table>

2.5.3.1. Single crowns

Single crowns have a small representation in published clinical observations. In a 2-year randomized control trial, 1 of 15 Cercon (DeguDent, Germany) zirconia crowns fractured in half only 1 month after cementation on a molar [81], so that the success rate for this study was 93% after 2-years. And, very interesting, no “chipping” of the veneering porcelain was reported after 2 years in the same study [81].

No framework fracture has been reported after 3 years in a study with 204 single crowns fabricated with Procera zirconia in a private practice setting [82]. However, 16% of the crowns had some difficulties, and 6% were recorded as a failure. Loss of retention and “chipping” of veneering porcelain e.g. were some of the complications reported in this study, which had a survival rate of again 93% at 3 years.

Although zirconia single crowns appear to demonstrate good short-term success and survival rates, these must be viewed with caution as they reflect data from studies
with a small sample size. A long-term observation has to be done to be sure on this system.

2.5.3.2. Fixed partial dentures

The most investigated PFZ dental restorations are the fixed partial dentures (FPD), with different clinical trials reporting on spans ranging from 3 to 10-units. Except for one study, all FPD used natural teeth as abutments; the other one used titanium implant abutments.

A relatively high success rate was found in most studies. A fairly small number of framework fractures have been reported during clinical trials and do not appear to have occurred spontaneously. An initiating factor event was determined by all studies to have been the basis of the fractured framework.

The longest fixed partial dentures spanned 10-units made with HIP-ed DC-Zirkon, DCS, Switzerland, and the used veneering porcelain was Vita Verblendkeramik D, VITA Zahnfabrik, Germany [73]. No framework fractures were reported after 3 years of follow-up; however, “chipping” of the veneering porcelain was described in 4 of the 65 bridges located both in the anterior and posterior regions.

In another study the success rate for 33 posterior zirconia fixed partial dentures was 100% [74]. All of these clinical studies suggest a promising future for all-ceramic posterior FPD with a zirconia framework.
2.5.3.3. Zirconia framework fracture

Fracture of Y-TZP framework mostly occurred for posterior FPD, nevertheless this was found to be rare, and was only reported in three studies shown on Table 3. The incidence of framework fracture was directly related to the design of the posterior FPD, where inlay retained partial dentures showed the highest failure rate of 30% after only 12 months [59]. The debonding of the inlay pontic of the natural tooth has been concluded to be the cause of the framework fractures.

In the review, Cercon zirconia (DeguDent, Germany) had the most framework fractures compared to all other investigated zirconia brands [66]; but it must be kept in mind that it is also the most investigated brand and had also some clinical trials without fracturing and with a 100% success rate.

The probability of fracture of zirconia posterior fixed partial dentures has been estimated to be almost 0% after a simulated 10-year clinical service study [83] still; framework fracture has been reported in several in vivo trials of less than 5-years [66].

As an example, in a study by Sailer [67], a 5-unit Cercon zirconia (DeguDent, Germany) maxillary posterior FPD fractured at the connector between two pontics at the first and second premolars after 38 months in function [67]. The dimension of the fractured connector was greater than all manufacturers recommended for the connector area (9–16 mm²), which was introduced by Raigrodski [75]. Biting on a stone was reported in this observation to be the main reason for the failure [67].
Some other fractures came from night-time bruxism and the major reported reason, debonding of the retainers resulted in some framework fracture primarily when just one retainer debonded. This fact overloaded the connectors to failure. Debonding was explained by the reduced area of adhesion, because of the small surface area of the inlay retainers, as shown in the study by Ohlmann [59].

The longest follow-up period found in a literature review was 5 years, where two papers reported results on patients restored with zirconia all-ceramic fixed partial dentures [67]. Interesting was that the survival rate of the observed Cercon zirconia-based FPD over 5 years were 100% [79] and 74% [67].

2.5.3.4. Low-temperature degradation

Catastrophic failure of zirconia restorations has been a major concern in the progress for dental restorations because of the ageing problem of zirconia in the presence of saliva [39]. Low-temperature degradation (LTD) was first described 1981 by Kobayashi [84], where in a humid environment, spontaneous transformation from the tetragonal to the monoclinic phase arose in zirconia grains at low temperatures of just 150°C – 400°C.

In contrast, in another early study (1984) about zirconia used in orthopaedic are - according to Cales et al.[92]- state-of-the-art Y-TZP materials capable of resisting degradation at 37°C. Chevalier [37; 49] refuted this statement after an excessive fracture concern in joint replacements. But, how excessive this ageing problem is for zirconia-based dental restorations is presently unknown!
The weakness of zirconia to ageing is impaired by the fact that it differs between different zirconia blocs from different manufacturers, and even in zirconia from the same manufacturer, which have been processed differently [84]. This may be reflected clinically, but before this can be confirmed, further studies with larger sample sizes following a longer review period must be completed.

Each observed case of framework fracture was caused by an introduced influence, such as accidents, improper dental technique, and inadequate thickness of the framework design and so on. This leads to the point that by avoiding this, a longer restoration lifetime can be expected.

2.5.4. Comparison on clinical success of PFM and PFZ

The objective there is to compare the clinical success and advantages while focusing on the rate of “chipping” of the veneering porcelain in both groups; some studies have enabled a direct comparison between zirconia and metal-based restorations.

To evaluate the influence of different materials on the failure rates of zirconia-based crowns, the results from studies reporting different manufacturing procedures were compared separately with those from studies reporting on metal–ceramic crowns.

Fig. 13 presents a comparison of the US market presented by the CRA newsletter in 2008. It was mainly a counting on fractures and chippings of PFM and PFZ restorations reported by dentists of the USA. At least more than 5000 restorations were calculated. It was clearly observable that the PFM restorations had better clinical success than the PFZ restorations. Only the zirconia-based frameworks
veneering CZR press material (Noritake, Japan) show similar result to PFM materials.

![Bar chart showing percentage of porcelain cracking](image)

*Fig. 13: Comparing the percentage of porcelain cracking between PFM (left side) and PFZ (right side) materials according to the CRA newsletter [96]*

For comparison, porcelain problems on metal–ceramic restorations over a 10 year observation period was reported to be approximately 4% for a gold–palladium alloy, never higher than 6% for the most alternative alloys and only as high as 15% for a nickel-based alloy without beryllium [93]. Consistent findings have been reported for a gold-based alloy with 98% completely intact porcelain after 5 years [94]. As mentioned before, lower survival rates are only reported for porcelain fused to titanium (84–87% survival at 5 years) [94; 95]. Consequently, porcelain–zirconia compatibility appears more problematic than past experience with metal–ceramic systems.
It is common dental knowledge that some of zirconia-based restorations have resulted in disappointing failures after a few years in the mouth. Zirconia frameworks are stated to have problems clinically comparable with that of metal substructures [96; 97]. If patients wish or demand to have non-metal indirect restorations, zirconia-based restorations are a logical choice. It appears after nearly 15 years that the frameworks are working as well as metal frameworks, but only continuing clinical research can verify this assumption [96].

However, almost all dentists and research projects have described some clinical failures with zirconia frameworks. Also, they appear more frequently in zirconia-based restorations than in PFM restorations used as control group [96].

The potential of PFM restorations seems to be more expected than that of zirconia-based all-ceramic restorations, but it is likely that this difference may soon be overcome. Skilled dental technicians can enable every all-ceramic restoration appear like a natural tooth [96; 98].

It is deceptive that zirconia–based frameworks for all-ceramic restorations can be made relatively rapid and predictable. When the digital information concerning the tooth preparation is placed into the computer, the technician is free to do other things while the framework is milled. This relatively simple task replaces the process of waxing, investing, burning out, casting and finishing frameworks that is familiar to dentists and technicians.
Zirconia–based and PFM restorations require nearly the same clinical procedures [99]. However, to allow for an optimum combination of the zirconium-oxide framework thickness and the superficial ceramic, tooth preparations for the zirconia-based restorations need to be somewhat deeper on the proximal and lingual surfaces than do tooth preparations for PFM restorations. This fact is known from other all-ceramic framework materials as In-Ceram. Impressions, also digital, and cementation are about the same for both systems [96].

When restoring a single maxillary central incisor, most dentists prefer to make the restoration from all-ceramic materials to achieve an optimum aesthetic result. This advantage is related to the difficulty in blocking out the colour and opacity of the metal framework.

The margins of PFM restorations in observable areas of the mouth usually are placed sub-gingival. After a few years, gingival tissues always retreat and the margins of the PFM restoration are exposed. Even when all-ceramic margins have been placed on PFM restorations, the exposed margins of these restorations often are still unpleasant and are immediately recognizable when patient smile. In fact, the exposed margins of the zirconia-based all-ceramic restorations are less disappointing aesthetically than exposed PFM margins [100].

Insufficient clinical trials involving Y-TZP-based restorations were found in the literature, some were randomized control trials, the majority of studies investigated all-ceramic fixed posterior dentures, while a very small number investigated purely
single crowns, implant abutments and just one study was found on implant-supported zirconia fixed partial dentures [100].

Certainly, the published clinical trials demonstrate a careful approach in their treatments with steps taken to insure that the zirconia frameworks are delivered at their best possible condition before cementation. Furthermore, it was interesting to note that all found studies included bruxism in their exclusion criteria, and therefore this should indicate a potential limitation [100].

Metal–ceramic crowns have been inserted in patients since 1962 [21] and been considered to be the so-called “gold” standard in reconstructive dentistry for a long time. It was amazing that few studies have estimated the long-term survival of metal–ceramic crowns and moreover, most of these studies regarding PFM clinical success were published within the last 4 years [98].

2.6. Veneering porcelain fracture (“Chipping”)

Zirconia has a white colour. Some manufacturers provide a colouring liquid to give zirconia a more natural appearance, but it still needs a covering especially in the anterior region. Veneering with translucent and coloured porcelain brings a more acceptable natural aesthetic result as with metal-based restorations.

The most common problem observed in the clinical with zirconia-based restorations is fracture and cohesive failure of the veneering porcelain.

This fact is established clinically as “chipping” fractures of the veneering porcelain. It appears that in some cases the underlying Y-TZP framework is exposed. It does not
appear that restorations have needed to be replaced in any studies due to porcelain cracking or minor “chipping”. Fig. 14 presents a cohesive failure in the veneering porcelain of a molar crown with zirconia framework in three steps from the fresh inserted perfect crown (left part) to the “chipped” fractured crown (right part of the figure). The crack fracture is initiated (middle part) from the mesio-lingual cusp and propagates within the porcelain layer.

Fig. 14: "Chipping" fracture initiating from the occlusal surface of the fractured crown

“Chipping” can dissatisfy both the clinician and the patient. Since the introduction of zirconia-based restorations, it has been known as a serious problem [85], initiating a large number of studies investigating this phenomenon and a challenge to solve.

As stated above the incidence of “chipping” fractures ranged from 0% [74] to as high as 54% in just 1-year time of observation [80]. No brand of Y-TZP and also no brand of porcelain have completely escaped from this problem, and it has been reported in nearly every clinical observation regarding zirconia-based restorations.

Fig. 15 presents a typically “chipping” fracture on a molar crown, where the cohesive failure runs through the veneering porcelain. The chipped porcelain fracture lies directly next to the crown.
"Chipping" fractures were also found to arise in non-loaded areas, such as mesio-lingual cusps on a mandibular molar [86] and the lingual area of a fixed partial denture pontics [67]. At non-loaded regions sometimes even no set fracture pattern has been identified. The second molars have a higher incidence of "chipping" than the rest of the dentition because of the higher occlusal forces [75].

Trends in the "chipping" location have been recognized including the premolar and molar regions [77] particularly -as just described- the second molars [75] and the connector area in mandibular dentures [73]. HIP-ed zirconia frameworks veneered with Triceram (Dentaurum, Germany) had the highest extent of "chipping" namely
54% in a year. In this particular study the dentures were mounted on titanium implant abutments [80].

In one study of 3-unit FPDs placed on natural teeth the results after 5 years showed a 36% rate of irregularity on the occlusal surface with the same zirconia framework material when veneered with either a feldspathic porcelain or a leucite reinforced pressed ceramic [79].

It seems important to know that a high number of chip fractures reported were undetected by patients. The dentist found these fractures during reviews [71]. Some patients were satisfied with just polishing the rough surface [86] or repairing with composite resin [87]. In some cases, the patients chose even not to have the fracture polished at all [75]. Nevertheless, some restorations did require total replacement. The reasons were major “chipping” fractures, which could not be polished, or they presented aesthetic worries for both patients and dentists [67].

Numerous reasons for chipping have been suggested, such as mismatch of the CTE between the veneering porcelain and the zirconia substructure [88], mechanically imperfect micro-structural regions in the porcelain, areas of porosities [59], surface defects or improper support by the framework [85], overloading and fatigue [89], low fracture toughness of the veneering porcelain [74] and finally the low thermal conductivity of zirconia [16].

Delamination, as opposed to chip fractures, has also been suggested as a cause for failures. But as mentioned before, it seems quite possible that all fractures that have
been classified as delamination may in fact be “chipping” fractures as Kappert [12] declared. He mentioned that all of these fractures were cohesive.

In a long test series [90] regarding bonding of zirconia-based systems all test samples showed a crack running above the interface within the porcelain and no delamination could be detected. A typical crack surface within the porcelain just above the zirconia framework is presented in Fig. 16 and Fig. 17.

By visual (“eye/loops”) observations “chipping” seemed to expose the framework, whereas under SEM observation a thin cover of translucent veneering porcelain is usually found on top of the zirconia surface. Even by changing procedures such the porcelains used or grinding the zirconia surface, the zirconia remained slightly covered by the porcelain [90].

![Fig. 16: Bonding porcelain to zirconia showing the crack prolongation above the zirconia surface in the porcelain layer (300 X)](image)

![Fig. 17: Surface of a "chipping" fracture; the zirconia is not visible (1.00 KX)](image)

This speculation and observation is supported by the result of an investigation that the bond strength between zirconia and a large number of veneering porcelains with varying CTEs was higher than the cohesive strength of the porcelain itself [88].
The veneering porcelain is the weakest link in this system, and improving its strength and fracture toughness could reduce the “chipping” is one possible suggestion [88]. Unfortunately, “chipping” fractures have also been reported by using high-strength and pressed ceramics in clinical trials on zirconia and do not seem to solve this “chipping” problem [59].

Some observations propose that tempering residual stress is the basis for the majority of “chipping” [16]. Swain [16] determined three factors, which are a source of residual stresses and may be the origin of the unstable “chipping” fractures in zirconia:

- Mismatch of the CTE of porcelains bonded to zirconia
- Thickness of the veneering porcelain layer
- Cooling rate during the firing process of the porcelain

The cooling rate generates significant thermal gradients within the porcelain and is directly related to the low thermal conductivity of zirconia, which is much lower than that of metal-alloys, which do not result in similar “chipping” fracture rates [16].

It is possible to prevent the development of high residual stresses in the porcelain by slow cooling the restoration from above the glass transition temperature of the porcelain. High residual stresses may result in unstable cracking or “chipping” [16]. Most dental porcelain suppliers now recommend a slow cooling rate in the final firing procedure for the past two years.
The design of the zirconia framework has also been suggested to be a contributing factor in “chipping” fractures, because of the inadequate support provided by as thin as possible zirconia copings commonly milled.

Recently, an improved customised zirconia-coping design has been recommended to provide anatomically support to the veneering porcelain. Marchack [85] demonstrated in a case report the design of zirconia crowns taken from the conventional PFM technique. It was a full contour wax-up, which was then cut back to give the veneering porcelain still enough space for an aesthetic restoration.

Tinschert [73] approved this modified framework design as presented in Fig. 18 with a “balcony” support for the veneering porcelain. However, “chipping” fractures still happened in 4 of 65 fixed partial dentures in this clinical trial spanning 3 years.

Another study by Lorenzoni [91] showed that a framework design modification did not improve the fatigue life of the Y-TZP crowns system investigated. Both different
designs of the zirconia framework showed comparable fatigue to the metal ceramic control groups observed in his investigation. On the other hand, the failure mode itself varied according to the different crown system [91].

Some authors suggested sandblasting prior to the veneering to be a possible reason why they had “chipping” fractures. Yet, in this case complete delamination of the porcelain would be expected. This was never observed; rather only “chipping” fractures of and within the porcelain layer could be detected [25].

Another finding was in a study sponsored by DeguDent, Germany, that the “chipping” rate was depended also on the dentist [101]. One clinically significant finding was the rough and uneven surface that was detected at one clinician with the highest number of “chipping” failures. Clinical recommendations demand a perfectly polished surface after occlusal adjustments [102; 103].

![Graph](image.png)

*Fig. 19: Study sponsored by DeguDent with the focus on 3 different dentists [101]*

Fig. 19 presents the dependency on the dentist with chipping fractures. DeguDent sponsored this study, where 2 dentists had nearly no fracture and a survival rate of
about 97% after 5 years and the third had a loss of 17% in the same time, while all dental zirconia-based restorations were prepared at the same laboratory by the same technician [101].

A novel approach in veneering zirconia copings has been described by Beuer [74] by sintering a CAD/CAM - milled lithium-disilicate veneer “cap” onto the zirconia coping significantly increasing the mechanical strength of the restoration. To date, there are no clinical trials supporting this method and suggestions.

### 2.7. The future of zirconia-based dental restorations

The cost of zirconia-based all-ceramic restorations is for example in the USA and Northern Europe is higher than comparable PFM restorations. The higher cost generally is related to a cost addition by milling centres for the zirconia frameworks [98].

The average clinical fee, including laboratory cost, as reported by the American Dental Association for a PFM crown in 2005 was US-$808, and the average cost of a zirconia-based ceramic crown in 2005 was US-$834. Certainly both fees are slightly higher now. The cost will come down eventually as milling is perfected and milling devices of lower cost are introduced and really used [98]. In addition the high price of gold content alloys will also have an effect on that situation [98].

Case reports of large multi-unit bridge restorations and implant fixed partial dentures suggest that the dental public may have some confidence in zirconia as a restorative
material, with some restoring full mouth rehabilitations using zirconia abutments and frameworks despite limited scientific evidence [73].

The issue of porcelain “chipping” appears to be relevant to zirconia frameworks despite their fundamental superior mechanical properties and that porcelain mechanical properties are almost framework independent.

The same subject, the porcelain “chipping”, gave some manufacturers the idea to provide their customers monolithic Y-TZP zirconia products to avoid “chipping” fractures. These new zirconia materials are more translucent and appear more naturally and aesthetically than the known Y-TZP zirconia products. It is claimed that the abrasion is not an issue with this zirconia, when it is perfectly polished, and the opposite teeth will not be defected [104].

At this time, investigations appear to have been directed towards different zirconia materials with stabilizers other than yttria, which are less disposed to LTD, such as magnesia partially stabilized zirconia (Mg-PSZ) [105] and ceria-stabilized zirconia-alumina composites (Ce-TZP/A) [88]. These non-yttria-stabilized zirconia materials may be less liable to LTD and spontaneous phase transformation, however, their fracture toughness is higher with a lower flexural strength compared to YTZP [88]. Whether these zirconia materials are suitable for long-span fixed partial dentures is not observed yet. Therefore, long-term in vivo studies must be sensibly evaluated before non-yttria-stabilized zirconia materials could be recommended.
In addition as long as no other framework material can be found with such a “natural” appearance as shown in Fig. 20, zirconia will be in demand. In the presented dental case (Fig. 20) VITA In-Ceram YZ and VITA VM9 were used and produced by the technicians Rutten, Belgium, and the dentist Gamborena, Spain.

Fig. 20: Dental restoration of a 4-unit zirconia-based bridge as teamwork of I. Gamborena, Spain and the Rutten brothers, Belgium
2.8. Conclusion

Zirconia-based restorations seem to have an acceptable longevity that accompanies their aesthetic advantages. In the future, transformation-toughened zirconia may stand out as the most successful all-ceramic system, regardless of the clinical indication.

With the limited number of published clinical trials, it can be concluded that Y-TZP has the potential for being accepted as a suitable material for fixed partial dental treatments; however, larger sample sizes and longer in vivo studies are needed.

Nevertheless, “chipping” of the veneering ceramic on zirconia restorations continues to be a problem. The results based on this review are:

- Based on the limited short-term studies available, zirconia is suitable for nearly all kind of dental restorations (e.g. posterior single crowns, long-span fixed partial dentures and implant-abutments)
- Up to 3-unit dental restorations the all-ceramic system with In-Ceram and densely sintered alumina materials have better clinical results than zirconia-based restorations.
- PFM and alumina-based restorations have a higher success rate than PFZ restorations especially regarding “Chipping” fractures.
- Zirconia framework fractures seems not to be a concern in dental clinical cases
- “Chipping” of the veneering porcelain is confirmed to be the major problem with zirconia-based restorations without a complete clarification of this problem; up to 54% clinical chipped porcelain fractures [80] were observed within 2 years’ of placement.
• Delamination seems to be not an issue for zirconia-based restorations but there are no studies about the interface between porcelain and zirconia

• Handling recommendations for dental technicians have still not resulted from the clinical chipping observations

In this thesis, the following issues will be investigated because of the above-mentioned limited understanding:

• To determine the influence of the processing of a dental restoration by a dental laboratory on the mechanical properties of the veneering porcelain as one reason for possible cohesive fracturing of the porcelain.

• To explore the interface of the zirconia porcelain dental restoration by SEM high resolution imaging to clarify the interaction between the two materials.

• To investigate the changes of the crystal structure of the nucleation growth process of zirconia during its veneering with a new approach using XRD$^2$ diffraction through the veneering porcelain layer without touching the surface of zirconia.

• To study and identify residual stresses within the porcelain layer on a zirconia coping with anatomical unsupported and supported design by using thermocouples and optical polarimeter methods.

• To present an approach how a dental technician and his dentist can give their patient successfully zirconia-based dental restorations.
3. Materials, Methods and Theoretical basis

3.1 Firing of the sample for the determination of the properties

3.1.1 Pre-Test

Before starting the different observations on various porcelains the correct firing degree was determined. This was evaluated by using the firing degree test developed and introduced by Claus [107], to identify a starting position for further tests. This test is necessary to obtain near perfectly fired porcelain. For all testing three different brands of porcelain for the all-ceramic system with Y-TZP framework were used.

The first porcelain was VITA VM 9 material, which is the VITA Zahnfabrik porcelain for zirconia-based restorations with a coefficient of thermal expansion (CTE) of $9.2 \times 10^{-6} \text{ K}^{-1}$, the second was DeguDent Cercon Ceram Love with a CTE of $9.2 \times 10^{-6} \text{ K}^{-1}$, both feldspar-based, and the third one was the nano-fluor-apatite porcelain Ivoclar Vivadent e.max Ceram with a CTE of $9.5 \times 10^{-6} \text{ K}^{-1}$, both also suitable for zirconia based restorations.
Fig. 21: Schedule of the firing degree test introduced by Claus [107]. On the vertical axis is the maximum hold temperature while the horizontal axis is the time taken to achieve this temperature during the heating up phase.

With this test it was possible to observe the influence of firing time and maximum temperature on the firing response of the porcelain. Fig. 21 illustrates this dependency for the translucent version porcelain VM 9 (VITA Zahnfabrik, Germany). A pre-drying time of 6 minutes was used for all porcelains at a lift position 75% (setting for VITA Vacumat 6000, the furnace used in this examination, shown in Fig. 22). The holding time at the maximum temperature was 2 minutes for all samples. It is also mentioned that because of the flat disc samples used they must be fired to a slightly higher temperature than a veneered crown to achieve the correct firing degree.
All samples (0.7 g of weight with a diameter of 12.5 mm and a height of 3 mm) were positioned on a firing tray on the floor of the furnace chamber; they do not receive the same degree of heat as in the centre of the furnace chamber, where dental restorations are positioned. As such it was not possible to follow the presented instructions of the manufacturer to develop a uniformly and perfectly sintered sample.

The firing degree of the samples was determined on the basis of their transparency, shade intensity and edge angle of the disk-shaped sample using the same methods as described in the following paragraphs.

### 3.1.2 Test according to ISO 6872

After this pre-test the exact firing temperature was determined, the tests were done by following the instructions of the ISO 6872:2008 for the production of the specimens for the flexural strength measurement, CTE, chemical solubility testing and for $K_{IC}$.
The starting temperature for every sample was 500°C with the same lift position as for the determination of the firing degree. The temperatures and the heating up time used for VM9 are shown in Table 4. The firing temperatures for the other porcelains are slightly different, depending on the material and associated manufacturers’ instructions. All samples were placed on a firing tray in the middle of the furnace, so that the position for the sample was not in the centre, where dental restoration usually are placed, which is the reason for changing the recommended firing schedule. The heating speed plus the vacuum time also varies with the size of the sample. Bigger samples need longer time to reach the same sintering degree for the same end temperature.

Table 4: Firing temperatures for the test sample with VITA VM9

<table>
<thead>
<tr>
<th></th>
<th>Pre-Drying [min.]</th>
<th>Heating Speed [min.]</th>
<th>Holding time [min.]</th>
<th>Holding Temperature [°C]</th>
<th>Vacuum Time [min.]</th>
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<tr>
<td>Recommended Firing</td>
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<td>7:36</td>
<td>1:00</td>
<td>910</td>
<td>7:36</td>
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<tr>
<td>Flexural Strength</td>
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<td>8:00</td>
<td>2:00</td>
<td>930</td>
<td>8:00</td>
</tr>
<tr>
<td>CTE</td>
<td>6:00</td>
<td>10:00</td>
<td>2:00</td>
<td>930</td>
<td>10:00</td>
</tr>
<tr>
<td>Chemical solubility</td>
<td>6:00</td>
<td>8:00</td>
<td>2:00</td>
<td>930</td>
<td>8:00</td>
</tr>
<tr>
<td>Fracture toughness</td>
<td>6:00</td>
<td>9:00</td>
<td>2:00</td>
<td>930</td>
<td>9:00</td>
</tr>
</tbody>
</table>

The specimens for the three point bending test to determine the flexural strength had a width of 4.0 mm, a thickness of 1.2 mm and a length of 20 mm. The three point bending test was performed in a Z010 Universal testing machine (Zwick, Ulm, Germany) and the two rollers made of hardened steel had a 15 mm gap between them. The equation used for the calculation of the flexural strength was

\[
\delta = \frac{3Pl}{2wb^2},
\]
where \( P \) is the breaking load, \( l \) the test span, \( w \) the width of the specimen and \( b \) the thickness.

The specimens for the CTE measurements were 25 mm long and had a 5 mm\(^2\) cross-sectional area. A dilatometer (“DIL 803” Baehr, Germany) was used to determine the CTE. The expansion measurement was determined between 25°C and 500°C.

For the test of chemical solubility the specimens were disk-shape with a diameter of 13.5 mm and a thickness of 1.75 mm. The specimens were washed in water and dried at 150°C for 4h. Then the samples were placed in 4% (by volume) acetic acid in water at a temperature of 80°C for 16h, afterwards they were again washed and dried at 150°C. The samples were weighed before and after the procedure and with the known density to measure the volume loss.

All specimens for these three test methods were fired according to Table 4 and also with a maximum temperature 30°C higher and lower than that recommended to identify any effect of firing temperature. For each temperature evaluated, the tests used 20 samples for the flexural strength, 6 for the CTE and again 20 samples for the chemical solubility.

To illustrate the influence of time at the maximum temperature on the flexural strength, only VM9 material was used. In this case the end temperature and the holding time stayed the same and only variations of 4, 8 and 12 minutes in the heating rate with vacuum were done.
To determine the fracture toughness the single edge V-notched beam method was used. The specimen dimensions were 25 mm long by 4 mm wide and 3 mm thickness. Twelve samples were prepared for each test. The test was performed after fast cooling, which means opening the furnace at the max temperature and after slow cooling by removing the samples from the furnace below the glass transformation point (T_G) for each porcelain brand.

The furnace opening temperature for slow cooling was determined by the T_G of the porcelains, which for VM 9 is 603°C, for Cercon Ceram love 596°C and for the e.max Ceram 482°C. To generate a sharp notch a diamond saw was used and the specimen were mounted in a special machine with a razor blade and diamond paste to cut the notch. The notch shape and depth was examined under a microscope. A four point bending system was applied to load the specimen. For the calculation of the fracture toughness (K_{IC}) the equation was according to the ISO 6872:2008, namely:

$$K_{IC} = \frac{P}{b\sqrt{w}} \sqrt{\frac{S_1 - S_2}{w}} Y \frac{3\sqrt{\alpha}}{2(1-\alpha)^{1.5}} Y,$$

where P is the fracture load, b the thickness of the specimen, w the width, S_1 and S_2 the outer and inner support spans, a=a/w and Y the stress intensity shape factor.

### 3.1.3 Shade determination

To determine the influences on the shade of the restoration ten samples as for the firing degree test were produced. The optical properties were then measured with the Spectraflash 600 D65/10°C and SAV aperture by Datacolor AG, Switzerland (see Fig. 23), which is a dual-beam spectrophotometer for reflection and transmission
control of colour matching and colour quality. It is usable for translucent materials such as dyes, plastics and porcelains. In this test the maximum temperature was in any case the same. The software for the data analysis was X-Rite colour meter 8.4.2 by X-Rite, USA.

Fig. 23 Spectraflash 600 by Datacolor AG, Switzerland

The differences were observed only for shade 3M2 (base dentine material) of VITA VM9 (10 samples), the effect of pre-drying time, lower end temperature. In addition tests were made with the translucent effect mass “window” of VM9 (10 samples) fired with and without vacuum according to the outcomes of the chemical solubility results (Table 4).

The colour difference was expressed as $\Delta E$ (E stands for the German word “Empfindung” = sensation), the quantified form in three-dimensional space. This colour definition is based upon Grassmann’s law, an empirical result about human colour sensitivity [108]. The value of $\Delta E$ between the terms $(L^*,a^*,b^*)_p$ and $(L^*,a^*,b^*)_v$ according to ISO 12647 and ISO 13 655 calculated with the Euclidean distance [108]:
\[ \Delta E_{p,v} = \sqrt{(L_p^* - L_v^*)^2 + (a_p^* - a_v^*)^2 + (b_p^* - b_v^*)^2} \]

The three coordinates, specified by the International Commission on Illumination, of the three-dimensional space (CIELAB) represent the lightness of the colour (\(L^* = 0\) yields black and \(L^* = 100\) indicates diffuse white), its position between red and green (\(a^*\), negative values indicate green while positive values specify red) and its position between yellow and blue (\(b^*\), negative values indicate blue and positive values specify yellow) as presented in Fig. 24.

![CIELAB](image)

*Fig. 24: CIELAB specified by the International Commission on Illumination (by X-Rite)*

### 3.2 SEM observations of the interface

#### 3.2.1 Firing of the samples

In this part of the study yttria partially stabilized tetragonal zirconia polycrystalline ceramic (Y-TZP, VITA in-Ceram® YZ, VITA Zahnfabrik, Germany) is used as a framework material. This material was prepared by sintering blocks, suitable for
CAD/CAM machines Cerec® and InLab® (Sirona, Germany), at a temperature of 1530°C for 2 hours. For the observations of the interface bonding system, 8 blocks with the dimensions of 10x10x1 mm³ were used. As veneering porcelain, VITA VM® 9 (colour shade 2M2), prepared in a variety of methods was built up on the zirconia surface in the manner listed in Table 5.

Table 5: Preparation methods of the Y-TZP frameworks

<table>
<thead>
<tr>
<th>No.</th>
<th>Liquid Medium</th>
<th>Porcelain</th>
<th>Firing Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>No</td>
<td>No</td>
<td>Wash-Firing (950°C)</td>
</tr>
<tr>
<td>2.</td>
<td>No</td>
<td>VM9</td>
<td>Wash-Firing (950°C)</td>
</tr>
<tr>
<td>3.</td>
<td>VITA VM-Liquid</td>
<td>VM9</td>
<td>Wash-Firing (900°C)</td>
</tr>
<tr>
<td>4.</td>
<td>VITA VM-Liquid</td>
<td>VM9</td>
<td>Wash-Firing (950°C)</td>
</tr>
<tr>
<td>5.</td>
<td>VITA VM Liquid</td>
<td>VM9</td>
<td>Wash-Firing thicker layer (950°C)</td>
</tr>
<tr>
<td>6.</td>
<td>VITA VM-Liquid</td>
<td>No</td>
<td>Wash-Firing (950°C)</td>
</tr>
<tr>
<td>7.</td>
<td>Distilled Water</td>
<td>VM9</td>
<td>Wash-Firing (950°C)</td>
</tr>
<tr>
<td>8.</td>
<td>Alcohol</td>
<td>VM9</td>
<td>Wash-Firing (950°C)</td>
</tr>
</tbody>
</table>

To evaluate the initial wetting of the Y-TZP a so-called wash-dentin-firing procedure was used. This involves the firing of a thin layer of veneering porcelain (approximately 0.05 mm thick) to 950°C at a heating rate of 45°C/min with a holding time of 2 min, following by a preheating temperature at 500°C for 6 min. The wash-dentin firing temperature cycle was used for each preparation method, except for sample number 3, where the maximum firing temperature was 900°C in order to evaluate the role of different firing temperatures. In all preparation methods vacuum was applied from the closing up of the furnace chamber, after preheating at 500°C for 6 min, to the holding period at the highest temperature.
For sample number 5 a thicker layer (approximately 2mm thick) of veneering porcelain was applied prior to initial heating. To observe only the initial bonding reaction between the two different materials no further firing process was conducted and no other porcelain layer was applied. The liquid application medium for the porcelain was systematically varied from complete absence in sample 2, the standard proprietary wetting liquid (VITA VM Modelling Liquid, VITA-Zahnfabrik, Germany) for samples 3 to 6, distilled water for sample 7 and ethyl alcohol for sample 8. The furnace used during this study was a VITA Vacumat 4000 T (VITA Zahnfabrik, Germany).

3.2.2 Preparation of the samples

To enable an expanded view of the interface, taper sections at approximately 5 degrees to the interface of all samples were cut with a water-cooled diamond saw (600 microns Struers, Germany) and polished with diamond paste (3µm VITA Zahnfabrik, Germany). In all instances the narrow porcelain-Y-TZP interface sections were etched using 5% hydrofluoric acid (VITA ETCH Gel) for 20 seconds in order to reveal the interface region in detail.

3.2.3 Observation of the samples

The cross-sections of the samples were observed using SEM (LEO 438 VPi Carl Zeiss SMT and LEO 1530 Gemini, field emission microscope), which is shown in Fig. 25.
Fig. 25: LEO 438 VPi Carl Zeiss SMT and LEO 1530 Gemini, field emission microscope

3.2.4 Brief introduction in the FE-SEM technology

Field Emission Scanning Electron Microscopy (FE-SEM) is an analytical technique used in materials science to investigate molecular surface structures and their electronic properties [109]. Invented by Erwin Wilhelm Müller in 1936, the FE-SEM was one of the first surface analysis instruments that approached near-atomic resolution [109].

Microscopy techniques are used to produce real space magnified images of a surface. In general microscopy information concerns surface crystallography (e.g. how the atoms are arranged at the surface, surface morphology and surface composition).
In FE-SEM, the phenomenon of field electron emission is used to obtain an image on the detector on the basis of the difference in work function of the various crystallographic planes on the surface. A Field Emission Scanning Electron Microscope is composed of a metallic sample in the form of a sharp tip and a conducting fluorescent screen enclosed in ultrahigh vacuum (UHV). The tip radius used is typically of the order of 100 nm, composed of a metal with a high melting point, such as tungsten [109]. The sample is held at a negative potential (1-10 kV) relative to the fluorescent screen. This gives the electric field near the tip apex to be the order of 1010 V/m, which is high enough for field emission of electrons to take place. Fig. 26 shows the set up for the LEO 1530 Gemini, field emission microscope.

---

**Fig. 26**: Operating principle of the LEO with 1530 Gimini column; $V_1$ - extractor at first anode; $V_0$ Accelerator at second anode; $V_B$ booster voltage
The field-emitted electrons travel along the field lines and produce bright and dark patches on the fluorescent screen giving a one-to-one correspondence with the crystal planes of the emitter.
3.3 XRD$^2$-Diffraction observation of the interface

3.3.1 Firing of the samples

In this study yttria partially stabilized tetragonal zirconia polycrystalline ceramic (Y-TZP, VITA In-Ceram® YZ, VITA Zahnfabrik, Germany) is used as a framework material. This material was prepared by sintering blocks, suitable for CAD/CAM machines Cerec® and InLab® (Sirona, USA), at a temperature of 1530°C for 2 hours. For the observation of the ceramic interface, rectangular plates with dimensions of 10x10x1 mm$^3$ were used. As veneering porcelain, VITA VM® 9 (colour shade 2M2), prepared in three variations were built up on the zirconia surface using the methods listed in Table 6 and presented in Fig. 27.

Table 6: Preparation methods of the Y-TZP frameworks

<table>
<thead>
<tr>
<th>No.</th>
<th>Liquid Medium</th>
<th>Porcelain</th>
<th>Firing Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>VITA VM-Liquid</td>
<td>VITA VM9</td>
<td>Wash-Firing (950°C)</td>
</tr>
<tr>
<td>2.</td>
<td>VITA VM Liquid</td>
<td>VITA VM9</td>
<td>Wash-Firing thicker layer (950°C)</td>
</tr>
<tr>
<td>3.</td>
<td>No</td>
<td>VITA VM9</td>
<td>Wash-Firing (950°C)</td>
</tr>
</tbody>
</table>

Fig. 27: Setup of the preparation methods
Prior to veneering the samples the flat zirconia surface was evaluated by X-ray diffractometry to determine the crystal phases of the sintered zirconia grains. This step ensured that changes at the zirconia interface following by porcelain build up were not associated with transformations due to exposure to room temperature humidity prior to porcelain veneering.

To assess the initial wetting of the Y-TZP a so-called wash-dentin-firing procedure was used. This involves the firing of a very thin layer of veneering porcelain (approximately 0.05 mm thick) to 950°C at a heating rate of 45°C/min with a holding time of 2 min, following by a preheating temperature at 500°C for 6 min in a 70% closed furnace chamber. The same wash-dentin firing temperature cycle was used for each preparation method. For all preparation methods, after preheating at the holding period for 2 min, vacuum was applied upon closing of the furnace chamber before heating to the highest temperature. For sample method number 2, a thicker moist layer (approximately 2mm thick) of veneering porcelain was applied prior to initial heating.

To observe only the initial bonding reaction between the two different materials no further firing process was conducted and no other porcelain layer was applied. The liquid application medium for the porcelain was systematically varied from complete absence in sample method 3 of the standard proprietary wetting liquid (VITA VM Modelling Liquid, VITA-Zahnfabrik, Germany) while for samples prepared according to method number 1 and 2 this was included. The choice of the standard liquid was based upon observations in the previous study where faceting of the zirconia grains occurred in the presence of both distilled water and the VITA VM liquid [110]. The
furnace used during this study was a VITA Vacumat 4000 (VITA Zahnfabrik, Germany).

3.3.2 Preparation of the samples

To enable a magnified view of the interface, taper sections at approximately 5 degrees to the interface of all samples were cut with a water-cooled diamond saw (600 microns Struers, Germany) and polished with diamond paste (3 µm VITA Zahnfabrik, Germany). The cross-sections of the samples were examined by scanning electron microscopy (LEO 438 VPi Carl Zeiss SMT and LEO 1530 Gemini, field emission microscope) and a XRD²-micro diffractometer (BRUKER-D8 DISCOVER with General Area Diffraction Detection System (GADDS) equipped with a specially developed focusing microlens to generate an analysing spot of approximately 50 µm diameter (FWHM) [111]).

3.3.3 Observation of the samples

Traditionally X-Ray diffractometers used for the purpose of local area analysis are typically equipped with pinhole collimators to generate a small analysis spot on the sample surfaces. The use of such pinhole collimators however decreases the intensity of the X-ray beam on the sample dramatically, which results in long measurement times. In the last decade pinhole collimators have been replaced by mono-capillary optics and in the last few years by focussing polycapillary microlenses in order to focus the generated X-ray beam on the sample. This has increased the localised intensity on the sample by orders of magnitude depending on the X-ray source and type of optics in comparison to a standard pinhole collimator [111].
The X-ray microdiffractometer (µ-XRD²) used in this study was a modification of typical powder diffractometer with a focussing microlens to achieve a micrometer-sized X-ray beam and a 2-dimensional detector system (BRUKER-HiStar; see Fig. 28), which covers app. 30° in 2θ and app. 30° φ at the same time [111]. The advantage of such a focussing polycapillary microlens instead of the common pinhole-collimator or a monocapillary is the short measurement time required, down to a few seconds, due to the high brilliance of the X-ray beam on the sample combined with a spot size currently down to approximately 50 µm diameter FWHM as presented in Fig. 28.

![X-ray microdiffractometer](image)

*Fig. 28: The set-up of the X-ray microdiffractometer (µ-XRD²) used in this study*

A general disadvantage of small spot sizes in powder diffraction setups is the potentially poor crystallite statistics in the analysed volume depending on the
crystallite size. In addition, and to avoid this disadvantage the additional 2-
dimensional HiStar-detector provides direct assessment of texture effects and
crystallite size in the analysed sample.

Before commencing the $\mu$-XRD$^2$ analysis of the ceramic interface region various
sample preparation methods of the taper sections were examined by locally
scanning the surface with the microdiffractometer. This indicated that the cutting and
polishing preparation [110] did not generate significant t$\rightarrow$m transformation of the
zirconia grains on the surface. Monoclinic peaks and broadening of the
tetragonal/cubic peak were only observed on the ground surface of the prepared
area and not on the polished area in the vicinity of the veneered interface with the
relatively low spatial resolution of the X-ray diffraction system used in the former
study [110].

All three different preparation procedures were scanned with the microdiffractometer
in the manner shown in Fig. 29. The veneered part and the polished zirconia
surfaces were measured at 8 different positions in steps of 50 $\mu$m across the
interface with a measurement time of 120 seconds per pattern using the 50 $\mu$m micro
lens and Co-K$\alpha$ (radiation with 30 kV/30 mA setting) with a fixed incident angle of
10° to the flat interface. Due to this incident angle the measurement spot has an
elliptical geometry with a length of app. 400 $\mu$m and a width of app. 50 $\mu$m.

Three of the scanning positions are shown as an example for the working area in
Fig. 29 where the middle position focuses on the location directly at the interface
between Y-TZP and porcelain and the others on the adjacent positions. The
schematic on the left hand side vertically through the tapered interface sample shows positions of the spots indicated by the elliptical areas on the right hand side. No etching process such as HF content gel was used to ensure no other potential influences on the framework material.

Fig. 29: Measurement points on the samples, on the left a schematic illustration vertically through the tapered sample across the interface while on the right hand side the elliptical scanned surface locations are shown.
3.4 Thermal gradients observations of the interface

3.4.1 Crown/sample model

A rotationally symmetric crown form similar to that previously invested by Lenz et al. [112] was selected to ensure the production of identical samples and to simplify the experimental determination of the surface temperature corresponding with the geometry of a premolar tooth. Anatomically precise crowns, whilst possible to evaluate in a similar manner would have drastically increased the difficulty of production, especially regarding thermocouple placement and subsequent cross-sectioning of similar veneered copings.

The copings were designed by the inLab software (inLab 3.80, Sirona, Germany) and milled using an inLab milling machine (inLab MC XL, Sirona, Germany). The Y-TZP partially sintered frameworks (VITA In-Ceram YZ) were sintered to full density for 2 h at 1530°C in a furnace (VITA ZYrcomat, VITA, Germany). After sintering the wall thickness was on average 0.7 mm with constant thickness frameworks. The anatomically supported frameworks had a wall thickness of 0.7 mm at the cervical region, which increased within the middle and cusp range from 1.3 mm and within the occlusal region to 1 mm. The overall height of all copings, constant wall or supported framework was 6.95 mm (see Fig. 30, crown with constant wall thickness).
The first veneering step with the dentine porcelain (VM9; VITA, Germany) was the application of a very thin so called “wash-dentin layer” and fired at 950°C. The first built up dentine firing was at 910°C and the second was fused at 900°C. Finally a glaze firing of the porcelain was carried out in each case at 900°C in a Vacumat 4000 Premium T (VITA, Germany).

The veneer thickness of all samples (Fig. 32) was identical and performed with a special veneering setup (Fig. 31). At the cusp, complete thickness (framework and porcelain) of 1.4 mm was developed. Thus the porcelain thickness resulted in constant wall thickness framework copings of 0.7 mm on average. The porcelain of the anatomically supported crown had a maximum layer thickness of 0.4 mm.
3.4.2 Thermal measurement configuration

As a basis for supporting the firing of the samples a refractory honeycomb tray was used (Renfert, Germany). The honeycomb tray was drilled centrically to which a thermocouple protective glass with a length of approx. 23 mm was fixed. This length was selected, as the cervical edge of the samples was positioned approx. 6 mm above the tray, which corresponds to the position used in dental labs.

To add retention to the crown a bent wire with protective glass sheath to support the thermocouples was included. The thermocouples were then placed on the internal and external selected measuring points (see Fig. 30) prior to being connected to the appropriate channels of data logging system (SCXI 1303, National Instrument, USA). For data recording and evaluation of the results the software LabView 8.5 was used.

To enable comparative measurements of the cooling profiles with the attached thermocouples, a different furnace was used, namely a Programat P95 (Ivoclar Vivadent, Liechtenstein). The sample was located in this furnace more securely than in a furnace with mobile base as presented in Fig. 33. The more rapid mouth
opening like mechanism of this furnace enabled the sample to be more quickly exposed to air movements of the environment than for the plinth lowering furnaces.

![Set-up of the firing of the samples](image)

**Fig. 33: Set-up of the firing of the samples**

The thermocouples wires were led out of the firing chamber of the Programat P95, sealed with an insulating firing pillow, so that no air movement would falsify the measurement and vacuum could be used during the firing process. During all measurements the temperature at positions 1 and 10 were used as references to ensure comparability. Due to the measurement setup and the possible errors of temperature measurement in the furnace by using too many thermocouples, simultaneous measurement at all 10 points was not accomplished. Instead there were only 3 thermocouples in addition to the reference ones at positions 1 and 10 at
the same time in the furnace. The temperature was recorded in total at five different measuring points during a firing process. Each sample was heated up and cooled down twice for the thermocouples placed at every measurement point. Altogether 48 measurements were accomplished.

Every sample was placed in the middle of the furnace chamber and the furnace was heated to the final temperature (840°C) at a heating rate of 60°C/min and held there for 10 minutes to achieve a homogeneous initial test temperature. The selected final temperature was 70°C below the recommended dentine porcelain firing temperature to enable sintering and retention of the thermocouples into the soft porcelain on the surface as without this step the results would be inaccurate. After 10 minutes at the maximum temperature the chamber was opened directly and the furnace was switched off. The only difference between the slow and fast cooling was that for the former the furnace remained completely closed, until it reached 600°C (the glass transition temperature of VITA VM9 is 603°C), and thereafter was opened. The samples were not touched until they reached room temperature.

3.4.3 Polarimeter method

The uniform thickness framework samples for the polarimeter (StrainMatic® M3/250, ilis GmbH, Germany) were produced following by exactly the same firing steps and in the same sizes as for the thermo-couple measurements. After the firing, a thin slice 0.5 mm thick was cut using a water-cooled diamond saw from the mid-point of the coping and mounted in the polarimeter. With the polarimeter the turn value or angular rotation of the light through the crown was determined. The change of the angle of the linear polarized light was determined with passage through the samples [113;114].
Even slight inherent stresses lead to deformations of the microstructure in the material and thus to direction-dependent changes of the refractive index. Glass is optically isotropic in a fully relaxed condition; i.e. the refractive index is not dependent upon orientation. However, glass becomes birefringent under stress. This effect is designated as stress birefringence (SBR). Of necessity, local changes of the refractive index have an effect on the imaging properties of optical systems manufactured from this material.

One uses the effect of photoelasticity for the quantitative determination of stress birefringence; If linearly polarised light strikes a birefringent material, then the emergent light wave is no longer linear, but elliptically polarised in the general case, i.e. its field vector describes an ellipse.

An elliptically polarised light wave is the superimposition of two linearly polarized waves at right angles to one another and with a certain phase difference. The phase difference results from the optical retardations of the light waves, which are propagated with different velocities in the material corresponding to the differences in refractive index. The resulting optical retardation determines the minor to major axis ratio of the imagined ellipse, and depends upon the ratio of the refractive indices as well as the optical path lengths. Therefore the change in ellipticity of the polarised light is a direct measure of the birefringence and thus of the underlying inherent stresses [113].
Fig. 34: Basic forms of polarisation: A) There is no phase shift without birefringence and the resulting light wave is again linearly polarized; B) If the optical retardation is exactly one quarter of the wavelength, the field vector describes a circle and one speaks of circular polarization; C) If the optical retardation is larger or smaller than one quarter of the wavelength, then the resulting light wave is elliptically polarised.

Fig. 34 illustrates the different polarisation states. The elliptically polarised light is converted by means of a quarter wave plate (named retarder) back into linearly polarized light, the oscillation plane of which is changed by a certain angle in relation to the original polarisation direction. This angle is directly proportional to the optical retardation and can be determined relatively simple by a second, rotatable linear polarizer (named analyser) [113].

Compared with a simple intensity evaluation with crossed polarisation filters, this method has the advantage that it is independent of the transmission of the measured object and the brightness of the illumination – calibration depending on the measured object or on the light source is not necessary [113].
This value along with the characteristic stress optical coefficient, which carried the designation optical activity, enabled determination of the principal residual stresses perpendicular to the optical path within the veneering porcelain [113].

The above approach could not determine the stresses within the more opaque zirconia framework [113; 114]. The differences between the rapid and slow cooled samples are observable in a colour-coded residual stress distribution. The residual stresses revealed are those of a radial nature, as such the magnitude of these stresses at the external surface is minimal. In addition the act of sectioning the axial symmetric crowns would have modified the hoop stress components.
4. Critical role of firing temperature on the physical properties of dental porcelains

4.1 Introduction

A great milestone in the field of the veneering technology was laid with the development of porcelain firing furnaces with vacuum possibility in 1949 [3]. Despite this significant improvement, however, the decisive breakthrough in ceramic metal dental restoratives was not to be achieved until 13 years later by Weinstein [116]. In 1962 he filed the US Patent 3,052,982 for a dental ceramic capable of being veneered to metal [4; 5]. Almost at the same time, in 1962, the first metal-ceramic system to be developed in Europe was brought onto the dental market by the German companies VITA Zahnfabrik and Degussa Dental [6]. This technology, referred to as the VMK® (VITA Metall Keramik, i.e. VITA Metal Ceramic) technique is still used today. This porcelain was veneered to a high gold alloy, DeguDent U manufactured by Degussa Dental (today DeguDent, Germany). Today's dental porcelains no longer have very much in common with those of 1962, particularly with

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1 This chapter is based on the following submitted manuscript with similar title: Tholey MJ, Thiel N, Swain MV. Critical role of firing temperature on the physical properties of dental porcelains. Submitted to Journal of European Ceramic Society 07/2011; and basis of an invited lecture at the Society’s annual meeting held in Stockholm June 2011
regard to aesthetic considerations and have more abrasion or antagonist-friendly properties [6; 118].

However the chemical composition of the current dental porcelains is still very similar, that is mainly feldspar and quartz porcelains except Ivoclar Vivadent, Lichtenstein, who are using nano-fluor-apatite containing porcelains for their products. The feldspar-based materials consist of an amorphous glass matrix and a crystalline leucite phase within the matrix as a stabilization factor [119; 120], which increase the fracture toughness and other physical properties of porcelains [1; 121 - 124]. Another reason for including a mixture of leucite in the glass matrix is to adjust the coefficient of thermal expansion for each framework material [1; 121].

When firing veneering porcelain, problems can still occur -despite 50 years of these improvements- within the porcelain layer and consequently with the resulting dental restoration. Even if several identical furnaces are in use in a dental laboratory, each furnace can yield a different result with different firing degrees of the porcelain, even with the same firing parameters being used [6].

In terms of the end result, this therefore means that mechanical properties and the shade effects differ with every furnace. This can mean that with one particular furnace, the fired veneering ceramic does not match the ceramic manufacturer's shade specification. For instance, the result for the shade A3 (VITA classical A-D shade guide) from one furnace looks too grey, while with the other furnace a perfect shade result is obtained despite exactly the same firing parameters being used.
With the furnace of one type or one manufacturer, the differences can additionally be caused by different batches of thermocouples. The ageing of the thermocouples can be one of the causes for deviant firing results. The shade differences shall not be observed in this investigation with such an extension to all different influencing factors, such as modelling liquid e.g., only some factors are included. The main focus is on the mechanical properties variations creating failures regarding the dental restoration.

The precondition for all physical and chemical properties of the veneering porcelains set by the manufacturer is the determination of the correct firing degree of the porcelain. If veneered restorations differ in their firing degree, this will also alter the physical and chemical properties of the fired porcelain [107].

The human eye perceives only the increasing transparency and shade intensity of a material [6]. In general these differences are attributed only to the end or the highest firing temperature. Other factors, however, have an equally decisive impact on the veneering porcelain. In addition to this maximum firing temperature, the firing degree of a dental ceramic depends also on the other parameters, which are used in a normal firing procedure for dental porcelain [107].

These other parameters include the pre-drying time and the position of the firing tray in the furnace closing steps, and hence also the temperature of the object during pre-drying. The heating speed, until the maximum firing temperature is reached, and the holding time at the maximum firing temperature have an influence. The cooling time has been shown in other observations by the authors regarding thermal
stresses developing between the veneering porcelain layers [16]. Vacuum and modelling liquid also have an influence particularly on the shade of the dental restoration [5; 21; 107].

*Fig. 35: Dependence on height on residual stresses by Lenz et al. [112]*

An examination by Lenz showed that the firing condition influences the properties of the porcelain [112]. He described the position of the dental crown placed on its firing stamp, when the crown is located 6 mm from the bottom of the firing tray, results in less residual stresses in between the porcelain layer compared to 3.5 or 12 mm (Fig. 35) [112].

Repeated firings and certain heat treatments are known to alter the leucite content of dental porcelain and resulting thermal expansion behaviour, and such changes in expansion could induce cracking of the veneering porcelain [123; 124]. This aspect is not an object of this investigation.

In this investigation it shall be shown how maximum temperature and heating rate influences affect the different properties of porcelain, which is used in the all-ceramic system with Y-TZP framework. The reason for observing this special type of porcelain is that one major concern of all-ceramic dental restorations is still the so-called “Chipping” fractures. Until now it has not been proven in numerous studies that the porcelain is fired correctly. Porcelain, which has not been fired in the correct
firing degree, seems for the authors a possible reason for fractures, especially as a consequence of the resulting property differences.

4.2 Materials and methods

The sample preparation was done using the methods and materials outlined in more detail in Chapter III.

4.2.1 Pre-Test

Before starting the different observations the correct firing degree was determined. This was evaluated using the firing degree test developed and introduced by Claus [107], to identify a starting position for further tests. With this test it was possible to observe the influence of firing time and maximum temperature on the firing degree of the porcelain.

All samples (0.7 g in weight with a diameter of 12.5 mm and a height of 3mm) were positioned on a firing tray on the floor of the furnace chamber; they do not receive the same degree of heat as in the centre of the furnace chamber, where dental restorations are usually positioned. As such it was not possible to follow the presented instructions of the manufacturer to develop a uniformly and perfectly sintered sample.

4.2.2 Test according to ISO 6872:2008(E)

After this pre-test the exact firing temperature was determined, the tests were done following by the instructions of the ISO 6872:2008 for the production of the specimen for the flexural strength measurement, CTE, chemical solubility testing and for $K_{IC}$. 
4.2.3 Shade determination

To determine the influences on the shade of the restoration, ten samples as for the firing degree test were produced. The optical properties were then measured with the Spectraflash 600 D65/10°C and SAV aperture by Datacolor AG, Switzerland, which is a dual-beam spectrophotometer for reflection and transmission control of colour matching and colour quality. It is usable for translucent materials such as dyes, plastics and porcelains. In this test the maximum temperature was in any case the same. The software for the data analysis was X-Rite colour meter 8.4.2 by X-Rite, USA.

4.3 Results

The following tables illustrate the dependency of the end temperature on the flexural strength, the coefficient of thermal expansion (CTE) and the chemical solubility. All tested material properties are affected. Significant points are the altered flexural strength and the high differences of the coefficient of thermal expansion. The chemical solubility remains in all cases clearly below the value of 100 µg/cm², which is the barrier result of the ISO 6872. On the one hand it is possible to increase the flexural strength by achieving a different degree of firing, but on the other hand the CTE of the porcelain is changing considerably.

Table 7: Result of the mechanical properties measurement according to ISO 6872 with VITA VM9

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Flexural strength [MPa]</th>
<th>CTE $[10^{-6} \text{ K}^{-1}]$</th>
<th>Chemical solubility [$\mu g/cm^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 30°C</td>
<td>117,48 +/- 6,36</td>
<td>9,01</td>
<td>4,77</td>
</tr>
<tr>
<td>Recommended</td>
<td>111,21 +/- 8,09</td>
<td>9,12</td>
<td>7,02</td>
</tr>
<tr>
<td>- 30°C</td>
<td>87,68 +/- 5,03</td>
<td>9,25</td>
<td>8,45</td>
</tr>
</tbody>
</table>
Table 8: Result of the mechanical properties according to ISO 6872 with DeguDent Cercon Ceram

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Flexural strength [MPa]</th>
<th>CTE [10⁻⁶ K⁻¹]</th>
<th>Chemical solubility [µg/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 30°C</td>
<td>126,13 +/- 14,83</td>
<td>8,56</td>
<td>1,94</td>
</tr>
<tr>
<td>Recommended</td>
<td>97,62 +/- 15,89</td>
<td>9,17</td>
<td>6,97</td>
</tr>
<tr>
<td>- 30°C</td>
<td>82,58 +/- 8,74</td>
<td>9,54</td>
<td>8,67</td>
</tr>
</tbody>
</table>

Table 9: Result of the mechanical properties according to ISO 6872 with Ivoclar e.max Ceram

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Flexural strength [MPa]</th>
<th>CTE [10⁻⁶ K⁻¹]</th>
<th>Chemical solubility [µg/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 30°C</td>
<td>116,22 +/- 16,47</td>
<td>9,57</td>
<td>11,19</td>
</tr>
<tr>
<td>Recommended</td>
<td>95,28 +/- 9,10</td>
<td>10,07</td>
<td>13,38</td>
</tr>
<tr>
<td>- 30°C</td>
<td>86,51 +/- 12,97</td>
<td>10,41</td>
<td>15,49</td>
</tr>
</tbody>
</table>

Table 10: Results of the flexural strength of VITA VM9 with different heating up rates

<table>
<thead>
<tr>
<th>Heating time</th>
<th>Flexural strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 min</td>
<td>85,40 +/- 10,01</td>
</tr>
<tr>
<td>8 min</td>
<td>102,32 +/- 4,82</td>
</tr>
<tr>
<td>12 min</td>
<td>108,72 +/- 8,31</td>
</tr>
</tbody>
</table>

The effect of the variations of the heating speed showed the same influence in the results of the flexural strength as the variations of the end temperature as presented in Table 10.

The cooling time is a further factor, which is significant for the veneering porcelain. One influence of the cooling period is on the thermal residual stresses, which is well known and a further influence is presented in the Table 11. In the case of samples of a dental ceramic, which has undergone fast cooling, a lower nominal crack resistance ($K_{IC}$) result is determined.
Table 11: Results of the fracture toughness

<table>
<thead>
<tr>
<th>KIC [MPa√m]</th>
<th>VM9</th>
<th>C.C. Love</th>
<th>e.max Ceram</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast Cooling</td>
<td>0,69 +/- 0,05</td>
<td>0,64 +/- 0,07</td>
<td>0,77 +/- 0,10</td>
</tr>
<tr>
<td>Slow cooling till T_G</td>
<td>1,26 +/- 0,11</td>
<td>1,05 +/- 0,10</td>
<td>0,92 +/- 0,06</td>
</tr>
</tbody>
</table>

The optical influence on the shade brilliancy of different firing program is illustrated in Fig. 36. Samples A and B are fired in the same way except that sample B had no pre-drying time, respectively, the measured results for the samples are presented in Table 12. Sample C and D were fired in vacuum (sample C) and no vacuum (sample D). As shown in

Table 13 the influence of vacuum during sintering is very high with a ΔE* of 16,79.

![Figure 36](image)

**Fig. 36**: Different fired sample of VITA VM9 to determine the shade differences; A: Original shade; B: Shade influences without pre-drying; C: window mass correct fired; D: window mass fired without vacuum

Table 12: Shade measurement with Datacolor and no pre-drying before the firing

<table>
<thead>
<tr>
<th></th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h*</th>
<th>ΔE*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard (example A)</td>
<td>68,53</td>
<td>4,74</td>
<td>21,82</td>
<td>22,33</td>
<td>77,75</td>
<td></td>
</tr>
<tr>
<td>No Pre-Drying (example B)</td>
<td>72,50</td>
<td>1,03</td>
<td>16,27</td>
<td>16,30</td>
<td>86,37</td>
<td></td>
</tr>
<tr>
<td>Difference</td>
<td>3,97</td>
<td>-3,70</td>
<td>-5,55</td>
<td>-6,03</td>
<td>2,87</td>
<td>7,77</td>
</tr>
</tbody>
</table>
Table 13: Shade measurement with Datacolor and no vacuum

<table>
<thead>
<tr>
<th></th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h*</th>
<th>ΔE*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard (example C)</td>
<td>63,62</td>
<td>0,05</td>
<td>1,31</td>
<td>1,31</td>
<td>87,70</td>
<td></td>
</tr>
<tr>
<td>No Vacuum (example D)</td>
<td>80,37</td>
<td>-0,23</td>
<td>2,54</td>
<td>2,55</td>
<td>95,09</td>
<td></td>
</tr>
<tr>
<td>Difference</td>
<td>16,75</td>
<td>-0,28</td>
<td>1,23</td>
<td>1,24</td>
<td>0,24</td>
<td>16,79</td>
</tr>
</tbody>
</table>

The influence on the shade with a 30°C lower end temperature is illustrated in Table 14, the ΔE* is not as high as with the other variations of the firing. Sample with higher maximum temperature of 30°C had too rounded edges, which made measuring dimensions with this method impossible.

Table 14: Shade measurement with Datacolor and 30°C less high end temperature

<table>
<thead>
<tr>
<th></th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h*</th>
<th>DE*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>68,77</td>
<td>4,79</td>
<td>21,93</td>
<td>22,45</td>
<td>77,69</td>
<td></td>
</tr>
<tr>
<td>No Pre-Drying</td>
<td>69,95</td>
<td>1,76</td>
<td>17,59</td>
<td>17,68</td>
<td>84,28</td>
<td></td>
</tr>
<tr>
<td>Difference</td>
<td>1,18</td>
<td>-3,02</td>
<td>-4,34</td>
<td>-4,76</td>
<td>2,29</td>
<td>5,41</td>
</tr>
</tbody>
</table>

4.4 Discussion

The overview in Fig. 21 illustrates the dependency of the firing degree on maximum temperatures and heating up times. It can also be seen here that the samples must be capable of being fired to a higher temperature than a veneered restoration. Since the firing samples were positioned on a firing support on the floor of the firing chamber, they do not receive the same degree of heat as in the centre of the firing chamber. As mentioned in the introduction Lenz made the observation that the positions where the samples are placed have an immense influence on the stresses between the metal and porcelain [112]. This fact leads to the resultant firing not according to manufacturers’ recommendations to generate the correctly sintered
sample. The manufacturers´ recommendations have to be seen as a basis for the firing procedure.

If the firing degree of the samples is determined on the basis of their transparency, as illustrated in Fig. 21, a clear general principle can be observed with these samples. As shown samples with the same firing degree, i.e. with the same firing outcome, are situated approximately on a straight line running from the top left to the bottom right-hand corner. The further this straight line is shifted parallel in the direction of the top right-hand corner, the more transparent the samples become. This straight line demonstrates that at higher temperatures and shorter heating up times, the same firing result will be achieved as in the case of lower temperatures and longer heating-up times.

The desired degree of firing, therefore, can be controlled not only by the maximum temperature alone, but also by the heating-up time. With longer heating up times a higher degree of firing, and hence greater transparency can be achieved than with a short heating up time. If the individual stages of porcelain sintering or fusion are passed through more slowly, the release of the air present within the veneering ceramic will function better. If the heating up rate is too fast, the air present between the grains has less time to escape, which then leads to higher porosity and associated opacity.

An even more intensive shade effect and increased translucency can be achieved even although an optimum degree of firing has been reached. The specimen demonstrates a perfect degree of firing when the edges are recognisable and a slight
surface glaze can be observed. These samples, which have undergone further firing are over fired, and their edges are visibly rounded. This means that they were too viscous for a dental restoration regarding the resultant shape.

Clearly observable is the influence of the different sintering maximum temperatures, which have a negative effect on some of the physical properties of the porcelain. On the one hand it is possible to increase the flexural strength by sintering at a higher temperature, this also decreases the chemical solubility at the same time. This means that the veneering porcelain can less easily be "attacked" by saliva or food in the oral environment.

On the other hand this higher sintering temperature is also decreasing the CTE, which will create additional stresses between the porcelain layer with its framework material as the CTE difference between the two materials is increased. This is also due to the altered proportion of leucite to glass phase compared with the optimum degree of firing of a restoration [127]. It is therefore essential to determine the exact degree of firing in order to guarantee the patient the ceramic manufacturer's material property specifications. Dental laboratories must guarantee the optimum material properties. In the oral situation non-optimum outcomes can cause potential fracture problems when biting forces are involved.

A higher temperature has also an effect on the shade value as presented in Table 14. The optical properties such as translucency and the influence on the shade brilliancy of an incorrect firing program were sufficiently illustrated by means of the results obtained with the test specimens (eg Fig. 35). This point is very important for
patients after insertion of the restoration, if the dentist is taking the shade and the technician is creating another shade result.

The $K_{IC}$, the next detected property, is a nominal material property, which cannot be easy influenced by the firing itself. The $K_{IC}$ of a material is given by the composition and phase content of the materials. Lower firing temperature and a shorter time may result in more porous porcelain with a lower toughness [127]. The dissolution of leucite at higher firing temperatures is also a possible factor for a reduction of the $K_{IC}$ [127]. In this case, the results of the fast cooling schedule are not really presenting the real fracture toughness. It is presenting the fracture toughness influenced by the position on the firing tray on the bottom of the furnace and tempering stresses created due to the thermal gradients developed during rapid cooling.

A slow cooling reduces the tempering stresses and only in this case the effective toughness of the material is measured. Rapid cooling results in a lower value because of the presence of internal tensile residual stresses combined with intrinsic toughness or resistance of the material.

What is to be learnt from these measurements?

The samples were all placed on a firing tray and this limits the heat and resultant temperatures the underside of the samples is exposed to. As shown and expected from the Claus-Test [107], sintering, densification and transparency of the samples are all controlled by the heating speed and end temperature.
The cooling rate may create thermal and residual stress gradients through the specimen and may influence the mechanical properties depending upon which side of the specimen are placed on the firing tray. In a dental restoration the heat can also diffuse through a metallic framework even to a lesser extent during rapid cooling. In the case of zirconia frameworks which is a poor thermal conductor [16] leading to poor heat transmission and resulting in significant thermal gradients through the porcelain upon rapid cooling. This situation results in the development of thermal tempering stresses leading to a lower fracture resistance of a crack that penetrates the outer compressive layer of the porcelain. This situation is what maximizes the “chipping” possibility in this kind of all-ceramic dental restoration material.

The tempering stresses within the porcelain were the focus in Chapter VII [16; 112; 126], where the outcome was that slow cooling decreases the stresses in the porcelain layer dramatically. Together with the results presented here it shows that a slow cooling procedure creates a better fracture resistance of the porcelain layer. This situation will result in the less chipping.

The pre-drying time of the porcelain has another particular influence on the final shade result of the veneering ceramic as shown in Fig. 36 and in Table 12. The veneering material used was taken from the same ceramic bottle of the same batch and weighed, and the specimens fired one after the other on the same day, in the same furnace, at the same lift position, and up to the same end firing temperature at the same heating up rate. In this way, identical conditions except of the pre-drying time were created for the individual firing cycles.
It becomes evident that the shade increases in intensity from A to B (Fig. 36) although the test specimens originated from the same ceramic powder. The only difference is that sample B was not pre-dried at all, but heated up immediately, while sample A was pre-dried for 6 minutes. This illustrates that saving time in the laboratory by specifically shortening the pre-drying time has a considerable influence on the end result. The reason for this could be, as already mentioned, the surface of the veneering ceramic has already begun to melt, and the liquid and air trapped in the interior can no longer escape. As a result, any air bubbles as well as modelling liquid residue remain trapped within the porcelain.

The samples may also heat up more slowly as some of the thermal energy is consumed evaporating the moisture still present. This effect will also have the same effect as a faster heating up of the sample.

These issues can be solved by longer pre-drying times. The pre-drying temperature must also remain below the glass temperature point, since otherwise the surface may begin to melt, so that the air and modelling liquid cannot escape.

The same effect can also been seen in Fig. 36 and Table 13. The samples fired without vacuum are far less translucent than those fired under vacuum, even though both were fired for the same length of time in the same furnace according to the same firing parameters. When fired without vacuum, the appearance of the porcelain remains milky and opaque. The air remains trapped
within the microstructure as porosity and scatters the light generating the observed greater opacity.

With these outcomes other influencing factors on the porcelain can be discussed. The exact lift position, and therefore the temperature which the firing object actually reaches during the pre-drying procedure, likewise have an influence on the subsequent translucency and shade effect of the restoration. Samples (with the firing chamber e.g. 25% closed) will, although the furnace has displayed the same temperature as in other firings, receive less heat, and will therefore be pre-dried at a considerably lower temperature. The sample then enters the heating up phase when it is still too moist. As a result, tiny air bubbles and modelling liquid residue remain in the dental ceramic, and this causes the subsequent restoration to become more opaque on account of the increased light refraction at the air bubbles.

The results for the various samples shown here are intended to demonstrate the principle of the influence of different firing procedures. On account of their position in the furnace, however, they had to be heated to a slightly higher temperature than a dental restoration in order to obtain the optimum degree of firing. Lenz has shown the effect on the residual stresses in the porcelain determined with different positions of the metal-ceramic crowns [112]. All together it shows how important the position of the dental restoration and equally of the porcelain for the result is.
4.5 Conclusions

- This work shows that a simple maximum firing temperature-heating time matrix readily enables the optimisation of most aesthetic and mechanical properties of veneer porcelains.

- Under firing has a more drastic effect on the mechanical and optical properties while over firing influences the coefficient of thermal expansion and the shape of the dental restoration.

- The cooling procedure after the final firing is critical to minimise residual tempering stresses and hence potential chipping of dental porcelains.

- Recommendations by manufacturers regarding firing steps for the porcelain have to be critically evaluated to achieve optimum outcomes.
5. SEM observations of the Interface between Y-TZP and its veneering material

5.1 Introduction

Dental crown and bridge restorative materials are changing from porcelain fused to metal (PFM) to all-ceramic systems. Techniques, which have been developed over decades in the case of PFM systems, must now be redeveloped for all-ceramic systems. These changes include issues such as the need for veneering porcelains with better matching coefficients of thermal expansion because of the inability of the ceramic copings to accommodate high tensile stresses by plastic deformation as with metallic copings. In addition the type of bonding and inter-diffusion that occurs at the interface is not well understood.

Recently with the advances in computer aided design and computer aided manufacturing (CAD/CAM) there has been marked interest in all-ceramic systems [5; 129]. This has also been encouraged by the very high strength and toughness reported of some of these ceramics especially yttria partially stabilised tetragonal zirconia polycrystalline (Y-TZP) materials [130]. The same material has been widely

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2 This chapter is based on the following published manuscript: Tholey MJ, Thiel N, Swain MV. SEM observations of porcelain YTZP interface. Dental Materials 2009; 25 (7): 857-862
used in orthopaedic surgery as a hip prosthesis ball because of its high mechanical properties as well as its fine grain size and excellent surface finish [131]. However there have been reports of moisture induced destabilisation of Y-TZP ceramics including a significant number of fractured implanted hip prosthesis that have been extremely harmful for this application [131]. Chevalier et al. [132] in a major review of Y-TZP for biomedical purposes recently summarised the influence of humidity at modest temperatures (lower than 250°C) on the metastability of Y-TZP. This group over the course of many investigations found that impurity content, grain size, density and temperature all led to destabilisation of the tetragonal to the monoclinic phase. The problems with hip implants were shown to be associated with the transformation instabilities of the tetragonal phase [133; 134]. More recently in the case of all-ceramic crowns and bridges there have been clinical reports of excessive chipping of the veneering porcelain for zirconia based systems, although the origin of this failure is not well understood [12; 53; 67; 135].

Pure ZrO$_2$ exists as a monoclinic crystal structure at room temperature and transforms to tetragonal (1173°C) and cubic (2370°C) structures at increasing temperatures. The volume change associated with the cubic to tetragonal to monoclinic transformation induces very large stresses within the material, and will cause pure zirconia to crack on cooling down from high temperatures [136].

Zirconia for dental applications in its tetragonal crystalline state, which is achieved by the addition of 3-mole% yttrium oxide (Y-TZP), is metastable. An applied stress, magnified by the stress concentration at a crack tip, or associated with high stresses, caused by grinding, can result in the tetragonal phase converting to monoclinic, with
an associated approximate 4%-volume increase. This zone of transformation around the crack tip can result in closure forces about the tip enhancing the fracture toughness. This mechanism is known as transformation toughening [137].

Porcelain fused to metal crowns have been developed over more than 50 years with great attention being paid to the preparation of the interface prior to building up of the porcelain layer as well as the reactions that enhance adhesion of the porcelain to the underlying metallic substrate [138; 139]. Non-precious elements in alloys produce metal oxides at the surface of the alloy, which enables a chemical bond to develop with the porcelain [140]. Mechanical bonding is also very important for a good clinical performance of metal-ceramic restorations. Sandblasting with aluminium oxide creates a keying effect, which provides a good surface for retention of the porcelain. In addition the Coefficient of Thermal Expansion (CTE) mismatch between the veneering porcelain and Y-TZP must be small so as not to jeopardise the interface bonding by generation of high residual stresses [141].

The aim of this chapter is to use scanning electron microscopy (SEM) and HF etching to evaluate the interface between veneering porcelain and Y-TZP prepared using different dental technology build-up procedures. It is hypothesised that the micro-structural changes of the Y-TZP grains observed at the interface are associated with moisture induced tetragonal to monoclinic zirconia.
5.2 Materials and Methods

The sample preparation was done using the methods and materials outlined more detailed in Chapter III.

In this part of the study yttria partially stabilized tetragonal zirconia polycrystalline ceramic (Y-TZP, VITA In-Ceram® YZ, VITA Zahnfabrik, Germany) is used as a framework material. For the observation of the interface bonding system, 8 blocks with the dimensions of 10x10x1 mm\(^3\) were used. As veneering porcelain, VITA VM® 9 (colour shade 2M2), prepared in a variety of methods was built up on the zirconia surface in the manner listed in Table 5, in chapter III.

To enable an expanded view of the interface, taper sections at approximately 5 degrees to the interface of all samples were cut, polished and the veneering porcelain was etched. The cross-sections of the samples were observed using SEM (LEO 438 VPi Carl Zeiss SMT and LEO 1530 Gemini, field emission microscope).
5.3 Results

Observations of the initial grain structure of the sintered Y-TZP prior to building up of the porcelain layer are shown in Fig. 37 after firing under conditions associated with the wash-dentin at 950°C procedure. The resultant grain size as determined using the linear intercept technique after sintering of this material was 540 +/-240 nm. On such a sintered surface the veneering porcelain was fired for samples 2 to 8 as listed in Table 5. The pure Y-TZP (Sample 1) does not show any influence of the 20 sec. exposure to the HF gel. Additionally in Fig. 37 the grain structure of the sputtered thin (approximately 5 nm thick) gold coating deposited prior to SEM observation may be detected. This appeared as approximately 50 nm grains with random grain structure. Such coating structure was present on every surface observed because of the very high resolution of the SEM system used.
Fig. 37: Sample No.1: pure Y-TZP refired at 950°C after the recommended sintering process. Note the very fine irregular grain structure of the sputtered gold coating at a magnification of 100.00 KX

The taper sections cut at approximately 5 degrees to monitor the interface of a veneered sample at a higher resolution showed the zirconia slightly covered by the veneering porcelain after HF etching and a typical example is shown in Fig. 38. The structure of the grains of the framework material in some instances, following the different sample preparation procedures as listed in Table 5 was obviously affected during the veneering process. Also in all of the SEM figures the fine irregular grain structure of the sputtered gold coating as in Fig. 37 is detected.
Fig. 38: SEM observation of the HF etched polished taper section of the interface region. The grains of the Y-TZP below the surface of the veneering porcelain are visible in the region adjacent to the interface at a magnification of 10.00 KX.

Twenty seconds exposure to the HF gel at the polished taper section specimen revealed the grain structure of the Y-TZP grains below the porcelain layer as shown in Fig. 38. On the left hand side of the image the remnant veneering porcelain, still in contact with the YZ material, is evident.

A typical high-resolution observation of the HF etched tapered interface is shown in Fig. 39. The veneering porcelain has been completely removed by the HF gel and the underlying grains of the Y-TZP may be seen. The surface shown in Fig. 39 was that for the porcelain powder without any liquid application medium, specimen
number 2. The zirconia grains in this image are very similar to those shown for the Y-TZP material wash fired without any veneering porcelain (Fig. 37).

![Image](image_url)

**Fig. 39:** Sample No.2: Image of etched surface showing the Y-TZP interface following removal of the veneering porcelain after the firing of veneering powder particles without a liquid onto the Y-TZP at 950 °C at a magnification of 100.00 KX.

The etched interface and associated Y-TZP grains for sample number 3 (wash dentin fired at 900°C with VM-Liquid) are shown in Fig. 40. The grain structure of the zirconia was unaltered but there were a few larger more linear crystallographic features on the surface of the Y-TZP grains than observed for 950°C fired surfaces in the absence of veneering material.
Observations of the Y-TZP grains with the same veneering porcelain layer thickness and modelling liquid but fired at 950°C (specimen 4) are shown in Fig. 41. The surface reveals crystallographic faceting of the YZ grains more extensively than specimen 3. These faceting features are present on nearly all grains. These features are shaper and clearly linear unlike the fine grain structure of the sputtered gold coating as revealed in Fig. 37 with sample number 1.
Fig. 41: Sample No.4: extensive evidence of faceted Y-TZP grains following application of modelling liquid mixed with porcelain fired at 950°C at a magnification of 100.00 KX.

Fig. 42 reveals a more pronounced faceting of the zirconia grains below the thicker layer of wash-dentin (specimen 5) compared to sample number 4, also fired at 950°C. In this image the sharp faceting of the grains along with the fine grain structure of the gold coating is readily observable.
Fig. 42: Sample No.5: Severe faceting of Y-TZP grains following application of a thick layer of porcelain with modelling fluid fired at 950°C at a magnification of 100.00 KX.

Also Specimen 6, VM-Liquid without any veneering porcelain powder, indicated that even in this case some faceting of the Y-TZP grains was observed. At some grain boundaries the grain structure has started to change. By using the wash-dentin firing cycle with the powder mixed with the same amount of distilled water (specimen 7), as with the modelling liquid there were again the same features observed. Sample 8, prepared with alcohol instead of modelling liquid or distilled water, also showed the same noticeable features on the surface of the zirconia grains as with all other used liquids in this study. All the above observations were found to be very repeatable in that all surfaces prepared in the same manner showed near identical features to those presented above.
5.4 Discussion

The SEM observations presented above clearly indicate a number of features that develop on the Y-TZP grains at the zirconia-porcelain interface. The use of only the porcelain powder without any liquid resulted in no obvious faceting of the zirconia grains, indicating that the powder itself cannot be the reason for this development of the Y-TZP grains. In contrast, the changes observed using a liquid medium with the same porcelain powder clearly show a visible effect. This noticeable change does not appear to depend on the type of moisture medium used although the intensity of the faceting does. Distilled water, alcohol and the corresponding modelling liquid together with porcelain powder had a similar effect on the zirconia grains although the intensity appeared to increase with aqueous based solutions. The percentage of powder and liquid used during all tests was the standard recommended mixtures for dental technicians to build porcelain-veneered restorations, for fusing to metal and to zirconia.

There exists also an influence of the amount of moisture present in the veneering porcelain, as it did appear to have an influence on the extent of grain faceting. The Y-TZP grains beneath a thicker coating of porcelain (sample number 5, Fig. 42) had a greater degree of faceting. It is also observed that the complete grain structure on the surface is more severely faceted and not just with some of the grains as for the thinner wash coating. The implications of these observations are that more moisture and higher final heating temperature accelerates the observed faceting of the Y-TZP grains at the interface to the veneering porcelain.
Another clear outcome is that of increasing firing temperature. Comparing the results in Figure 3 and Figure 4 for firing of exactly the same porcelain application liquid coating at 900°C versus 950°C, shows the more severe faceting at the higher temperature fired porcelain. From the observations in Fig. 37 it is clear that the 950°C firing temperature itself does not affect the surface crystal structure of the zirconia grains. In addition the firing of dry veneering powder did not lead to the Y-TZP grains at the interface developing a faceted nature. These observations point to the clear role of moisture leading to the faceting behaviour of the interface Y-TZP grains. This behaviour is in agreement with the well-documented phenomenon of degradation of Y-TZP in the presence of moisture [37].

The present results of the faceting of the Y-TZP grains are very similar to the initial stages of moisture induced tetragonal to monoclinic phase transformation observed for these materials using atomic force and optical microscopy by Chevalier and colleagues [132]. The AFM observations presented in Chevalier’s recent revue paper are almost identical with the high-resolution SEM images seen in many of the figures above. At the onset of such surface features the volume fraction of transformation is very small and only within the very surface layer of the individual grains exposed to moisture. In addition Chevalier et al. [132] were unable to detect the presence of monoclinic phase using X-ray diffraction as the layer thickness and amount of tetragonal transformed to the monoclinic phase was very limited. Indeed during this study it was also impossible to detect the presence of monoclinic zirconia using X-ray diffraction of such surfaces as those shown above.
What is the cause for such a reaction occurring on the surface of the Y-TZP grains? According to Schubert et al. [142] the diffusion of water radicals into the Y-TZP crystal grains leads to a lattice contraction, which results in the formation of tensile stresses in the surface grains that can destabilize the tetragonal phase and the martensitic transformation to the monoclinic phase will than proceed. This process is also influenced by the size of the tetragonal grains and their composition. The higher the initial firing temperature of the Y-TZP the coarser the resultant grains with cubic grains growing faster than tetragonal grains. In addition the smaller tetragonal grains surrounding the larger cubic grains will have a lower yttria stabilising content as may be deduced from the yttria-zirconia phase diagram [37].

Another feature that contributes to the destabilisation of the tetragonal grains is the porosity of the Y-TZP with fully dense structures showing less propensity for transformation than slightly porous materials with equivalent grain sizes. In their studies Chevalier et al. claim that the moisture induced tetragonal to monoclinic transformation is a classic Avrami-Johnson nucleation and growth reaction [132]. It starts mostly at grain corners, where residual tensile stresses are largest and that one given grain does not transform all at once but progressively due to water attack. That is, the transformation of the surface of Y-TZP takes place by an apparent nucleation and growth mechanism, i.e. once a grain is transformed, the extension of the transformation occurs not only at random sites on the surface but also at the neighbouring grains because of additional localised stress concentrations [132].

The implications of this study are that there are two distinct parts of the process that results in the observed faceting of the Y-TZP grains at the interface with the
porcelain. During initial preparation water is incorporated in the veneering build up procedure. Upon preheating the moist veneering powder on the Y-TZP the temperature rapidly exceeds 100°C and the moisture is converted to steam that with time escapes from the heated veneering powder and supporting Y-TZP framework. At the temperatures between 100°C and 250°C the rate of tetragonal to monoclinic transformation in a damp environment is most rapid [132] and this is the regime that the Y-TZP will be experiencing during the evaporation of the moisture within the veneering powder. Once the monoclinic phase is formed at the surface it will persist in some parts to temperatures in excess of 1000°C [128]. The absence of creep in Y-TZP materials till much higher temperatures means that there will remain persistent residual stresses at the boundaries between monoclinic and tetragonal portions of the same grain. At elevated temperatures the veneering porcelain will become almost fluidic and some degree of dissolution of the zirconia grains will occur in the feldspathic glass. This reaction is anticipated to be enhanced by the presence of localised regions where high stresses persist, such as grain boundaries and at the tetragonal to monoclinic boundary interfaces within individual grains of the original Y-TZP.

Etching with HF gel (20 sec.) most rapidly dissolves the glass phase and areas where the glass has preferentially dissolved the Y-TZP grains such as the grain boundaries and tetragonal to monoclinic interfaces as mentioned above. Thus for the higher fired veneered materials (950°C versus 900°C) with the same veneering moisture content, as the pre-heating process was identical, then the moisture exposure of the Y-TZP interface grains would have been identical. That is, a similar extent of tetragonal to monoclinic transformation would have occurred. However
upon further heating to the final maximal temperature one would expect greater dissolution of the zirconia grains by the porcelain at the higher firing temperature. This would enable more dissolution of the stressed tetragonal to monoclinic interfaces and grain boundaries, which upon subsequent HF etching would result in deeper faceting of the Y-TZP grains as seen in Fig. 41 specimen 5 heated to 950°C versus Fig. 40 (specimen 4) heated to only 900°C.

In the present study the chemical dissolution by the veneering porcelain of the Y-TZP would be much higher at 950°C than at 900°C. The powder itself has not affected the Y-TZP as shown with sample number 2 (Fig. 39). Only with the presence of liquid in the veneering porcelain to initiate the tetragonal to monoclinic transformation will this stress enhanced glass dissolution accelerate at this high temperature (950°C) and will also attack the grain boundaries.

The extent to which the presence of moisture induced tetragonal to monoclinic transformation influences debonding of the veneering porcelain in clinical situations is unknown. Limited interfacial fracture toughness tests using the Charalambides test [128] of freshly bonded specimens indicate that crack extension occurred through the porcelain rather than at the porcelain/Y-TZP interface. Other shear bond strength tests of porcelain-Y-TZP interfaces observed fracture also within the porcelain [136] in contrast to porcelain fused to metal where cracking occurs directly at the interface layer on top of the framework surface [141]. There have been reports of a higher incidence of failure of zirconia based compared with porcelain fused to metal crowns [67; 135], however the basis of this increased incidence of failure in the zirconia based materials is not understood. Further observations on the role of the surface
preparation of the zirconia and prior to veneer to ascertain whether sandblasting or
grinding of the Y-TZP surface further influences the transformation effects at the
interface are required. However, due to the metastability of tetragonal zirconia,
stress-generating surface treatments such as grinding or sandblasting are liable to
trigger the $t \rightarrow m$ transformation with the associated volume increase guiding to the
formation of surface compressive stresses, thereby increasing the flexural strength
but decreasing the resistance to aging [31]. More detailed cross-sectional
transmission electron microscopy and possibly AFM observations are required to
completely prove the proposed hypothesis and substantiate the plausible
interpretation provided above.
5.6 Conclusion

Veneering porcelain appears to wet and bond well to zirconia frameworks. However upon HF etching the interface it is observed that moisture present in the veneering powder during the preparation of these porcelain to Y-TZP structures, which were identical with all-ceramic crown firing procedures, generates grain faceting at the surface of the zirconia grains beneath the veneering porcelain. The extent of this surface faceting is dependent upon the moisture content of the porcelain powder and the firing temperature. The nature of the surface faceting of the zirconia grains is almost identical with the observations of the moisture induced tetragonal to a monoclinic structure observed by Chevalier et al. [132] using AFM.

It is argued that the observed increased faceting seen after high veneering porcelain firing temperatures are a consequence of the glass induced dissolution at sites of higher residual stresses at the tetragonal/monoclinic interfaces. The long-term consequence of the presence of such transformed grains at the porcelain Y-TZP interface needs to be further investigated.
6. XRD² Micro-Diffraction Analysis of the Interface between Y-TZP and Veneering Porcelain: Role of Application Methods³

6.1 Introduction

Zirconia holds an exclusive place amongst dental restorative materials compared with other oxide ceramics, such as alumina, because of its excellent mechanical properties as a consequence of transformation toughening that was identified in the mid-1970s [6]. Pure zirconia can exist in three different crystal structures depending on temperature. At room temperature up to 1170°C, the symmetry is monoclinic, the structure is tetragonal between 1170 and 2370°C and cubic above 2370°C up to the melting point [142] The transformation from tetragonal (t) to monoclinic (m) during a cooling process is accompanied by a volume increase (approximately 4%) and shear distortion, sufficient to cause catastrophic failure. Alloying pure zirconia with stabilizing oxides such as Y₂O₃ allows the preservation of the meta-stable tetragonal structure at room temperature and therefore the potential to enable stress-induced

³ This chapter is based on the following published manuscript:
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t→m transformation, which can enhance resistance to crack extension leading to higher toughness compared to alumina [26; 29; 30].

As a consequence of the metastability of tetragonal zirconia, stress-generating surface treatments, such as grinding or sandblasting, are able to trigger the t→m transformation with the associated volume increase leading to the formation of surface compressive stresses, thereby increasing the flexural strength. However such metastability of the material also increases the susceptibility to aging [31]. The Low Temperature Degradation (LTD) of zirconia is a well-documented phenomenon, dependent upon the presence of moisture and modest heat [37; 144; 145; 146; 147; 148]. The consequences of this aging process are multiple and include surface degradation with grain pull-out and micro-cracking as well as strength degradation. Although LTD has been shown to be associated with a series of orthopaedic hip prostheses failures in 2001 and despite a well-established definition of the conditions under which LTD occurs, there is currently no clear relationship between LTD and failure predictability when zirconia is used as a dental bio-ceramic [39].

3Y-TZP is now widely used in dentistry for the fabrication of dental restorations, mostly processed by machining of partially-sintered blanks followed by sintering at high temperature. The mechanical properties of 3Y-TZP strongly depend on its grain size [40; 149; 150]. Above a critical size, Y-TZP is less stable and more vulnerable to spontaneous t→m transformation than smaller grain sizes (<1 µm) [151]. Moreover, below a certain grain size (≈0.2 µm), the stress-induced transformation is not possible, leading to reduced fracture toughness [152].
Porcelain fused to metal (PFM) restorations developed over decades have placed great attention on the preparation of the interface prior to building up of the porcelain as well as the reactions that promote adhesion. The nature of the interface between Y-TZP and its veneering porcelains however has not been carefully studied. Although diffusion processes are time-dependent, chemical reactions may occur between the two ceramic materials [110; 150]. In Chapter V the authors used high resolution SEM to investigate the surface features of Y-TZP bonded to porcelain and found that wet thick layers of porcelain when sintered generated highly textured Y-TZP grains [110]. The aim of this paper is to use X-ray micro diffraction to evaluate the interface region between veneering porcelain and Y-TZP prepared using standard dental fabrication techniques.
6.2 Materials and Methods

The sample preparation was done using the methods and materials described in detail in Chapter III.

In this study yttria partially stabilized tetragonal zirconia polycrystalline ceramic (Y-TZP, VITA In-Ceram® YZ, VITA Zahnfabrik, Germany) is used as a framework material. This material was prepared by sintering blocks, suitable for CAD/CAM machines Cerec® and InLab® (Sirona, USA), at a temperature of 1530°C for 2 hours. For the observation of the interface system rectangular plates with dimensions of 10x10x1 mm³ were used. As veneering porcelain, VITA VM® 9 (colour shade 2M2), prepared in three variations were built up on the zirconia surface using the methods listed in Table 6, in chapter III.

All three different preparation procedures were scanned with the microdiffractometer in the manner shown in Fig. 29, chapter III. The veneered part and the polished zirconia surfaces were measured at 8 different positions in steps of 50 µm across the interface with a measurement time of 120 seconds per pattern using the 50µm micro lens and Co-Kα (radiation with 30 kV/30 mA setting) with a fixed incident angle of 10° to the flat interface. Three of the scanning positions are shown as an example for the working area in Fig. 29 (chapter III), where the middle position focuses on the location directly at the interface between Y-TZP and porcelain and the others on the adjacent positions. The schematic on the left hand side vertically through the tapered interface sample shows positions of the spots indicated by the elliptical areas on the
right hand side. No etching process such as HF content gel was used to ensure that other potential influences on the framework material were minimised.
6.3 Results

The zirconia surfaces were scanned, as described above, before the veneering process to ensure that the zirconia was completely tetragonal and had no observable monoclinic peak.

*Fig. 43: Typical GADDS frame of the diffraction pattern observed for untreated Y-TZP with a solid angle of incidence of 10°. The major peak is associated with the 100 tetragonal/cubic peaks while the less intense peaks to the right are of the 220 series of tetragonal and cubic peaks.*

The GADDS frame in Fig. 43 shows only the tetragonal crystal structure on the surface of the Y-TZP sample. In all samples reflections no monoclinic Baddeleyite structure of ZrO₂ was detectable. After the phase composition of the Y-TZP surfaces was established they were veneered using the different sample preparation methods listed in Table 6.
The result of the $\mu$-XRD$^2$-measurements from one typical sample prepared with a Wash-Dentin (preparation method no. 1) coating and prepared as schematically shown in Fig. 29 are presented in Fig. 44. The black arrow on the left side at position 1 identifies the location of the interface of the taper section between the veneered zirconia grain surface and the polished zirconia. Scans of intensity versus $2\theta$ at 8 measurement points were performed, starting in the veneered surface, proceeding across the interface region and ending in the substrate zirconia.

Both measurements at position 1 (green coloured patterns) show only low intensities of both, monoclinic and tetragonal/cubic Zirconia due to the overlying veneering glass, which absorbs the X-ray beam.

At the locations 2 and 3 (red patterns) the intensities from the zirconia surface beneath the porcelain layer were significantly increasing, due to the decreasing thickness of the overlying veneering. It should be point out that the observed monoclinic (-111)-reflection which appears at app. 33° $2\theta$ seems to be significantly more intense than for the other locations. Also in both green patterns (Pos. 1, 2) there is a significantly intense monoclinic reflection at this position.

At positions 4 to 7 (black patterns) no porcelain is covering the zirconia substrate due to the geometry of the sample, therefore the information comes from the ground and polished zirconia at areas below the interface. These areas are beneath the veneered zirconia interface and so they provide a basis for comparison with the diffraction patterns near the interface. These results are similar to position 2 and 3 (red patterns). The X-ray patterns show broader tetragonal/cubic peaks and weak
and significantly broad monoclinic peaks at $2\theta$ 33° in all of these areas. As such the influence of the veneering process can be compared with the grinding/polishing preparation of the taper section.

The right hand side of Fig. 44 presents the scan from $2\theta$ 32° to 37° at a higher magnification superimposing results from all locations. The slight broadening in width of the known cubic/tetragonal peak at about $2\theta$ 35° is evident for the black traces and an increase in intensity and sharpness of the monoclinic peak at $2\theta$ 33° for some of the green and red traces is also obvious.

![Fig. 44: X-ray scans across the interface area of the Wash-Dentin (method 1) prepared sample measured using a 50 µm micro lens, Co-Kα, 30 kV/30 mA, fixed incident angle 10°, 120 sec/frame.](image)

Another feature evident in Fig. 44 is the two reflections in the range around 70° $2\theta$, the cubic (311)/tetragonal (013 and 121) peaks. Both show a switch of tetragonal peaks intensity (121 to 013), starting under the veneering (red patterns 2, 3). This
grinding induced intensity flip phenomenon of these tetragonal intensities is well known on zirconia surfaces [153].

The \( \mu \)-XRD²-results for the “normal” Wash-Dentin layering technique (preparation method no. 1) coating and the thicker veneered specimen (preparation method no. 2) show similar results. It was impossible with the diffraction method to recognize dissimilar effects between the zirconia samples from these two preparation methods as anticipated from other studies [110]. In both cases clear monoclinic zirconia peaks were detectable directly under the porcelain layer from the zirconia surface, but they were not stronger or more clearly recognizable from those associated with the preparation with the thicker layer (method no.2) than the layering technique (method no.1).

To understand the reason for the sharp and increasing (-111)-reflection of the monoclinic phase especially in the interface region in Fig. 44 the related GADDS – frames from the Hi-Star detector are shown in Fig. 45 for the 6 patterns which are in the direct neighbourhood of the interface region.
Fig. 45: X-Ray scans across the interface area of the thin layer of porcelain coated zirconia (preparation procedure 1) measured using a 50 μm micro lens, Co-Kα, 30 kV/30 mA, fixed incident angle 10°, 120 sec /frame. An arrow at position 2 correlates the intense single crystal reflection with the corresponding monoclinic (-111)-reflection in the XRD²-pattern.

The GADDS frame especially for position 2 shows a very strong single crystal reflection, which is the reason for the monoclinic (-111) reflection in the corresponding pattern (The arrow indicates this single crystal diffraction spot within the corresponding reflection pattern).

Higher magnification X-Ray patterns provide a better appreciation of the structural phase change with the Wash-Dentin coating and the thicker layer of the porcelain on top of Y-TZP (preparation no. 1 and no.2). Fig. 46 A to Fig. 47 B present azimuthal projections from positions at similar distances from the interface region with preparation methods 1 and 2 within the veneered areas measured in this case with a 500 μm monocapillary optic with a 300μm exit pinhole to analyse a larger surface
area for better statistics. Again in both cases similar single crystal reflection spots from the monoclinic phase are detectable in the area under the porcelain independent of the preparation method.

![Image](image1.png)

**Fig. 46** (A) Area a in the veneered part of preparation method no. 1; 500 µm monocapillary optic with 300 µm pinhole Co-Kα, 30 kV/30 mA, fixed incident angle 10°, 600 sec/frame. (B) Diffraction pattern from Spot a showing the tetragonal diffraction rings and isolated spots caused by single crystal (111)-reflections of the monoclinic structure.

![Image](image2.png)

**Fig. 47** (A) Area b in the veneered part of preparation method no. 2; 500 µm monocapillary optic with 300 µm pinhole Co-Kα, 30 kV/30 mA, fixed incident angle 10°, 600 sec/frame. (B) Diffraction pattern from Spot b again highlighting the presence of intense monoclinic single crystal (111)-reflections of the monoclinic structure.

A clearly identifiable difference in the Y-TZP surface region prepared in the absence of a liquid medium by the veneered process (preparation method no.3, Fig. 48) was the absence of a detectable monoclinic peak through the porcelain very close to the interface.
Fig. 48: Interface area of the without liquid veneered zirconia (preparation procedure 3) measured using a 50 µm micro lens, Co-Kα, 30 kV/30 mA, fixed incident angle 10°, 120 sec/frame, only diffraction rings caused by the tetragonal ZrO₂ are observable.
6.4 Discussion

The present results indicate that prior to the veneering procedures on the surface of the zirconia samples only a tetragonal/cubic crystalline structure is detectable. After two different sample preparation methods 1 and 2, with either a thick wet porcelain layer or a thin wash coat layer with the presence of modelling liquid, the monoclinic phase was detectable by micro diffraction beneath the porcelain layer. Furthermore in the polished and ground areas of the unveneered area, a noticeable increase in the width of the tetragonal/cubic peak intensity and a small broad monoclinic peak was visible. The observation was similar to what Coldea et al [154] and Denry et al. [155] observed following different grinding and polishing procedures on Y-TZP-surfaces. The difference here is that the same observations were made after veneering on a zirconia surface, which was not affected by any grinding procedure.

These clearly observable features appearing after the veneering process point to crystal changes that develop on the Y-TZP grains directly at the zirconia-porcelain interface from t→m transformation as a consequence of the veneering. It indicates that a significant structural change has developed during the veneering process with the presence of a liquid medium during furnace firing. There is clear evidence of broadening of the tetragonal/cubic zirconia diffraction peak accompanying a limited rise of the monoclinic (111) intensity after firing the damp porcelain (preparation method no.1, Fig. 44 and no. 2, Fig. 47)

An approximate estimate of the extent of the monoclinic present in the diffraction patterns shown in Fig. 44, Fig. 47 and Fig. 48 for the different preparation methods may be obtained using the simple analysis proposed by Garvie and Nicholson [29]. It
utilises the intensities of the monoclinic and tetragonal/cubic diffraction peaks. The results are given in Table 15 below.

*Table 15: Monoclinic volume percentage from the analysis of Garvie and Nicholson [29]*

<table>
<thead>
<tr>
<th>Preparation</th>
<th>Monoclinic V% @ Red line position 2</th>
<th>Monoclinic V% @ Black line position 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method 1 (Wash firing)</td>
<td>11.5 %</td>
<td>3.5 %</td>
</tr>
<tr>
<td>Method 2 (thick layer)</td>
<td>13 %</td>
<td>4 %</td>
</tr>
<tr>
<td>Method 3 (no liquid)</td>
<td>&lt; 2 %</td>
<td>4 %</td>
</tr>
</tbody>
</table>

These results indicate the in the presence of liquid (Methods 1 and 2) the monoclinic content from the surface (position 2) is far greater than for the same position in the absence of liquid (Method 3) and also greater than the extent of monoclinic generated by cutting, grinding and polishing of the zirconia (position 5) for all methods below the interface. But due to a more detailed and critical examination of the GADDS-frame from the 2-dimensional Hi-Star detector shown in Fig. 45 especially at Pos. 2, it is important to point out, that the monoclinic information is caused by one single crystal reflection in contrast to the tetragonal/cubic reflection which shows complete diffraction rings typical for a random crystal orientation of this phase. For this reason an analysis like that proposed by Garvie and Nicholson [29] of these samples is not entirely appropriate.

However even without a quantitative measurement, the samples consisting only of the porcelain powder and no liquid medium exhibited far less observable monoclinic phase than the two other preparation methods. These results are consistent with other observations that humidity at elevated temperatures causes the $t \rightarrow m$ nucleation and growth [110; 132].
A significant feature of the 2-dimensional HiStar-detector associated with the \( \mu \)-
XRD\(^2\)-setup is that from the intensity distribution along the diffraction ring of each
reflection, direct information of crystallite size and texture could be estimated. In the
case of the tetragonal/cubic zirconia crystals present the intensity distribution is
completely uniform which indicates that the crystallites are statistically randomly
distributed in the measurement volume. However for the monoclinic phase only
isolated peaks as indicated with arrows in Fig. 45, Fig. 46 and Fig. 47 are observed.
This suggests the monoclinic crystals present are highly aligned. This arises
because the nucleation of the tetragonal to monoclinic transformation at a surface
will be governed by both the strain energy constraints and also specific orientation
requirements between the tetragonal and monoclinic phases [132]. These authors
also show that at a surface transformation of the tetragonal to monoclinic can only
occur by one lattice correspondence. That is, certain oriented grains will be more
susceptible to this transformation and result in highly textured or oriented monoclinic
volumes, which is what the GADDS images indicate. In addition the highly oriented
X-ray beam will show the presence of these diffraction peaks at localised spots as
observed.

The use of only porcelain powder (preparation method no.3) without any liquid
medium resulted in no obviously detectable transformation of the zirconia grains
structure, indicating that the powder itself, even with the same temperature exposure
as with the other preparation methods, cannot be the reason for developing a
monoclinic peak from the Y-TZP grains. In contrast, the changes observed using the
liquid medium with exactly the same porcelain powder and the same firing procedure clearly shows an observable effect.

These observations support previous studies [37; 110] on the role of humidity during the initial stages of the moist porcelain powder heating up leading to the destabilisation or LTD of the veneered Y-TZP tetragonal grains. This behaviour is in agreement with the well-documented occurrence of instability of Y-TZP in the presence of humidity [31; 37; 39; 110]. The present results for the Y-TZP grains are similar to the initial stages of moisture induced tetragonal to monoclinic phase transformation observed for these materials using atomic force and optical microscopy by Chevalier [31; 37; 39]. In addition Chevalier et al. were unable to detect the presence of monoclinic phase using X-ray diffraction as the layer thickness and amount of tetragonal transformed to the monoclinic phase was very limited. The X-ray micro diffraction setup used in this case study with the 10° incident angle using a focussing micro lens to achieve a 50 by 200 micrometer-sized localized beam had the advantage to enable phase stability of the near surface layer of the zirconia interface to be evaluated. This specially designed X-ray polycapillary micro lens system also enabled detection of the zirconia through thin layers of the porcelain surface.

This structural t→m change at the interface creates localised residual stresses as a consequence of the volume dilation as well as the different coefficient of thermal expansion of the framework material. Such localised residual stresses at the interface may weaken the porcelain to zirconia adhesion and may have influenced the shear interfacial strength tests by Fischer et al [156]. However to date there have
been no published reports of clinical adhesion failure between porcelain and Y-TZP frameworks despite increasing observations of chipping induced failures within the porcelain on such frameworks [157].

The localised stresses developed between the veneering and the reliability of the dental restoration in the clinical situation are not completely established and further investigations with a focus on these topics need to be undertaken.
6.5 Conclusions

The present observations using the locally resolved $\mu$-XRD$^2$ technique have clearly established that the porcelain veneering process, especially with a wet veneer during firing, results in a localized tetragonal to monoclinic structural transformation at the surface of the zirconia framework material during preparation of these all-ceramic dental restorations.

In the case of moist veneering porcelain a highly textured or oriented monoclinic crystalline phase was observed at the zirconia/porcelain interface. In the absence of moisture within the veneering porcelain no transformation of the Y-TZP tetragonal phase was identified.

As a consequence of the findings in this study, it is strongly recommended to use a porcelain layering technique that is very thin and as dry as possible for the initial layering application to prevent destabilisation of the tetragonal crystals of the Y-TZP framework at the interface, which will otherwise induce local mechanical stress into the overlying porcelain layer and therefore could decrease the mechanical stability of the final product.
7. Thermal gradients and residual stresses in veneered Y-TZP frameworks

7.1 Introduction

The introduction of metal-ceramic system in 1962 enabled dentists and dental technicians to produce highly aesthetic dental restorations. More recently with the development of dental all-ceramic systems especially with yttria partially stabilized zirconia (Y-TZP) or alumina as framework materials, aesthetics have been further improved. These enhanced dental restorative materials come ever closer to that of natural teeth. In 2008 in Germany over 40 % manufactured dental restorations were all-ceramic, but according to the broad-based consumer surveying company since then the demand has decreased to less than 25%. The reason for the decline is the clinical concern about failures and long-term stability of restorations especially with Y-TZP frameworks.

This apprehension, especially the occurrence of “chipping” of all-ceramic restorations with Y-TZP frameworks, has generated considerable research within the dental materials community [128]. Failures within the porcelain layer or breakage at the

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4 This chapter is based on the following published manuscript:

Tholey MJ, Swain MV, Thiel N. Thermal gradients and residual stresses in veneered Y-TZP frameworks. Dental Materials 2011; 27, 11, 1102-1110
interface in metal-ceramic restorations are well known since their introduction. But this special “chipping” failure mode appears to arise predominantly with Y-TZP all-ceramic systems especially in the cusp area. The term “chipping” according to the dictionary definition implies that splinters occur, which realistically describes the characteristic features of this failure mode. The crack propagation occurs exclusively within the porcelain layer and does not appear to run to the interface between the veneering and the framework material. Added to the outer surface of a zirconia framework is generally a thin veneering layer beneath where the chipping event occurs [7; 128].

With all-ceramic framework materials, especially with Y-TZP, the processing guidelines have been modified by most commercial suppliers compared with the well-known technique of the metal-ceramic systems. The consensus, although not as yet genuinely verified, is that residual stresses develop within the porcelain during rapid cooling and these contribute to chipping induced fracture. Residual stresses can be introduced during the firing process inside the porcelain layer and can be of two major origins; due to thermal expansion mismatch and tempering stresses associated with temperature gradients during cooling [14; 112]. These residual stresses, which remain after the cooling in the porcelain layer, are one possible explanation for the differences of “chipping” failures between metal and Y-TZP based all-ceramic restorations. The materials parameters of all-ceramic restoration such as Young’s modulus or coefficient of thermal expansion of the material partners as well as the glass transition temperature of the porcelain do not differ significantly from those of the well-known metal-ceramic porcelains. It has been argued that the drastically different thermal conductivity of the framework materials (gold has
approximately 150-times higher thermal conductivity than zirconia) may be the origin of this special failure mode [112].

One goal of this investigation was to determine experimentally the temperature differences arising during the firing process of all-ceramic crowns with Y-TZP frameworks by the use of a rotational symmetric crown model. In addition two slightly different models (one framework with constant wall thickness and the other with anatomical supported structure) were cooled after firing in two different ways (fast and slow cooling). Another objective was the determination and visual presentation of the stress distribution with an optical imaging polarising system that can measure the optical polarization state of light transmitted through the porcelain. It is mainly based on the ability to build effective polarization state analysers that acquire the Stokes vectors corresponding to each pixel in the image [113; 114]. This is done traditionally by rotating birefringent optical elements such as quarter-wave plates in front of a fixed polarizer [113].

Reductions of residual stresses within the veneering porcelain will possible result in more secure zirconia framework based dental restorations. The hypothesis investigated in this paper is that temperature gradients produced at temperatures above the glass transition temperature of the porcelain during cooling generate higher residual stresses. Optical polarimeter images are used to verify this hypothesis.
7.2 Materials and Methods

The sample preparation was done using the methods and materials outlined in more detail in Chapter III.

7.2.1 Crown/sample model

A rotationally symmetric crown form similar to that previously invested by Lenz et al. [112] was selected to ensure the production of identical samples and to simplify the experimental determination of the surface temperature corresponding with the geometry of a premolar tooth. Anatomically precise crowns, whilst possible to evaluate in a similar manner would have drastically increased the difficulty of production, especially regarding thermocouple placement and subsequent cross-sectioning of similar veneered copings.

7.2.2 Thermal measurement configuration

As a basis for supporting the firing of the samples a refractory honeycomb tray was used (Renfert, Germany). The honeycomb tray was drilled centrically to which a thermocouple protective glass with a length of approx. 23 mm was fixed. This length was selected, as the cervical edge of the samples was positioned approx. 6 mm above the tray, which corresponds to the reality in dental labs.

7.2.3 Polarimeter method

The uniform thickness framework samples for the polarimeter (StrainMatic® M3/250, ilis GmbH, Germany) were produced following exactly the same firing steps and in the same sizes as for the thermo-couple measurements. After the firing, a thin slice 0.5 mm thick was cut using a water-cooled diamond saw from the mid-point of the
coping and mounted in the polarimeter. With the polarimeter the turn optical rotation value of the light through the crown was determined. The change of the angle of the linear polarized light was determined with passage through the samples [113; 114].

### 7.3 Results

Typical thermocouple observations (Fig. 49) were made of the normal firing program together with a fast cooling, which means that the furnace was opened directly after the designated holding time at the max firing temperature of the furnace. The thermocouples were based on the measuring points 1 and 10 (see Fig. 30 and insert in Fig. 49) of the rotationally symmetric veneered sample with constant framework wall thickness (0.7 mm). During heating almost parallel temperature plots resulted from both locations, with the inner temperatures always lower than the external temperature. This difference diminished during holding at the maximum temperature and then during cooling the temperature differences were inverted and diverged. The inner and the outer thermocouples were at the same end temperature after 20 sec at the max hold temperature point of the furnace, which means that the framework and the veneering layer reach the same temperature during the heating process as presented in Fig. 49. At four temperature points (during the heating process: 630°C and 920°C, during the cooling process: 305°C and 180°C) on the measured firing line of the porcelain deviation bars are included as explanatory of the little variation between repeats of the thermocouple results.

It was interesting to observe that at the reference points (MP1 and MP10) only a very low deviation of about 4°C - 7°C (see Fig. 49) in the heating process and 11°C- 16°C in the cooling was detectable, so that only the average of all measurements had to
be presented in all other measurements. The higher deviation during the cooling could be explained with the opening mechanism of the furnace combined with little movements of the thermocouples.

![Graph](image)

*Fig. 49: Temperature recorded during the complete process of firing porcelain to zirconia at the measurement points MP1 and MP10.*

On this basis in further observations only the cooling behaviour was examined as this was considered a direct guide to tension developed within the porcelain layer where the chipping occurs. Typical examples for measurement points 2 versus 8 for a sample with constant wall thickness are shown in Fig. 50.

An analysis of all measurements showed that the maximum temperature differences between the inside and the outside is present in the area of MP2, MP3 and MP8 (see Fig. 50). That is the maximum temperature difference, which was observed in the cusp as this in the thickest section of the samples.
The two plots of the direct temperature difference between the measurement points 2 and 8 versus time after opening the furnace at 850°C (Fig. 51: A) and also versus the outside surface temperature at measurement point 8 (Fig. 51: B) show more clearly that the maximum temperature difference occurs between 40 to 45 seconds after opening of the furnace. This is typically the time when the outer surface of the porcelain in the area of measurement point 8 reaches the glass transformation point of the VM 9 porcelain.
Table 16 presents an overview of the time when the glass transition point of the VM 9 porcelain (approximately 603°C) is reached at the different measurement points.

Table 16: Time at the measurement points when the glass transition temperatures arise

<table>
<thead>
<tr>
<th>Measuring Point</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>[sec.]</td>
<td>58</td>
<td>55</td>
<td>54</td>
<td>48</td>
<td>46</td>
<td>38</td>
<td>45</td>
<td>42</td>
<td>46</td>
<td>50</td>
</tr>
</tbody>
</table>

Evaluation of all measurements showed, that all differences were maximum during the opening process of the furnace and for a further 60 seconds.

The cooling curves of the anatomically supported samples, the second investigated series, showed a similar tendency. The maximum values of the time differences with the anatomically supported Y-TZP crowns are approximately 40°C higher than with the constant wall thickness samples. Fig. 52 presents the cooling behaviour of the porcelain supporting framework structure of Y-TZP from 850°C.
The plot of the temperature difference between the measurement points 2 and 8 versus the outside surface temperature at measurement point 8 (Fig. 52) indicates that the maximum temperature difference is also with anatomically supported zirconia frameworks happening between 40 to 45 seconds after furnace opening.

Table 17 presents an overview of the time after opening of the furnace for the different measurement points to reach the glass transition point of the porcelain (approximately 603°C). The outer surface (e.g. measurement point 8) is at 600°C at the same time after opening as the samples with constant wall thickness while the inner surface needs a longer cooling time to reach 600°C.

Table 17: Opening at 60 sec with supported framework structure

<table>
<thead>
<tr>
<th>Measuring Point</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>[sec.]</td>
<td>58</td>
<td>56</td>
<td>56</td>
<td>49</td>
<td>45</td>
<td>43</td>
<td>44</td>
<td>40</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

The maximum temperature differences arose between MP2, MP3 and MP8 as shown in the following table. The temperature difference between MP1 and MP10 was similar for both Y-TZP coping designs. The observed maximum differences are
presented in the following table. Another notable feature is that the temperature differences occur later with the anatomically supported framework than with a thin and constant wall thickness of the same framework material.

*Table 18: Maximum temperature difference in the cusp area during rapid cooling for the uniform framework thickness*

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant wall thickness</td>
<td>118</td>
<td>44</td>
<td>158</td>
<td>58</td>
</tr>
<tr>
<td>Constant wall thickness</td>
<td>101</td>
<td>48</td>
<td>148</td>
<td>62</td>
</tr>
<tr>
<td>Anatomically supported</td>
<td>64</td>
<td>62</td>
<td>62</td>
<td>66</td>
</tr>
<tr>
<td>Anatomically supported</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the third series the samples with constant and supported wall thickness were cooled down slowly, i.e. with a closed furnace, to 600°C. Here the maximum temperature difference arising between MP2 and MP8 was clearly lower than the previous results. At the start of more rapid cooling upon opening the furnace at 600°C the inner and outer layers were the same temperature. The start temperature of this observation series was lower than the glass transition temperature of the porcelain. The highest temperature differences also arose after the cooling time of 40 - 60 seconds as with the fast cooling, as presented in Fig. 53. The maximum temperature difference between MP2, MP3 and MP8 is shown in the Table 19.
Fig. 53: A: Cooling from 600°C at MP2 and MP8 for samples with constant wall thickness and B: Differences between MP8 and MP2 versus the temperature at MP8 (outer surface)

Table 19: Maximum differences in the cusp area

<table>
<thead>
<tr>
<th>Measurement points</th>
<th>Max. Difference [°C]</th>
<th>Max. Difference [Sec.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 - 8</td>
<td>88</td>
<td>48</td>
</tr>
<tr>
<td>3 - 8</td>
<td>79</td>
<td>58</td>
</tr>
<tr>
<td>1 - 10</td>
<td>51</td>
<td>60</td>
</tr>
</tbody>
</table>

The optical polarimeter observed residual stress results only for the uniform framework crown are presented in Fig. 54. These polarimeter images provide a non-destructive measurement of the residual stresses and show higher values within the veneering porcelain in the fast cooled sample. The clear differences between the cooling procedures are observable in the colour-coded stress distribution.

The residual stresses observed are those that highlight the radial values, as the magnitude at the external surface is minimal. For the section examined these radial stresses show the stresses developed above the porcelain zirconia interface. The image of the slow cooling method from 600°C indicates that lower residual stress
remain in the porcelain by using this different firing cycle compared with the standard fast procedure (Fig. 54).

Fig. 54: Differences of the residual stresses between slow and fast cooling measured with polarimeter. The lower values in the horizontal table are the magnitudes of the residual stress in MPa.

7.4 Discussion

Chipping of all-ceramic restorations is a phenomenon, which does not appear to exist to the same extent in metal-ceramic technology compared to all-ceramic system with Y-TZP framework [159]. Also it is not reported to occur to the same extent in other all-ceramic systems. Therefore the question arises, to what extent do dental porcelain systems differ? A significant difference as to the nature of the failures arises because of the material compositions, because chipping of the porcelain runs completely within the veneering of all-ceramics with a Y-TZP
framework, resulting in the surface of the framework remaining slightly covered by a thin layer of porcelain [13; 14; 16; 128; 159 - 164].

From the thermocouple data (Fig. 50 - Fig. 52) it was possible to determine the temperature difference between the various measuring points, especially from the measurement points in the cusp area where the focus was placed. The reason for observing these measurement points is that it is from the cusp area that most chipping occurs. The temperature gradients with the different test conditions may be compared against each other and with a geometrically simplified model [112; 159; 161].

The results observed in this study showed a clear difference in the temperature between the inner and outer surface of a veneered zirconia coping during the cooling procedure. It was also obvious that the temperature differences between the two surfaces were lower for slower cooling with a closed furnace chamber till 600°C. The temperature differences differ from 160°C with an anatomically supported design of the zirconia to nearly half of the difference with 88°C at the same measurement point for a slow cooled non-supported coping. This results in a lowering of the temperature gradients in the veneered coping in the cusp area. The temperature differences from the inside to the outside arise with the faster cooling method and are higher than in earlier reports of measurements with metal copings [112; 128]

It is observable that two completely different situations are occurring during the different cooling procedures. The first situation is the cooling from 850 °C as was
recommended from all manufacturers of veneering porcelain till 2009. The second observed situation is cooling from 600 °C.

In the first situation, the porcelain is above its glass transition (T_g) point. In the temperature range from 850°C to 600°C normally all porcelain stresses are able to relax by viscous flow until the temperature is equal to its T_g. In this case the cooling is very fast and when the outer surface reaches 600 °C the outer regions of the porcelain can no longer relax and essentially the temperature gradient through the porcelain becomes locked in [16; 164 - 166]. This results in residual stresses in the porcelain layer. These stresses do not change upon further cooling but additional stresses due to coefficients of thermal expansion (CTE) differences between Y-TZP and porcelain may additional develop [16].

The maximum stresses developed are a combination of CTE mismatches induced stresses and tempering residual stress in this all-ceramic combination. The poor thermal conductivity combined with the poor thermal diffusivity [168] of both materials results in a high temperature difference through the crown, especially at the thicker sections upon fast cooling, resulting in high residual tempering stresses. Thermal tempering creates a compressive stress on the surface of the porcelain. It is important to note that the compressive stresses at the surface of tempered porcelain are balanced by tensile stresses in the centre of the porcelain; therefore, once a crack penetrates the compressive layer, it is driven by the residual tensile stresses in the porcelain. The magnitude of tempering stresses is highly influenced by the elastic modulus, coefficient of thermal expansion, temperature point of the glass transformation and the temperature gradient [16; 167].
Changing the design of the core has been a heuristic process proposed for metal ceramic crowns [169] that has never been evaluated in clinical controlled trials, perhaps because the survival rates are known to be high in such systems [170]. Porcelain veneered zirconia failures have led to concerns regarding adequate porcelain support [168], differences in the CTE between the framework and the veneering porcelain and their respective processing techniques [168] or the low thermal diffusivity of zirconia compared with alumina or metal [168].

The second situation presented is for cooling below the glass transition temperature. In this situation the porcelain is completely elastic when the furnace has been opened. As at 600 °C, which is below the $T_G$ of the porcelain, there is no temperature difference and no temperature gradients between the inner and outer surfaces of the crown. Therefore no thermal stresses are present in the crown. The crown is like a sphere of zirconia, which is coated with porcelain thick layer. For such a body held at just above the $T_G$ (~600°C) no stresses are present as the porcelain can relax any CTE mismatch stresses. Below $T_G$ the zirconia will contract more than the porcelain as it has a higher CTE. Thus in the radial direction the stress at the porcelain-zirconia interface in both materials will be in tension. There will be a gradual decline in the radial tensile stress towards the surface in the porcelain as at the external surface the radial stress must be zero. However the hoop stresses at the external surface will be compressive whereas towards the interface they will also become tensile [171].
The final situation has some desirable aspects, namely surface compressive stresses in the porcelain, as well as undesirable subsurface compensating tensile stresses that increase towards the porcelain-zirconia interface. Whilst this is an attractive situation for the prevention of crack initiation from surfaces exposed to contact loading in the oral system, however if contact loading or clinical “adjustment” initiates a crack, which upon further loading and as a consequence of sub-critical crack growth, it may well couple into the internal tensile stresses and spontaneously extend [16; 167].

The polarimeter residual stress images (Fig. 54) support the measured thermocouple results for the two different cooling situations. The images present a clear reduction of the radial stresses for the slower cooling method. The stresses seen in the imaging polarimeter when the slow cooled sample is taken from the furnace at 600°C are, as outlined above, only due to the CTE differences.

Whereas the samples rapidly cooled from 850 °C contain CTE mismatch stresses plus tempering stresses due to locked in temperature differences as the porcelain cools through the glass transition temperature at 600°C. In other words the thermocouple plots for the slow cooled crown to 600°C, the T_G temperature, before opening of the furnace do not develop tempering residual stresses but do hint at transient stresses developed during cooling that disappear as the crown eventually cools to room temperature. Removing the crown from the sintering furnace at 850°C results in more rapidly cooling in the laboratory air and generates a superposition of a CTE mismatch and residual tempering stress in the porcelain.
In principle the polarimeter measures stresses by determining the propagation velocity of light along different axes. Imaging polarimeters facilitate fast and accurate determination of stress birefringence and its spatial distribution and orientation. To what extent such a polarimeter method is identifying the reality of stresses in this all-ceramic restoration is not absolutely clear because of the necessity of producing a thin section. The cutting and polishing of the thin slices may have caused differences from the actual 3 dimensional stress situation [112; 159].

Another outcome of this investigation was that anatomical support creates greater thermal differences from the inner to the outer surface within the restoration than an unsupported framework. This arises because of the higher heat capacity of zirconia than porcelain. But as shown the differences were lower by slowly cooling till 600°C. Further work is in progress to quantify the residual stresses with the polarimeter for the anatomical shaped framework.

At this time we are unable to address the question as to whether it is still favourable to support the porcelain as with the anatomical design. It is claimed in some studies that an anatomical support reduces the loading induced tension caused by biting and oral dysfunction [25; 162; 163]. In addition the thinner porcelain layer even if it did chip would result in thinner and a less consequential outcome compared with an unsupported framework [162; 163; 172]. The thicker section of zirconia and thinner porcelain veneer leads not only to smaller chippings, but in addition the contact induced biting forces result in slightly lower contact stresses because of the stiffer framework and with this the resistance to contact induced cracking in the oral system would be higher [14; 160 - 163; 172].
Bonfante et al. [168] presented a finite element analysis (FEA) simulation for an anatomical crown model, which showed a higher overall maximum stress in the framework compared with a non-supported framework, but also more stress distribution. Theoretically, his results were a positive indicator of potential beneficial geometric effect for an anatomical design [168].

Slow cooling is only important in the last firing step. This arises because the stresses introduced during the earlier firing steps in the porcelain layer will be relaxed upon reheating above the glass transition temperature so that only in the last firing is the importance of slow cooling critical [16; 167]. The last firing step is usually the glaze firing step, it is also important for healing and thereby reducing defects associated with clinical adjustment of the dental restoration.

Possible reasons for the big differences of zirconia framework based all-ceramic restorations in clinical failures compared to metal ceramic systems are the very low thermal conductivity values of $\lambda = 2 \text{Wm}^{-1}\text{K}^{-1}$ for the zirconia framework and $\lambda = 1.5 \text{Wm}^{-1}\text{K}^{-1}$ for the porcelain. The value for the zirconia material is very small versus those for metal (co/cr alloys: $\lambda_F \approx 90 \text{Wm}^{-1}\text{K}^{-1}$, gold alloy: $\lambda_F \approx 310 \text{Wm}^{-1}\text{K}^{-1}$) [14] so that the resultant temperature gradients during rapid cooling will be higher compared to these in metal-ceramic systems. Because of this extreme difference compared with other framework materials the thermal stresses will be different and in all instances higher with zirconia frameworks [16; 167].
Another short remark is that for samples used clinically in the oral system, many other parameters especially for bridgework also require slow cooling because of sizeable pontics for example, which will retain the heat even longer than a relatively thin walled crown.

Finally, it is pointed out that the observed temperature gradients and residual stress results with fast and slow cooling cannot be transferred directly to other all-ceramic crowns especially those with alumina frameworks. The reason is that the thermal conductivity of alumina is about 15 times higher than the conductivity of Y-TZP and it has lower CTE, so that the temperature gradients will be substantially reduced and the tempering induced residual stresses will be much lower.

A last remark is to the polarimeter method. The problem was to cut the very thin slices for this kind of method. Considerable difficulties were encountered especially for the rapidly cooled samples. There were 10 samples of each group produced for the cutting process but only one fast cooled sample was able to be cut without a crack developing in the veneering porcelain during sectioning, which supports also the other results of this study.

7.5 Conclusions

This investigation has shown that by a slow compared to a normal cooling procedure, the temperature gradients can be minimised through the porcelain layer of all-ceramic crowns. These observations for the uniform framework are directly correlated with optical polarimeter observed residual birefringence, which relates to stresses, which are much lower for the slower cooled crowns thereby confirming the stated hypothesis. The results clearly distinguish between stresses generated by
coefficient of thermal expansion mismatch between porcelain and the Y-TZP framework for slow cooling to 600°C and additive tempering stresses generated by fast cooling above the glass transition temperature. Therefore this simple change in cooling leads also to a clear reduction of the thermal gradient induced residual stresses, which represent one of the possible causes for chipping.

The largest temperature differences and associated thermal stresses arose within the cusp region of the porcelain veneer, within the area in which chipping of crowns are frequently observed.

An anatomically supported framework design generated greater temperature gradients between the porcelain layer and the inner surface of the framework because of the higher heat capacity and poor thermal conductivity of the zirconia. This result contrasts with other studies, where an anatomically designed framework is being recommended to minimise the likelihood of chipping.
8. Conclusions and Implications

8.1 Brief Summary

The importance of firing temperature of the veneering porcelain on its subsequent mechanical, optical, coefficient of thermal expansion and solubility properties was addressed in Chapter IV. The tests used in this part of the study are mainly based on the ISO 6872:2008 standards. The key outcomes were the critical role of the maximum temperature, firing time, vacuum and pre-drying on the porcelain on these parameters and also on differences of the resultant shade of a dental restoration.

The importance of sintering time and temperature is identified as being critical for the resultant properties most noticeably translucency (value) and strength. The results are discussed in terms of the basic mechanisms contributing to the physical properties. In addition a simple method for optimising porcelain firing procedures was proposed in Chapter IV.

In Chapter V and VI the interface of zirconia to its porcelain was the primary focus. During SEM observations at the interface, it was found out that in some instances the zirconia grains appear to show multiplicity of sub-grain faceting whereas in other instances they do not. It depended on the content of water present and with the amount of porcelain applied in the first firing step. The latter indicate destabilisation
of the tetragonal phase occurs during initial heating and in addition that the porcelain veneering material wets and results in some dissolution of the Y-TZP occurs.

Chapter VI proved that observations with the X-ray diffraction method were able to detect tetragonal to monoclinic transformation of zirconia grains at the interface during firing with moist veneering porcelains. These observations also indicated that destabilisation of the tetragonal to the monoclinic phase of zirconia occurs at the interface during veneering with porcelain with a specific orientation.

Chapter VII observed that slow cooling to the glass transition temperature decreases the temperature differences between the internal and external surfaces of a porcelain veneered zirconia crown but still differences of up to 88°C were observed. For the fast cooled crown form glaze firing conditions, temperature differences of more than 100°C for the uniform and 140°C for the anatomical framework at temperatures above the glass transition temperature were recorded. Optical polarimeter observations indicated much lower stresses within the porcelain layer upon slow cooling by removing the crown from the furnace below the glass transition temperature.

8.2 Conclusion

All chapters showed clear outcomes for the firing and veneering process of zirconia-based dental restorations

Chapter IV showed

- A simple firing temperature-time matrix readily enables the optimisation of the aesthetic and mechanical properties of veneer porcelains.
• Under firing has a more drastic effect on the mechanical and optical properties while over firing influences the coefficient of thermal expansion and the shape of the ceramic samples.

• The cooling procedure after the final firing is critical to minimise residual stresses and hence the likelihood for chipping of dental porcelains.

Chapter V identified:

• Veneering porcelain appears to wet and bond well to zirconia frameworks.

• However upon HF etching the interface it is observed that moisture present in the veneering powder during the preparation of these porcelain to Y-TZP structures, which were identical with all-ceramic crown firing procedures, generates grain faceting at the surface of the zirconia grains beneath the veneering porcelain.

• The extent of this surface faceting is dependent upon the moisture content of the porcelain powder and the firing temperature. The nature of the surface faceting of the zirconia grains is almost identical with the observations of the moisture induced tetragonal to a monoclinic structure observed by Chevalier et al. [132] using AFM.

• It is argued that the observed increased faceting seen after high veneering porcelain firing temperatures are a consequence of the glass induced dissolution at sites of higher residual stresses at the tetragonal/monoclinic interfaces.

• The long-term consequence of the presence of such transformed grains at the porcelain Y-TZP interface needs to be further investigated.

The present observations using the locally resolved $\mu$-XRD$^2$ technique of Chapter VI have clearly established the following:
The porcelain veneering process, especially with a wet veneer during firing, results in a localized tetragonal to monoclinic structural transformation at the surface of the zirconia framework material during preparation of these all-ceramic dental restorations.

In the case of moist veneering porcelain a highly textured or oriented monoclinic crystalline phase was observed at the zirconia/porcelain interface.

In the absence of moisture within the veneering porcelain no transformation of the Y-TZP tetragonal phase was identified.

The investigation in Chapter VII has shown

- By a slow compared to a normal cooling procedure, the temperature gradients can be minimised through the porcelain layer of all-ceramic crowns.
- These observations for the uniform framework are directly correlated with optical polarimeter observed residual stresses, which are much lower for the slower cooled crowns thereby confirming the stated hypothesis.
- The largest temperature differences and associated thermal stresses arose within the cusp region of the porcelain veneer, the area within which chipping of crowns are frequently observed.
- An anatomically supported framework design generated greater temperature gradients between the porcelain layer and the inner surface of the framework because of the higher heat capacity and poor thermal conductivity of the zirconia.
- The result contrasts with other studies, where it is being recommended that anatomical designs be used to minimise the likelihood of chipping.
8.3 Recommendations

These thesis research outcomes lead to clear recommendations for a dental laboratory and dental research regarding the procedures used for veneering zirconia-based dental restorations to minimize their clinical failure rates

- Each of the firing steps of veneering porcelain have to be rethought and maybe adjusted to obtain the perfect sintering degree combined with the correct properties of the veneering porcelain such as shade, flexural strength, chemical solubility, $K_{IC}$, CTE.

- A simple temperature-time matrix method for optimising porcelain-firing procedures is achievable and should be made for every dental firing furnace and program.

- It is strongly recommended to use a porcelain layering technique that is very thin and as dry as possible for the initial layering application; to prevent a destabilisation of the tetragonal crystals of the Y-TZP framework at the interface, which will otherwise induce local mechanical stress into the overlying porcelain layer and therefore could decrease the mechanical stability of the final dental product.

- The cooling study results clearly distinguish between stresses generated by coefficient of thermal expansion mismatch between porcelain and the Y-TZP framework for slow cooling till the $T_G$ of the porcelain (600°C with VITA VM9); additive tempering stresses have been generated by fast cooling above the glass transition temperature.

- A simple change in cooling procedure leads to a clear reduction of the thermal gradient induced residual stresses within the porcelain layer, which represent one of the possible causes for chipping.
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Tables

Table 1: Average composition of dental porcelain [22] ............................................. 13
Table 2: Different studies on PFM survival results ................................................. 35
Table 3: List of clinical studies with PFZ restorations ........................................... 39
Table 4: Firing temperatures for the test sample with VITA VM9 ............................. 63
Table 5: Preparation methods of the Y-TZP frameworks ....................................... 68
Table 6: Preparation methods of the Y-TZP frameworks ....................................... 73
Table 7: Result of the mechanical properties measurement according to ISO 6872 with VITA VM9 .......................................................... 92
Table 8: Result of the mechanical properties according to ISO 6872 with DeguDent Cercon Ceram Love .......................................................... 93
Table 9: Result of the mechanical properties according to ISO 6872 with Ivoclar e.max Ceram .......................................................... 93
Table 10: Results of the flexural strength of VITA VM9 with different heating up rates .......................................................... 93
Table 11: Results of the fracture toughness ............................................................ 94
Table 12: Shade measurement with Datacolor and no pre-drying before the firing .. 94
Table 13: Shade measurement with Datacolor and no vacuum ............................. 95
Table 14: Shade measurement with Datacolor and 30°C less high end temperature .......................................................... 95
Table 15: Monoclinic volume percentage from the analysis of Garvie and Nicholson [29] .......................................................... 134
Table 16: Time at the measurement points when the glass transition temperatures arise

Table 17: Opening at 60 sec with supported framework structure

Table 18: Maximum temperature difference in the cusp area during rapid cooling for the uniform framework thickness

Table 19: Maximum differences in the cusp area
Fig. 1: "Chipping" fracture at the mesio-buccal cusp on a first molar (Magnification: 44x) .......................................................................................................................... 5

Fig. 2: Three component composition diagrams of porcelain by Della Bona [23] with A: Presenting the raw materials in relation to the main ceramic components and B: Presenting various types of ceramics in relation to the main ceramic components.. 14

Fig. 3: Typical examples of currently available veneering porcelains. A) VITA VM9; B) DeguDent Cercon Ceram Kiss; C) Shofu Vintage Zr ; D) HeraCeram Zirconia. All images are at 1000x. ................................................................................................ 15

Fig. 4 Different zirconia crystal structures from monoclinic (on the left), tetragonal (in the middle) and cubic (on the right) [23]. .............................................................................. 16

Fig. 5: Schematic views of transformation zone and toughness increment ($\Delta K\text{c}$) development with crack extension by Evans [32] ......................................................... 19

Fig. 6: Low Temperature Degradation of the tetragonal to the monoclinic phase of zirconia (After Chevalier [39]) ............................................................................................... 20

Fig. 7: Grain size of zirconia depending on the sintering temperatures as reported by Piconi [42]. ................................................................................................................. 22

Fig. 8: Differently sintered 3Y-TZP resulting in different grain sizes. All images are at 50.00 KX .................................................................................................................. 23

Fig. 9: Phase diagram of zirconia stabilized with yttria [48]. ........................................... 24

Fig. 10: The mechanical, chemical and thermal problems associated with PFM dental replacements [21]. ................................................................................................. 28
Fig. 11 Metal Ceramic bond (metal, sandblasted with 130 µm alumina grit at 2 Bar pressure) at 1.00 KX magnification ................................................................. 30

Fig. 12: Results of a study of Prof Kerschbaum, University of Cologne, Germany, for the DKV, 2000, including the survival rates of PFM restorations for every 5 year [60] ........................................................................................................... 34

Fig. 13: Comparing the percentage of porcelain cracking between PFM (left side) and PFZ (right side) materials according to the CRA newsletter [96] ....................... 44

Fig. 14: "Chipping" fracture initiating from the occlusal surface of the fractured crown ................................................................................................................... 48

Fig. 15: „Chipping“ fracture on a molar crown along with the “chip”. ....................... 49

Fig. 16: Bonding porcelain to zirconia showing the crack prolongation above the zirconia surface in the porcelain layer (300 X)..................................................... 51

Fig. 17: Surface of a "chipping" fracture; the zirconia is not visible (1.00 KX) ........ 51

Fig. 18 Framework design for posterior fixed dentures by Tinschert [73] ............... 53

Fig. 19: Study sponsored by DeguDent with the focus on 3 different dentists [101]. 54

Fig. 20: Dental restoration of a 4-unit zirconia-based bridge as teamwork of I. Gamborena, Spain and the Rutten brothers, Belgium ........................................ 57

Fig. 21: Schedule of the firing degree test introduced by Claus [107]. On the vertical axis is the maximum hold temperature while the horizontal axis is the time taken to achieve this temperature during the heating up phase......................... 61

Fig. 22: VITA Vacumat 6000 M, VITA Zahnfabrik, Germany ......................... 62

Fig. 23 Spectraflash 600 by Datacolor AG, Switzerland ................................... 66

Fig. 24: CIELAB specified by the International Commission on Illumination (by X-Rite) .............................................................................................................. 67
Fig. 25: LEO 438 VPi Carl Zeiss SMT and LEO 1530 Gemini, field emission microscope

Fig. 26: Operating principle of the LEO with 1530 Gimini column; $V_1$ - extractor at first anode; $V_0$ Accelerator at second anode; $V_B$ booster voltage

Fig. 27: Setup of the preparation methods

Fig. 28: The set-up of the X-ray microdiffractometer ($\mu$-XRD$^2$) used in this study

Fig. 29: Measurement points on the samples, on the left a schematic illustration vertically through the tapered sample across the interface while on the right hand side the elliptical scanned surface locations are shown

Fig. 30: A section of the axially rotational crown showing the thermocouple measurement points

Fig. 31: Setup for veneering the copings

Fig. 32: Copings used for the test

Fig. 33: Set-up of the firing of the samples

Fig. 34: Basic forms of polarisation: A) There is no phase shift without birefringence and the resulting light wave is again linearly polarized; B) If the optical retardation is exactly one quarter of the wavelength, the field vector describes a circle and one speaks of circular polarization; C) If the optical retardation is larger or smaller than one quarter of the wavelength, then the resulting light wave is elliptically polarised.

Fig. 35: Dependence on height on residual stresses by Lenz et al. [112]

Fig. 36: Different fired sample of VITA VM9 to determine the shade differences; A: Original shade; B: Shade influences without pre-drying; C: window mass correct fired; D: window mass fired without vacuum
Fig. 37: Sample No.1: pure Y-TZP refired at 950°C after the recommended sintering process. Note the very fine irregular grain structure of the sputtered gold coating at a magnification of 100.00 KX ................................................................. 108

Fig. 38: SEM observation of the HF etched polished taper section of the interface region. The grains of the Y-TZP below the surface of the veneering porcelain are visible in the region adjacent to the interface at a magnification of 10.00 KX .......... 109

Fig. 39: Sample No.2: Image of etched surface showing the Y-TZP interface following removal of the veneering porcelain after the firing of veneering powder particles without a liquid onto the Y-TZP at 950 °C at a magnification of 100.00 KX. ................................................................................................. 110

Fig. 40: Sample No. 3: surface grains of Y-TZP after etch removal porcelain applied with modelling liquid fired at 900°C at a magnification of 100.00 KX......................... 111

Fig. 41: Sample No.4: extensive evidence of faceted Y-TZP grains following application of modelling liquid mixed with porcelain fired at 950°C at a magnification of 100.00 KX................................................................................................. 112

Fig. 42: Sample No.5: Severe faceting of Y-TZP grains following application of a thick layer of porcelain with modelling fluid fired at 950°C at a magnification of 100.00 KX......................................................................................................................... 113

Fig. 43: Typical GADDS frame of the diffraction pattern observed for untreated Y-TZP with a solid angle of incidence of 10°. The major peak is associated with the 100 tetragonal/cubic peaks while the less intense peaks to the right are of the 220 series of tetragonal and cubic peaks ........................................................................ 126

Fig. 44: X-ray scans across the interface area of the Wash-Dentin (method 1) prepared sample measured using a 50 µm micro lens, Co-Kα, 30 kV/30 mA, fixed incident angle 10°, 120 sec/frame. ........................................................................................................ 128
Fig. 45: X-Ray scans across the interface area of the thin layer of porcelain coated zirconia (preparation procedure 1) measured using a 50 µm micro lens, Co-K\(\alpha\), 30 kV/30 mA, fixed incident angle 10°, 120 sec /frame. An arrow at position 2 correlates the intense single crystal reflection with the corresponding monoclinic (-111)-reflection in the XRD\(^2\)-pattern. .......................... 130

Fig. 46 (A) Area a in the veneered part of preparation method no. 1; 500 µm monopapillary optic with 300 µm pinhole Co-K\(\alpha\), 30 kV/30 mA, fixed incident angle 10°, 600 sec/frame. (B) Diffraction pattern from Spot a showing the tetragonal diffraction rings and isolated spots caused by single crystal (111)-reflections of the monoclinic structure. ................................................................. 131

Fig. 47 (A) Area b in the veneered part of preparation method no. 2; 500 µm monopapillary optic with 300 µm pinhole Co-K\(\alpha\), 30 kV/30 mA, fixed incident angle 10°, 600 sec/frame. (B) Diffraction pattern from Spot b again highlighting the presence of intense monoclinic single crystal (111)-reflections of the monoclinic structure. ................................................................. 131

Fig. 48: Interface area of the without liquid veneered zirconia (preparation procedure 3) measured using a 5 0µm micro lens, Co-K\(\alpha\), 30 kV/30 mA, fixed incident angle 10°, 120 sec /frame, only diffraction rings caused by the tetragonal ZrO\(_2\) are observable. ........................................................................................................ 132

Fig. 49: Temperature recorded during the complete process of firing porcelain to zirconia at the measurement points MP1 and MP10. ........................................ 144

Fig. 50: Cooling after opening from 850°C with uniform thickness of the coping at the measuring points 2 and 8 ........................................................................ 145
Fig. 51: A: Differences between MP8 and MP2 during the cooling versus time and B: Differences between MP8 and MP2 during the cooling versus the temperature at MP8 ............................................................... 146

Fig. 52: A: Cooling after opening from 850°C for anatomical supported framework at MP2 and MP8 and B: Differences at MP2 and MP8 during the cooling for anatomical supported framework ................................................................................................................. 147

Fig. 53: A: Cooling from 600°C at MP2 and MP8 for samples with constant wall thickness and B: Differences between MP8 and MP2 versus the temperature at MP8 (outer surface) .......................................................................................................................... 149

Fig. 54: Differences of the residual stresses between slow and fast cooling measured with polarimeter. The lower values in the horizontal table are the magnitudes of the residual stress in MPa ........................................................................................................................................ 150