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THE INFLUENCE OF CERTAIN PROCESSING FACTORS ON THE DURABILITY OF YTTRIUM STABILIZED ZIRCONIA USED AS DENTAL BIOMATERIAL

by

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ABSTRACT

Jenni Hjerppe. The influence of certain processing factors on the durability of yttrium stabilized zirconia used as dental biomaterial. Department of Biomaterials Science, Institute of Dentistry, University of Turku, Turku, Finland. Annales Universitatis Turkuensis, Ser D, Medica-Odontologica. Painosalama Oy, Turku, Finland 2010.

In dentistry, yttrium partially stabilized zirconia (ZrO_2) has become one of the most attractive ceramic materials for prosthetic applications. The aim of this series of studies was to evaluate whether certain treatments used in the manufacturing process, such as sintering time, color shading or heat treatment of zirconia affect the material properties. Another aim was to evaluate the load-bearing capacity and marginal fit of manually copy-milled custom-made versus prefabricated commercially available zirconia implant abutments.

Mechanical properties such as flexural strength and surface microhardness were determined for green-stage milled and sintered yttrium partially stabilized zirconia after different sintering time, coloring process and heat treatments. Scanning electron microscope (SEM) was used for analyzing the possible changes in surface structure of zirconia material after reduced sintering time, coloring and heat treatments. Possible phase change from the tetragonal to the monoclinic phase was evaluated by X-ray diffraction analysis (XRD). The load-bearing capacity of different implant abutments was measured and the fit between abutment and implant replica was examined with SEM.

The results of these studies showed that the shorter sintering time or the thermocycling did not affect the strength or surface microhardness of zirconia. Coloring of zirconia decreased strength compared to un-colored control zirconia, and some of the colored zirconia specimens also showed a decrease in surface microhardness. Coloring also affected the dimensions of zirconia. Significantly decreased shrinkage was found for colored zirconia specimens during sintering. Heat treatment of zirconia did not seem to affect materials' mechanical properties but when a thin coating of wash and glaze porcelain was fired on the tensile side of the disc the flexural strength decreased significantly. Furthermore, it was found that thermocycling increased the monoclinic phase on the surface of the zirconia. Color shading or heat treatment did not seem to affect phase transformation but small monoclinic peaks were detected on the surface of the heat treated specimens with a thin coating of wash and glaze porcelain on the opposite side. Custom-made zirconia abutments showed comparable load-bearing capacity to the prefabricated commercially available zirconia abutments. However, the fit of the custom-made abutments was less satisfactory than that of the commercially available abutments.

These studies suggest that zirconia is a durable material and other treatments than color shading used in the manufacturing process of zirconia bulk material does not affect the material's strength. The decrease in strength and dimensional changes after color shading needs to be taken into account when fabricating zirconia substructures for fixed dental prostheses. Manually copy-milled custom-made abutments have acceptable load-bearing capacity but the marginal accuracy has to be evaluated carefully.

Keywords: zirconia, sintering, thermocycling, color, heat treatment, abutment, flexural strength, microhardness, load-bearing capacity, phase transformation

TIIVISTELMÄ

Jenni Hjerppe. Käsittelymenetelmien vaikutus hammaslääketieteellisenä biomateriaalina käytetyn yttrium stabiloidun zirkonian eräisiin mekaanisiin ominaisuuksiin. Biomateriaalitieteen oppiaine, Hammaslääketieteen laitos, Turun yliopisto, Turku. Annales Universitatis Turkuensis, Ser D, Medica-Odontologica. Painosalama Oy, Turku, Finland 2010.

Zirkoniasta on viimeaikoina tullut yksi käytetyimmistä metallittomista biomateriaaleista hammashoidossa. Tämän väitöskirjatutkimuksen tavoitteena oli selvittää vaikuttavatko tietyt hammassiltojen ja –kruunujen valmistuksessa käytetyt zirkonian käsittelyt, kuten tiivistyspolttoaika, värjäys- tai lämpökäsittelyt materiaalin ominaisuuksiin. Lisäksi tavoitteena oli selvittää yksilöllisesti valmistettujen hammasimplanttijatkeiden kuormankantokykyä ja marginaalialueen tarkkuutta verrattuna eräisiin kaupallisesti saataviin zirkonia-implanttijatkeisiin.

Eri tavoin käsiteltyjen (lyhyempi tiivistyspolttoaika, väri- ja lämpökäsittelyt) zirkoniasta valmistettujen koekappaleiden mekaanisia ominaisuuksia, kuten taivutuslujuutta ja pintakovuutta tutkittiin ja niitä verrattiin kontrolliryhmänä käytettyihin tiivistyspoltettuihin zirkoniakoekappaleisiin. Pyyhkäisyelektronimikroskooppia (SEM) käytettiin analysoimaan mahdollisia muutoksia zirkonia-materiaalin pinnassa. Röntgendiffraktio-analyysia (XRD) käytettiin arvioimaan mahdollisia faasimuutoksia monokliinisesta tetragonaaliseen kiderakenteeseen. Implanttijatkeiden muotoisten koekappaleiden kuormankantokykyä mitattiin staattisella testillä ja jatkeiden marginaalialueiden tarkkuutta implanttimallin päällä tutkittiin SEM:lla.

Tulokset osoittivat, että lyhyempi tiivistyspolttoaika tai lämpösyklikäsittely eivät vaikuttaneet kiekon muotoisten koekappaleiden kestävyyteen tai pintakovuuteen. Zirkonia-koekappaleiden värjäys heikensi materiaalin kestävyyttä verrattuna värjäämättömiin koekappaleisiin. Lisäksi värjääminen vaikutti koekappaleiden mittasuhteisiin, sillä värjätyt koekappaleet kutistuivat tiivistyspolton aikana vähemmän kuin värjäämättömät koekappaleet. Posliinin päällepolttoa jäljittelevät lämpökäsittelyt eivät vaikuttaneet zirkonian mekaanisiin ominaisuuksin. Sen sijaan, kun koekappaleiden pinnalle poltettiin lämpökäsittelyn aikana ohut pinnoitus päällepolttoposliinia kappaleen vetojännityspuolelle, heikentyi taivutuslujuus merkittävästi. Tutkittaessa kiderakenteen faasimuutoksia zirkonia-koekappaleiden pinnalla havaittiin, että termosyklikäsittely vedessä lisäsi monokliinista faasia, mutta väri- tai lämpökäsittelyt eivät saaneet aikaan faasimuutoksia. Kuitenkin monokliinista faasia oli nähtävissä hieman lämpökäsitellyissä koekappaleissa, joissa oli päällepolttoposliinipinnoitus. Yksilöllisesti valmistetut zirkonia-implanttijatkeet olivat mekaanisilta ominaisuuksiltaan yhtä lujia kuin kaupalliset verrokit. Marginaalinen mittatarkkuus ei ollut kuitenkaan yhtä hyvä.

Zirkonia on kestävä materiaali, jonka ominaisuuksiin monet siltojen ja kruunujen valmistuksessa käytetyt käsittelyt eivät vaikuta. Heikommat mekaaniset ominaisuudet ja koekappaleiden mittasuhteiden muutokset värjäyskäsittelyiden jälkeen tulee ottaa huomioon hammaskruunuja ja –siltoja valmistettaessa. Yksilöllisesti valmistetut implanttijatkeet ovat mekaanisesti kestäviä, mutta niiden marginaalista istuvuutta täytyy arvioida huolellisesti kliinisen käytön kannalta.

Avainsanat: zirkonia, sintrausaika, värjäysmenetelmät, lämpökäsittelyt, implanttijatke, taivutuslujuus, pintakovuus, kuormankantokyky, faasimuutokset

CONTENTS

ABBREVIATIONS

ANOVA	analysis of variance
c	cubic phase
CAD/CAM	Computer Aided Design / Computer Aided Manufacture
EDX	energy-dispersive x-ray analysis
FDP	fixed dental prostheses
FPD	fixed partial dentures
m	monoclinic phase
MPa	megapascal
n	number of specimen
N	newton
PFM	porcelain-fused-to-metal
PMMA	polymethylmetacrylate
SEM	scanning electron microscopy
t	tetragonal phase
t-m	transformation from tetragonal to monoclinic phase
VHN	Vicker's hardness number
Vol%	volume percentage
Wt%	weight percentage
XRD	x-ray diffraction

LIST OF ORIGINAL PUBLICATIONS

The thesis was based on the following original publications, which will be referred to by the Roman numerals I-IV in the text.

I Hjerppe J, Fröberg K, Vallittu PK, Lassila LVJ. Effect of sintering time on biaxial strength of zirconium dioxide. *Dent Mater* 2009;25:166-71.

II Hjerppe J, Närhi T, Fröberg K, Vallittu PK, Lassila LVJ. Effect of shading the zirconia framework on biaxial strength and surface microhardness. *Acta Odontol Scand* 2008;66:262-7.

III Hjerppe J, Fröberg K, Lassila LVJ, Vallittu PK. The effect of heat treatment and feldspathic glazing on some mechanical properties of zirconia. *Silicon* 2010, in press.

IV Hjerppe J, Lassila LVJ, Rakkolainen T, Närhi TO, Vallittu PK. Load-bearing capacity of custom-made versus prefabricated commercially available zirconia abutments. *Int J Oral Maxillofac Impl* 2010, in press.

1. INTRODUCTION

Dental ceramic restorations have been of increasing interest among dentists and patients, as expectations for more natural looking materials have increased. Traditional porcelain-fused-to-metal (PFM) restorations have proven to be durable and have been widely used in dentistry since the 1960s (Kelly et al., 1996; Shillingburg, 1997). Despite their good mechanical properties, the PFM restorations do not always provide optimal cosmetic-esthetic values (Blatz, 2002; Kelly, 1997), as the metal substructure can be visible on the marginal gingival border. When using titanium implant abutments the dark shade of the metal substructure can be transmitted through the peri-implant tissues and give an unnatural dark or greyish appearance, especially with patients with thin gingival biotype or a high lip line (Tripodakis et al., 1995; Yildirim et al., 2000).

Dental ceramics can be divided in to three groups: predominantly glassy materials (feldspathic ceramic), reinforced glass ceramics, and polycrystalline ceramics (Kelly, 2004). Glass-ceramics were introduced in the 1960s. Since then dental ceramic materials have undergone huge development. The ceramics that best mimic the optical properties of enamel and dentine are glass ceramics (feldspathic porcelain and reinforced glass ceramics). Feldspathic porcelain is used for veneering porcelain on metal or ceramic substructures. Leucite- or lithium disilicate reinforced glass ceramics are used for ceramic fillings, laminates and crowns. These ceramics do not have high mechanical strength but they reach high bond strength with resin cements and sufficient strength for restoring a tooth to bear occlusal forces (Blatz, 2002; Hooshmand et al., 2008). In the late 1980s high strength glass containing 70 vol% aluminum oxide was introduced (Hornberger and Marquis, 1995). This led to the use of high strength polycrystalline ceramics, such as alumina (Al_2O_3) and zirconia (ZrO_2). These polycrystalline ceramics have no glassy matrix and can be used as substructure materials for dental crowns. As such, the polycrystalline ceramics are relatively opaque and need more esthetic feldspathic veneering porcelain on their surface.

Due to its good mechanical properties zirconia has rapidly achieved a leading position among the polycrystalline dental restorative materials. Many studies on the use of zirconia have been conducted, but some features still remain unclear.

There is a lack of information of how sintering time, color shading or heat treatments affect the material properties. Custom-made implant abutments are widely used in the clinical field but data about the mechanical properties of these abutments is sparse. This series of studies attempts to discover whether various processing conditions affect the properties and fit of zirconia structures.

2. REVIEW OF THE LITERATURE

2.1 HISTORY OF ZIRCONIA

Zirconia (ZrO_2) is a metal oxide of zirconium. It was identified in 1789 by German chemist Martin Klaproth. After stabilization, high levels of toughness and strength as well as good wear resistance can be achieved. Because of these properties, zirconia has been used in many applications such as knife blades, thermal shock resistant liners in foundries and valves for combustion engines (Piconi and Maccauro, 1999).

In medical applications zirconia has been used in the femoral heads of hip prosthesis since the 1980s (Christel et al., 1988). Currently more than 600 000 zirconia femoral heads have been implanted world wide (Chevalier et al., 2007). In dentistry, zirconia has been widely tested, mainly as a prosthetic material. One of the first attempts was made in the 1990s by adding 50 wt% of ZrO_2 to glass porcelain, which resulted in 20 to 80 % higher bending strength and fracture toughness than with porcelain alone (Kon et al., 1990). Subsequently the development of zirconia as a dental material has been rapid and today it is used in root canal posts, brackets, substructures for FDPs, implant abutments and oral implants.

2.2 MATERIAL PROPERTIES

2.2.1 Physical properties

Certain zirconia-based materials have shown good mechanical properties. Zirconia has been shown to be stronger than other dental ceramic materials (Chen et al., 2008; Teixeira et al., 2007). Mechanical properties of some commonly used materials for FDPs are presented in Table 1. Flexural strength of zirconia ranges from 800 to 1500 MPa (Pittayachawan et al., 2007; Tinschert et al., 2000; Yilmaz et al., 2007). In addition to good flexural strength zirconia has shown high fracture toughness values, ranging from 6.3 to 11.5 MPa $m^{1/2}$ (Aboushelib et al., 2008b; Tinschert et al., 2007; Yilmaz et al., 2007).

Zirconia is chemically stable and does not dissolve in saliva (Chai et al., 2007; Piconi and Maccauro, 1999). The thermal conductivity of zirconia is low, which prevents the sensitivity of the abutment tooth during temperature changes in mouth. Zirconia contains small amounts of natural radionuclides as the element zirconium does not occur in nature in a pure state. However, the radiation dose of zirconia material is well below the dose from natural background radiation (Piconi and Maccauro, 1999).

Table 1. Mechanical properties of some materials used in the fabrication of fixed dental prostheses

Material	Flexural Strength (MPa)	Elastic modulus (GPa)	Hardness (VHN)	Reference
Zirconia (Y-TZP)	800-1500	210	1200	(Callister, 2007; Piconi and Maccauro, 1999)
Alumina (Al_2O_3)	500	380	2200	(Piconi and Maccauro, 1999)
Leucite reinforced glass ceramic (Empress 2)	283	96	550	(Aboushelib et al., 2007a; Hooshmand et al., 2008)
Feldspathic porcelain (Vita VMK 68)	83	57	703	(Seghi et al., 1992; Seghi et al., 1995; Tinschert et al., 2000)
Gold alloy Au-Pd	611 (tensile strength)	103	220	(O´Brien, 2008)
Gold alloy Type IV	759 (tensile strength)	99	250	(O´Brien, 2008)

2.2.2 Phase transformations – transformation toughening

Pure zirconia is a polymorphic material that occurs in three forms: monoclinic, tetragonal and cubic. The monoclinic phase (*m*) is stable below 1170 ºC. Zirconia is in tetragonal (*t*) form between 1170 and 2370 ºC and in cubic (*c*) form over 2370 ºC. The transformation of pure zirconia from the tetragonal to the monoclinic phase takes place during cooling after material sintering. Cooling is associated with a volume expansion of 3–5 %. Monoclinic zirconia is a very fragile material and may have some flaws and microcracks. By adding stabilizing oxides, such as Y_2O_3, MgO or CeO_2, zirconia can be stabilized in the more durable tetragonal phase also at room temperature (Garvie et al., 1975; Piconi and Maccauro, 1999). Y_2O_3 is the most commonly used stabilizer of dental zirconia material. The name zirconia is commonly used for dental ceramic material, that is partially stabilized with 3 Mol% of yttrium oxide. Other names used in the literature are Y-TZP (yttrium stabilized tetragonal zirconia polycrystal) and partially yttrium stabilized zirconium dioxide. In this series of studies the term zirconia is used for partially yttrium stabilized zirconium dioxide.

The high strength and durability of zirconia is based on a phenomenon called transformation toughening. When a crack occurs in the material, the local stresses can lead to *t-m* transformation at the crack tip and the local compressive stresses caused by volume expansion (3-5%) will prevent crack propagation (Figure 1) (Garvie et al., 1975; Piconi and Maccauro, 1999). This stress-induced phase transformation mechanism makes the material more resistant to crack propagation. However, in the presence of high enough stress the crack will propagate through the whole bulk of the material.

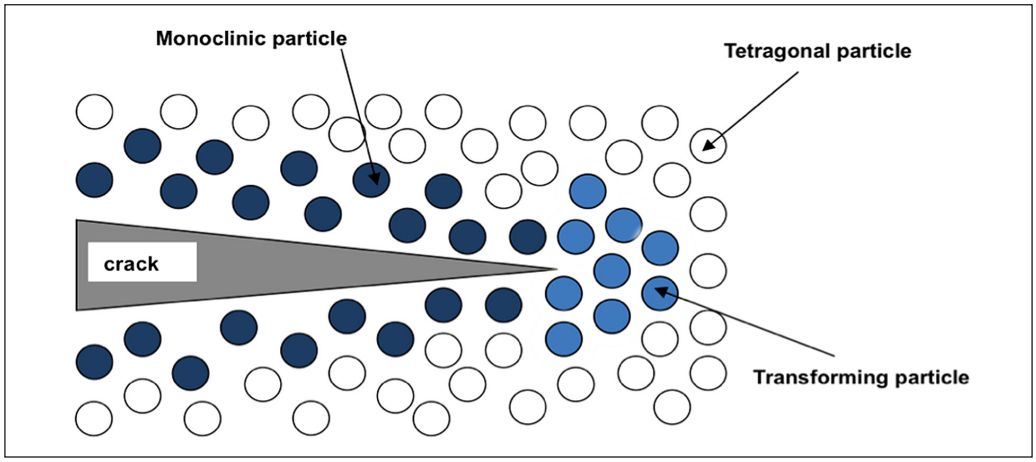

Figure 1. Illustration of the stress-induced transformation toughening process. The crack is propagating in the material and grains surrounding the crack are transforming from tetragonal to monoclinic. The figure is modified from Piconi and Maccauro (1999) and Butler (1985).

The tetragonal phase is meta-stable and the surface *t-m* phase transformation can be initiated by surface grinding, sandblasting, stress or temperature changes (Hannink and Swain, 1989; Kosmac et al., 1999; Swab, 1991). The transformation induced by grinding generates thin surface layer with compressive stresses. Thickness of the phase change on the surface depends on the severity of surface treatment.

2.2.3 Low temperature aging

Low temperature degradation or aging of zirconia is a negative phenomena related to the transformation ability of the tetragonal phase. Slow surface transformation to the stable monoclinic phase occurs through environmental stresses, usually in the presence of water molecules, hot water vapor or body fluids such as saliva (Kobayashi et al., 1981; Lawson, 1995; Schmauder and Schubert, 1986; Swab, 1991). Aging proceeds more rapidly in a warm environment and the critical temperature range is 200 - 300 ºC (Yoshimura, 1988). However, aging can occur even at room temperature. The water enhances aging process (Sato and Shimada, 1985; Yoshimura et al., 1987). It has been shown that water molecules can penetrate the zirconia lattice during exposure in a humid atmosphere. In the presence of water molecules the outer tetragonal grains of zirconia transform into monoclinic grains (Chevalier et al., 1999). This leads to a cascade of events as the transformation of one grain results in local volume expansion and causes stress to neighboring grains. Due to the stress the neighboring grains also transform into the monoclinic phase. The sudden volume expansion leads to swelling of the surface and the grains. This enables penetration of water molecules through the grain boundaries into the zirconia, causing the transformation of the grains deeper in the bulk of the material (Figure 2) (Chevalier and Gremillard, 2008; Deville and Chevalier, 2003). The *t-m* phase transformation leads to micro- and macro-cracking of the zirconia (Yoshimura et al.,

1987). The sintering temperature seems to play a role in the aging process. Chevalier and co-workers (2004) demonstrated that the amount of the cubic phase in zirconia increases when during a long sintering time (5h) the sintering temperature reaches 1500 ºC. The presence of cubic grains in zirconia material seems to diminish the resistance to low temperature degradation. The cubic grains are likely to be enriched with yttrium stabilizer ions while the surrounding tetragonal grains are less stable.

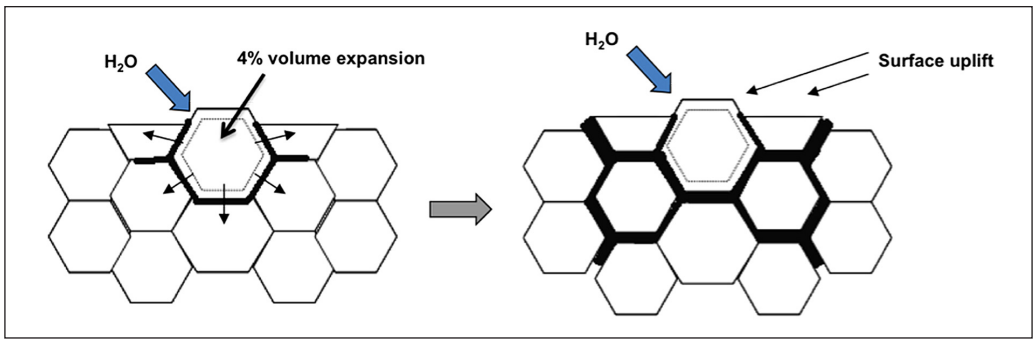

Figure 2. Illustration of low temperature degradation in zirconia. Water is penetrating in grain boundaries causing *t-m* transformation in grains, volume expansion and surface uplift. The figure is modified from Chevalier (2006).

The microstructure of zirconia material affects aging related phenomena. The higher the density zirconia has, the less aging occurs. The low density offers water molecules easy access to the bulk of the material and aging occurs internal surfaces of the material as well resulting in the decrease of mechanical properties (Chevalier and Gremillard, 2008). Grain size also has a role in aging. Tsukuma and co-workers (1984) have reported that in zirconia with grains bigger than 1μm a large amount of *t-m* transformation is seen together with the decrease in strength. In another study, the results showed a decrease of aging resistance for grain sizes above 0.6 μm (Munoz-Saldana et al., 2003). Surface stress of zirconia affects the aging process. The surface tensile stresses caused by machining can initiate the *t-m* transformation, because the stresses decrease the energy needed for phase transformation (Deville et al., 2006; Li et al., 2001). Compressive stresses do not seem to have a major effect on phase transformation as they stabilize the zirconia grains (Lawson, 1995; Li et al., 2001; Schmauder and Schubert, 1986). Aging during preparation of zirconia material can be prevented by careful machining of the restorations and avoiding the formation of scratches on the surfaces.

Aging seems to be a concern when using zirconia in moist environments such as in the mouth. However, some *in vitro and in vivo* studies have shown that aging does not affect the clinically related mechanical properties of zirconia (Cales et al., 1994) even if some *t-m* phase transformation has occurred (Shimizu et al., 1993). No problems with aging have been reported so far in the clinical use of zirconia in dentistry. However, in 2001 during a short period of time failures of several hundred hip prostheses were reported. Apparently,

the steam sterilization in the autoclave had caused the degradation in certain batches of Prozyr® zirconia ball heads which led to dramatic failures (Chevalier, 2006).

2.3 ZIRCONIA IN DENTISTRY

2.3.1 Root canal posts

Zirconia root canal posts were introduced at the beginning of the 1990s (Lüthy et al., 1995; Lüthy et al., 1993; Meyenberg et al., 1995; Simon and Paffrath, 1995). The white color of zirconia provides a more esthetic outcome for the posts and cores of ceramic crowns compared to dark metal posts. These metal-free constructions have excellent biocompatibility and do not exhibit galvanic corrosion that might be detrimental to the root of the teeth (Koutayas and Kern, 1999). Asmussen and co-workers (1999) showed that zirconia posts have high mechanical strength, but their plastic properties are inferior compared to less stiff prefabricated metal and fiber posts. In the study of Spazzin and co-workers (2009) zirconia root canal posts showed higher stress concentrations compared to glass fiber posts. Nissan and co-workers (2007) showed that there was no significant difference of the failure loads between ceramic and metal post systems. In short term clinical studies with zirconia posts no failures have been reported (Kakehashi et al., 1998; Nothdurft and Pospiech, 2006). In a four-year retrospective study of zirconia posts no failures were observed in teeth restored with direct resin composite crowns either (Paul and Werder, 2004). However, three failures out of 58 posts placed were seen in a group restored with indirect glass-ceramic crowns. The failures were all because of loss of retention. A recent 10-year retrospective clinical study showed a survival probability of 88.4% for zirconia posts with ceramic cores and 76.5% for posts with composite build-ups (Bateli et al., 2010). The main reason for failure was extraction of the tooth.

2.3.2 Orthodontic brackets

At the beginning of the 1990s tooth colored zirconia orthodontic brackets were introduced for achieving a better cosmetic outcome. Kittipibul and Godfrey (1995) reported that zirconia ceramic brackets have a clinically acceptable de-bonding shearing force. Some *in vitro* studies have been carried out on the frictional forces of zirconia brackets with arch wires (Keith et al., 1994; Tanne et al., 1994). In the study of Keith and co-workers (1994) no significant advantage of zirconia over alumina brackets was found in terms of their frictional properties. No clinical studies about zirconia brackets have been reported in the literature. Monocrystalline and polycrystalline aluminium oxide is a more commonly used material for ceramic brackets than zirconia (Russell, 2005). Zirconia brackets are opaque and for that reason may also be more visible compared to those made of alumina.

2.3.3 Oral implants

Ceramic materials, especially zirconia, have been suggested as an alternative to titanium as an implant material. The esthetic outcome and biocompatibility of ceramic implant materials and potential patient allergies to titanium have been increasing interest in the development of zirconia implants (Andreiotelli et al., 2009). Cellular behavior towards zirconia is favorable and several *in vitro* studies show that zirconia is not a cytotoxic material (Lohmann et al., 2002; Torricelli et al., 2001). Human gingival fibroblasts have good attachment and proliferation on zirconia material (Mustafa et al., 2008). This is important for early bone and soft tissue regeneration when treating patients with implants. Zirconia has shown low values for streptococci adhesion in *in vitro* studies (Hahnel et al., 2009). Adhesion of *Candida albicans* has been found to be similar on machined titanium and zirconia surfaces (Bürgers et al., 2009).

At the beginning of the 1990s Akagawa and co-workers (1993) reported using zirconia as oral implant material in animal experiments. Later *in vivo* and *in vitro animal* experiments on zirconia implants have shown acceptable osseointegration, cell metabolism and soft tissue response (Blaschke and Volz, 2006; Kohal et al., 2004; Oliva et al., 2007). The biological properties of zirconia implants seem to be comparable to titanium implants (Kohal et al., 2004; Wenz et al., 2008). A recent animal study showed that collagen fiber orientation is similar around titanium and zirconia implant necks (Tete et al., 2009). *In vitro* studies on zirconia implants have shown desirable mechanical behavior when the mean fracture loads after fatigue have been within the requirements for anterior teeth (Kohal et al., 2006; Silva et al., 2009). The results are promising but more long-term studies are needed before the clinical use of zirconia implants can be recommended (Andreiotelli et al., 2009; Kohal et al., 2008; Silva et al., 2009; Wenz et al., 2008).

2.3.4 Implant abutments

The use of implants for replacing missing anterior teeth is esthetically challenging. The tooth-like color of ceramic abutments is more natural for implant restorations than metal abutments. The dark shade of the metal abutment can be transmitted through the peri-implant tissues and give an unnatural dark or greyish appearance (Tripodakis et al., 1995; Yildirim et al., 2000). *In vivo* studies of microbial colonization on titanium and zirconia discs have shown that zirconia gathered less plaque on the surface compared to titanium (Rimondini et al., 2002; Scarano et al., 2004).

For ceramic abutments, zirconia has been a material of choice due to its good mechanical properties and better reliability in *in vitro* and *in vivo* studies compared to abutments made of alumina (Al_2O_3) (Glauser et al., 2004; Yildirim et al., 2003). The soft tissue reaction has also been found to be favorable as in an animal study the zirconia abutments demonstrated proper conditions for soft tissue healing (Welander et al., 2008). Two types of zirconia abutments are commonly used, all-zirconia and zirconia abutments with a metallic (titanium) insert at the implant-abutment interface (Nakamura et al.,

2010). In the study of Att and co-workers (2006) it was shown that the fracture resistance of titanium abutments with alumina crowns was higher than zirconia abutments with alumina crowns, 1454 N and 444 N, respectively, after cyclic fatigue in water. Mitsias and co-workers (2010) showed in their study that titanium abutments had higher strength and reliability compared to zirconia abutments. In other studies, the fracture loads of zirconia abutments in static loading tests have varied from 429 N to 576 N (Adatia et al., 2009; Sundh and Sjogren, 2008; Yildirim et al., 2003). These studies have shown that zirconia abutments can withstand clinical biting forces as in previous studies the maximal occlusal forces in the incisor area have been reported to range from 108 to 174 N (Helkimo et al., 1977), 93 to 368 N (Haraldson et al., 1979) and 161 to 299 N (Lujan-Climent et al., 2008). A recent review article concluded that because of its mechanical and biological properties zirconia is a suitable abutment material and could be used in the anterior region and premolar area of the dentition (Nakamura et al., 2010).

Zirconia abutments can be milled in a dental laboratory for an abnormal inter-dental space, occlusal conditions or when there is a need to modify soft tissue structure. In a study of custom-made titanium-zirconia bi-component abutments, marginal fit values varied horizontally from 8.96 to 11.65 μm and vertically from 3.75 to 7.0 μm (Canullo, 2007). The marginal gap of zirconia abutments was measured from longitudinally cut implant-abutment configurations by Baixe and co-workers (2010). The mean marginal gap was less than 2 μm in the study groups and the gap decreased quickly from the outer region to the inner region of the configuration.

2.3.5 Substructures for fixed dental prostheses

Substructures for zirconia FDPs can be fabricated with a manual copy-milling machine, computer aided design/ computer aided manufacturing (CAD/CAM) systems (Luthardt et al., 1997; Strub et al., 2006) or with the recently introduced direct inkjet printing (Ebert et al., 2009). In their study, Persson and co-workers (2008) showed that the computer aided method might be more accurate and precise than the traditional stone replica method in terms of the fit of zirconia restorations. When manufacturing substructures for FDPs the zirconia bulk material can be in the pre-sintered soft green-stage (Filser et al., 2001) or fully sintered form (Tinschert et al., 2001b). Milling the structures in fully sintered form offers higher precision but may introduce microcracks in the material (Luthardt et al., 2004). On the other hand, the manufacturing process of the pre-sintered green-stage material is easy but does not necessarily lead to high precision because shrinkage during sintering process imposes machine frameworks that are approximately 20% larger and the exact final dimensions after sintering are not known (Chevalier and Gremillard, 2008). After milling and sintering, the zirconia frameworks are veneered with veneering porcelain when the desired color and translucency cannot be achieved with zirconia alone.

Some surface treatments might be needed in the manufacturing process of zirconia restorations by laboratory technicians or by dentists in intraoral conditions. It has been

shown that coarse diamond burs are more efficient for cutting zirconia as machining with fine burs causes more ductile damage (Yin et al., 2003). Curtis and co-workers (2006) showed that fine grinding of zirconia does not affect the material strength but coarse grinding decreases it. However, grinding zirconia ceramics induces surface flaws and microcracks, which can decrease the fracture resistance of the material (Luthardt et al., 2004). Grinding, especially with coarse diamonds, causes some *t-m* transformation on the surface of zirconia and it seems to decrease the reliability and strength of zirconia material because of the increased surface roughness (Curtis et al., 2006; Kosmac et al., 2000). Grain size of the grinding diamond also has an effect on grinding damage, since it has been shown that the fine grain size leads to smoother zirconia surfaces after machining (Kou et al., 2006).

Some studies have shown that air-particle abrasion enhances the bond strength between zirconia and the luting cement (Derand and Derand, 2000; Kern and Wegner, 1998). The effect of air-particle abrasion on zirconia depends on the size of blasting particles (from 30 to 250 μm), particle shape, blasting distance and blasting pressure (from 0.1 to 0.5 MPa). It has been shown that air-particle abrasion increases the monoclinic phase on the surface of zirconia material and also increases the material strength (Guazzato et al., 2005; Karakoca and Yilmaz, 2009; Kosmac et al., 1999; 2000; Papanagiotou et al., 2006). Despite the increased strength, the reliability of the air-particle abraded zirconia decreased. In the studies of Ban and co-workers (2007; 2008) air-particle abrasion (particle size 70 μm Al_2O_3, pressure 0.4 MPa) increased the monoclinic phase but did not affect to the biaxial flexural strength of Y-TZP. Curtis and co-workers (2006) compared bi-axial flexural strength of zirconia material air-particle abraded with different Al_2O_3 particle sizes, 25, 50 and 110 μm with a pressure of 4.8 bar (0.48 MPa). They found that increasing the particle size resulted in decreased surface roughness of zirconia material. No statistical difference was seen in bi-axial flexural strength between the air-particle abraded groups and the non-abraded control group. Zhang and co-workers (2006; 2004) reported that in a fatigue strength test the degradation was seen when the air-particle abraded (particle size 50 μm Al_2O_3, pressure 0.276 MPa) surface of zirconia was on the cemented (tension) side of the specimen. In long term fatigue the small flaws and microcracks caused by air-particle abrasion can become crack origins. Compressive stresses caused by air-particle abrasion and phase transformation are not high enough to overcome the strength loss caused by microcracks. However, recent studies have shown that the low-pressure air abrasion (particle size 50 μm Al_2O_3, pressure 0.05 MPa) reduced the surface roughness without affecting the long-term bond strength of zirconia substructure (Kern et al., 2009; Yang et al., 2010). With low-pressure abrasion, possible surface damage effects can be minimized.

Phase transformation caused by surface treatments is assumed to decrease the materials long-term reliability (Denry and Kelly, 2008). When a crack propagates from the material surface the crack propagation cannot be prevented as the transformation toughening has already occurred during the surface treatment and the microcracks can propagate through the transformed monoclinic surface. Results from different studies seem to be conflicting

and yet no conclusions can be drawn whether the surface processing causes detrimental effects for long-term use.

Fixed dental prostheses have shown high load-bearing capacity in mechanical *in vitro* tests. In recent studies the fracture strength of incisal zirconia crowns has varied from 551 N to 1100 N depending on the crown thickness and preparation type (Luthardt et al., 1999; Reich et al., 2008). Fracture strength of molar zirconia crowns cemented to carbon steel or brass master die has varied from 2135 N to 4114 N (Sundh and Sjogren, 2004; Tsalouchou et al., 2008) depending on the framework thickness and type of veneering ceramics. The failure strength of zirconia fixed partial dentures has varied between 1192 N and 2131 N (Att et al., 2007a; Att et al., 2007b; Filser et al., 2001; Kokubo et al., 2007; Tinschert et al., 2001a). Finite element analysis of the stress distribution on the loaded zirconia fixed partial dentures has shown that the connector region is the potential failure site for these restorations (Dittmer et al., 2009b; Fischer et al., 2003; Ozen et al., 2007). A minimum diameter of 4.0 mm is recommended for the connector area of posterior zirconia fixed partial dentures (Larsson et al., 2007).

Maximal biting forces in the molar area measured by surface electromyography varied from 446 N to 1220 N in healthy young adults (Ferrario et al., 2004). Patients with bruxism are likely to have higher maximal biting forces. However, zirconia restorations are able to withstand normal biting forces in the molar area, especially when the maximal biting forces are not present all the time. The lifetime prediction for zirconia is good and it is reliable for long-term use (Studart et al., 2007; Tinschert et al., 2007).

In addition to the mechanical properties and appearance, one of the key factors in a long-term clinical success of zirconia restorations is marginal adaptation. Insufficient fit and open margins of the restoration can offer a niche for the attachment of oral bacteria, which may result in secondary caries and gingival irritation (Gardner, 1982; Knoernschild and Campbell, 2000). In their study, Beuer and co-workers (2008b) found that the preparation angles of the crowns did not influence the marginal fit of zirconia crowns. The preparation design was shown to affect the fracture resistance of zirconia substructures. In a previous study, the load required to break the zirconia crown or fixed partial denture was statistically higher with shoulder preparation than with deep chamfer preparation (Beuer et al., 2008a). Marginal gaps below 120 μm are considered clinically acceptable (Belser et al., 1985; Karlsson, 1993; Sulaiman et al., 1997). In recent *in vitro* studies the marginal fit of zirconia frameworks has been below this limit (Att et al., 2009; Beuer et al., 2009; Coli and Karlsson, 2004; Gonzalo et al., 2009; Tinschert et al., 2001b).

Inlay-retained fixed partial dentures made of zirconia were introduced in the 2000s. Some *in vitro* studies have shown that the fracture resistance is not high enough and zirconia inlay-retained fixed partial dentures cannot yet be recommended for clinical use (Gabbert et al., 2008; Ohlmann et al., 2005). Similar results have been shown in a preliminary clinical study (Ohlmann et al., 2008), where several complications were seen, such as the fracture of the substructure, de-laminations of the veneering porcelain

and de-cementations of the prostheses. However, according to the study of Rosentritt and co-workers (2008) zirconia resin bonded fixed partial dentures might be suitable as minimally invasive restoration to the anterior area of the mouth. Recent studies have shown positive development and with a big enough connector size the durability of inlay-retained fixed partial dentures might be strong enough for posterior biting forces (Mehl et al., 2010; Wolfart et al., 2007).

2.4 PROCESSING OF ZIRCONIA RESTORATIONS

2.4.1 Sintering

Green-stage monoclinic zirconia is sintered in a special sintering furnace to achieve the final form of the restorations; hard and durable partially yttrium stabilized tetragonal zirconia. Typical sintering temperatures vary between 1400 ºC and 1600 ºC depending on the manufacturer of the material. The sintering temperature and sintering time affects the grain size of the material. The higher the sintering temperature and the longer the time, the bigger the final grain size is (Chevalier et al., 2004; Swain, 1986). The sintering process can also be carried out with hot isostatic pressuring. After the HIP-procedure, zirconia material has been shown to be less prone to *t-m* phase transformation (Grant et al., 2001).

Managing the sintering temperature and time is important since the mechanical properties of zirconia material depend on the grain size (Ruiz and Readey, 1996). When the grain size is larger than 1 μm zirconia material becomes less stable and more spontaneous *t-m* transformations occur (Tsukuma et al., 1984). Smaller grains, in control, have a lower transformation rate but when the grain size is less than 0.2 μm the transformation is not possible and this results in lower fracture toughness (Cottom and Mayo, 1996).

2.4.2 Coloring

Pure zirconia is white in color and more opaque than other dental ceramics (Chen et al., 2008; Heffernan et al., 2002). From the point of view of appearance of the restoration it has been shown that the color of the underlying substructure affects the color of the veneered crown (Crispin et al., 1991). Because of the white color and opacity, the substructure of zirconia FDP may need to be colored before sintering. With coloring a more natural looking result can be achieved and the layer thickness of the veneering ceramic can be reduced (Devigus and Lombardi, 2004a; b).

To enhance the appearance of FDPs, some colorant oxides of Fe, Cu, Co, Mn and opacifying oxides of Sn, Zn, Al, Zr and Ti can be added to ceramic material (Milleding et al., 2003). In the study of Cales (1998) it was shown that iron oxide (Fe_2O_3), cerium oxide (CeO_2) and bismuth oxide (Bi_2O_3) gave brown to yellow colors and the use of combinations with different ratios were allowed to reproduce most of the color shades in the Vita classic scale (Vita, Zahnfabrik, Säckingen, Germany). Adding these coloring

oxides did not significantly change the physio-chemical properties of zirconia ceramics. There have been some studies on color shade effects on properties of zirconia. When comparing white and yellowish shades of zirconia, the yellowish specimens had higher flexural strength. The higher strength might have been related to components that were added to obtain different shades of zirconia such as CeO_2, Fe_2O_3 and Bi_2O_3 (Ardlin, 2002). The study of Pittayachawan and co-workers (2007) showed no difference in flexural strength between the shaded and unshaded LAVA (3M ESPE) specimens. Aboushelib and co-workers (2008a) showed in their study that the core-veneer bond strength was significantly weaker in colored zirconia compared to white zirconia substructures. The authors suggested that colored substructures need different surface treatments before veneering, as the color pigments tend to crystallize on the surface of the substructure, which can be the reason for weakening the bond with the veneering ceramic.

There are different ways of coloring zirconia frameworks. The zirconia material in the green-stage form can be dipped in or painted with a color liquid before sintering, or some coloring additives can be mixed to the zirconia powder before pressing the material to a block and before sintering (Cales, 1998).

2.4.3 Veneering

Zirconia frameworks are veneered with veneering porcelain for natural tooth appearance, as zirconia as such does not meet the high esthetic values needed for FDPs. Zirconia heat treatment is part of the veneering porcelain firing procedure. The firing temperature for veneering porcelain varies from 700 to 900 °C. Recent studies have reported that heat treatment by firing the veneering porcelain lowers the strength of zirconia when fabricated in a sintered form (Øilo et al., 2008; Sundh et al., 2005). Milling and grinding of sintered zirconia caused phase change from tetragonal to monoclinic on the surface of the zirconia. The results indicated that heat treatment influenced the surface of the ceramic material by reducing the amount of monoclinic zirconia grains, which was suggested to result in lower strength. Similar results were found in studies on surface treatments of zirconia. After air-particle abrasion, grinding or polishing the heat treatment of the zirconia specimen decreased the flexural strength of the material (Guazzato et al., 2005; Sato et al., 2008). It was suggested that compressive stresses caused by surface treatment such as sandblasting are released during heat treatment and the mean flexural strength is decreased by sandblasting-induced defects in the material.

In a study about marginal fit of fixed partial dentures Vigolo and Fonzi (2008) found that the firing cycle of veneering porcelain or the veneer glazing cycle does not affect the marginal fit of the specimens. The measurements were performed with a light microscope using a magnification of 50x prior to and after the simulation veneering process. However, Dittmer and co-workers (2009a) reported that stresses and distortions, occurring due to the veneering process, may influence the marginal and internal fit of fixed partial dentures. The results were based on finite element analysis performed prior to and after the simulation veneering process.

Zirconia substructure and veneering porcelain form a bi-layered structure, where the material that is placed on the bottom surface (tension side) has an impact on the strength (Guazzato et al., 2004a; White et al., 2005). The material on the bottom surface also dictates the fracture mode of the specimen (Guazzato et al., 2004b). White *et al.* found that by increasing the thickness of zirconia on bi-layered porcelain/zirconia material combination, the flexural strength of the tested specimens increases (White et al., 2005).

The failure mode of the porcelain/zirconia combination seems to depend on the form of tested specimens. In porcelain/zirconia bi-layer crack propagation very often extended along the porcelain/zirconia interface (Guazzato et al., 2004b). Cracks are unlikely to propagate from low-toughness porcelain to a high-toughness zirconia ceramic. Instead, an arrest and deflection of the crack on the porcelain/zirconia interface can be observed (Kim et al., 2006). When testing the porcelain/zirconia bi-layer with 30º off-axis sliding contact cone cracks were seen in the veneering porcelain layer and the cracks extended to the porcelain/zirconia interface but no damage was seen in the zirconia layer (Santana et al., 2009). When loading the veneered zirconia crowns in mouth-motion sliding-contact fatigue a cohesive fracture of veneering porcelain was noticed and it resulted in chipping of the veneer whereas a single load of zirconia crowns showed fractures through zirconia substructure (Coelho et al., 2009a; Coelho et al., 2009b).

In the study of Guess and co-workers (2008) shear bond strength between different zirconia and core ceramics varied between 9.4 and 12.5 MPa and was significantly weaker compared to the shear bond strength of porcelain-fused-to-metal control group (27.6 MPa). All of the metal ceramic failures were cohesive in veneering ceramic and the all-ceramic groups showed combined failure modes: cohesive in veneering ceramic and adhesive in the interface of core and the veneer. On the other hand, in another study the bond strength of veneering porcelain to zirconia substructure was similar to that of the porcelain-fused-to-metal control (Al-Dohan et al., 2004). Fisher and co-workers (2008) studied the effect of surface treatments on shear bond of porcelain/zirconia specimens. The shear bond strength varied between 23.5 and 33.0 MPa and sandblasting did not increase the bond strength. All of the failures were cohesive in the porcelain material. Aboushelib and co-workers (2006) showed that microtensile bond strength between zirconia and veneering ceramic varied from 17.2 MPa to 48.8 MPa depending on the manufacturing technique and veneering material used.

Some questions have arise, whether veneered zirconia restorations are more prone to chipping than the veneer of porcelain-fused-to-metal restorations. Quinn and co-workers (2010) compared the edge chipping resistance of porcelain-fused-to-metal and veneered zirconia specimens. They found that despite the difference of the substructure hardness the chipping behaviour was similar between the metal and zirconia combinations and the chipping extended to the porcelain/substructure border but not to the substructure with both material combinations.

A relatively common clinical failure of zirconia fixed partial dentures has been reported to be chipping of the veneering porcelain with minor loss of material (Sailer et al., 2007; Tinschert et al., 2008). The reason for the chipping is not yet fully understood. There are many possible explanations for porcelain chipping. It might be a material specific problem, but also substructure design and thickness of the veneering porcelain may play a role. Fast cooling after porcelain firing or mismatch in thermal expansion coefficients of porcelain and zirconia may also influence the chipping (Denry and Kelly, 2008). In the clinical study of Sailer and co-workers (2009a) the anatomical framework design was taken into account, but still some veneer chipping occurred. Recent studies have shown that thermal expansion and the glass transition temperature of the veneering porcelain can have an impact on the bond strength of porcelain/zirconia composites (Aboushelib et al., 2005; Fischer et al., 2009). The cooling rate has an impact on the development of residual stresses in porcelain/zirconia specimen. In the study of Taskonak and co-workers (Taskonak et al., 2008) slowly cooled specimens had significantly lower failure stresses than fast cooled specimens. Compressive residual stresses increase the flexural strength of bi-layer zirconia materials. However, the residual stresses caused by uneven cooling of the bi-layered specimens can be a reason for chipping of the ceramic layer when contact damage is present. The uneven heat distribution may also result in insufficient firing of the veneering ceramic and possibly cause pores in the veneering porcelain and to the porcelain/zirconia interface leading to chippings (Swain, 2009). There is evidence that the roughness of the veneering ceramic by occlusal function or grinding is associated to chipping of the veneer (Sailer et al., 2009a). This has to be taken into account when adjusting zirconia FDPs in a clinical situation. Careful polishing of the veneering ceramic surface is needed to remove the roughness.

2.4.4 Bonding of zirconia substructures to luting cement

There have been several studies on the bonding of zirconia substructures to luting cements. The bonding procedure differs from silica-based glass ceramic restorations. The etching of zirconia surface with hydrofluoric (HF) acid does not improve the bond strength because the high crystalline structure is resistant to acid etching (Chaiyabutr et al., 2008; Derand and Derand, 2000; Özcan and Vallittu, 2003). Additionally, silane coupling agents, such as 3-methacryloxypropyltrimethoxysilane (MPS) used for bonding silica-based glass ceramics does not provide adequate bond to zirconia ceramics (Derand et al., 2005; Kern, 2009).

The bonding of zirconia substructures should be based on both micromechanical and chemical bonding since the micromechanical retention supports chemical bonding and if bonding is based only on chemical compounds some debonding might happen in moist environments such as in the mouth (Kern, 2009). Airborne-particle abrasion with Al_2O_3 abrasive particles, tribochemical silica coating or firing glass pearls as a monolayer to the inner surface of zirconia substructure can be used as surface pre-treatments prior to bonding to achieve better bond strength between the zirconia material and resin cement

(Aboushelib et al., 2007b; Atsu et al., 2006). Airborne-particle abrasion has been shown to be a good method for cleaning and roughening the zirconia surface after clinical try-in procedures, since the contamination with saliva is known to decrease the bond strength (Yang et al., 2008; Yang et al., 2007). Tribochemical silica coating is a system where a silica layer is formed on the surface of zirconia ceramic by airborne-particle abrasion with silica coated alumina particles. MPS silane can be used on the surface of silica coated zirconia substructure and afficient chemical bonding can be achieved. However, according to a recent review article tribochemical silica coating seems to produce durable bonding with some zirconia ceramics, whereas silica coating particles do not seem to attach well enough to the surface of denser zirconia ceramics (Kern, 2009). Recently, a modified zirconia surface was introduced for better bond strength. In this procedure, the pre-sintered copings are ground and slurry containing zirconia ceramic powder and pore former is applied to the inner surface of the coping. When the coping is sintered the inner surface then has many micromechanical pores for the cement to attach to (Phark et al., 2009a). Another method for improved micromechanical bond strength is selective infiltration etching (Aboushelib et al., 2007b). In this method, a thin layer of an infiltration glass is applied over a sintered and heat-treated zirconia surface. The molten glass infiltrates between the grain boundaries and results in a porous surface optimal for bonding.

To improve the chemical bond between zirconia and cement adhesive phosphate monomer 10 –methacryloyloxydecyl dihydrogen-phosphate (MDP) can be added to the resin cement or primers (Blatz et al., 2004; Kern and Wegner, 1998). The use of phosphate monomer containing cement has been shown to increase bond strength after air-particle abrasion treatment. Derand and co-workers (2005) showed in their study that treating the zirconia surface with plasma spraying (hexamethyldisiloxane) increases shear bond strength. The plasma is partially ionized gas containing ions, electrons, atoms and neutral species.

Many studies have shown that treatments simulating the conditions in the mouth, such as thermocycling, decrease the bond strength between zirconia and some luting cements (Lüthy et al., 2006; Matinlinna et al., 2007; Oyagüe et al., 2009; Phark et al., 2009a). The shear bond strength of adhesive resin composite cement in previous studies has varied from 10.6 to 26.4 MPa depending on the surface conditions (Heikkinen et al., 2007; Phark et al., 2009b). After tribochemical silica coating shear bond strength has been as high as 67.1 MPa (Tsukakoshi et al., 2008). Microtensile bond strength has varied from 16.2 to 40.6 MPa depending on the surface conditions (Aboushelib et al., 2008c; Piascik et al., 2009). The zirconia samples with no surface treatment had lower microtensile bond strength, 2.1 - 7.6 MPa (Aboushelib et al., 2008c; Piascik et al., 2009).

However, the airborne-particle abrasion and the tribochemical silica coating may have a detrimental effect on the treated zirconia surface by creating microcracks. This can reduce the strength of the ceramic (Zhang et al., 2006; Zhang et al., 2004). In the recent studies of Kern, Yang and co-workers (2009; 2010) low-pressure air abrasion reduced the

surface roughness without affecting the long-term bond strength of zirconia substructure and the bond strength was on the same level compared to commonly used air abrasion treatment. Low-pressure air abrasion was achived with 50 μm Al_2O_3 particles at 0.05 MPa air-pressure when the commonly used pressure is 0.25 MPa. With low-pressure abrasion, the possible surface damage effects can be minimized.

Resin cementation seems to be the one of the most favorable choices for cementing zirconia restorations, as the adhesive primers and phosphate monomers seem to improve the bond strength (Kern et al., 2009; Kern and Wegner, 1998). However, luting can be done as well with zinc phosphate cement or glass ionomer cement. When comparing the bonding strength of zirconia copings cemented with resin cement and zinc phosphate cement, the latter cement showed lower bond strength values (Derand et al., 2008). It has been shown that shear bond strength of zirconia increases in the order of adhesive resin composite cement > glass ionomer cement > zinc phosphate cement (Uo et al., 2006). Decrease in bond strength can be compensated with good retention and resistance of the substructures.

2.5 ARTIFICIAL AGING AND CLINICAL OUTCOME OF ZIRCONIA RESTORATIONS AND IMPLANTS

Several clinical studies have shown that zirconia substructures have sufficient strength in function and the success rate of the prostheses has been excellent (Molin and Karlsson, 2008; Raigrodski et al., 2006; Sailer et al., 2006; Tinschert et al., 2008; Vult von Steyern et al., 2005). The success rate of the zirconia FPDs varied between 74 % and 97 % (Crisp et al., 2008; Sailer et al., 2007; Sailer et al., 2006; Schmitt et al., 2009; Wolfart et al., 2009) after one to five year observation periods. Compared to porcelain-fused-to-metal posterior fixed partial dentures the zirconia-ceramic FDPs showed similar a survival rate (Sailer et al., 2009a). In the study of Wolfart and co-workers (2009) the four year success rate for cantilever zirconia FDPs was 92 % .

For mimicking the clinical behavior of zirconia restorations, *in vitro* artificial aging studies have been performed. Mechanical loading and thermal cycling is commonly used for artificial aging. In the study of Kohorst and co-workers (2008) the artificial aging decreased the load-bearing capacity of zirconia fixed partial dentures. It has been calculated that aging zirconia specimens at 134 ºC with hot water or steam for one hour corresponds to 3-4 years use at body temperature (Chevalier et al., 1999; Chevalier et al., 2007). Oral fluids are known to cause stress corrosion on the ceramic surface, resulting to slow crack growth. This might lead to failure of the ceramic restoration (Zhang et al., 2005). Testing the material in water or performing thermal cycling before mechanical testing is used to imitate this water effect in the mouth. As the chewing cycle in posterior dentition involves the sliding contact between the mandibular buccal cusps and maxillary lingual cusps, off-axis sliding contact testing seems to imitate the oral conditions better than uni-axial loading (Kim et al., 2008; Santana et al., 2009). Mouth-motion simulation

is carried out in water by step-stress fatigue using 30º off-axis sliding contact. Off-axis sliding contact induces more occlusal surface damage whereas axial loading can cause more radial fractures from the bottom of the specimen (Kim et al., 2008).

Clinically, complications seen in studies of zirconia FDPs are chipping of the veneering ceramic, secondary caries, the need for endodontic treatment and technical complications such as the discrepancy of marginal integrity or discoloration of the margins, loss of cementation or fracture of the substructure caused by trauma (Molin and Karlsson, 2008; Sailer et al., 2006; Sailer et al., 2009c; Tinschert et al., 2008). Chipping of the veneering porcelain has been seen in 6-13 % of the zirconia FPDs after three years in use (Sailer et al., 2006; Tinschert et al., 2008) and 15 % after a five-year observation time (Sailer et al., 2007). In the study by Larsson and co-workers (2006) the chipping rate was 54 % over one year of observation time. The probability for success of the veneer after a 4 year observation period was 88-91 % in the study of Roediger and co-workers (2010). However, chipping of the veneering ceramic on the metal-ceramic FDPs has also been seen (Sailer et al., 2009a). Periodontal health has been reported to be good around zirconia FPDs (Schmitt et al., 2009; Tinschert et al., 2008). In a clinical study of marginal fit of FPDs the mean marginal gap for zirconia FPDs and porcelain fused to metal FPDs was 65 μm and 54 μm respectively (Reich et al., 2005). Some clinically unacceptable marginal gaps have been reported and it tends to lead to secondary caries (Sailer et al., 2007).

Clinical studies of zirconia abutments, including the individually designed and milled custom-made abutments, have shown good survival rates and comparable properties to titanium abutments in the posterior jaw regions (Sailer et al., 2009c; Zembic et al., 2009). A study of zirconia abutments placed in the anterior jaw regions showed no failures during the eight year clinical follow-up (Döring et al., 2004). In another study, zirconia abutments in anterior and premolar regions showed good stability and favourable soft and hard tissue reaction, but abutment screw loosening was reported for two restorations out of 53 (Glauser et al., 2004). A six month clinical investigation of prefabricated zirconia implant abutments for posterior single-tooth replacement showed a high success rate and healthy periodontal soft tissues (Nothdurft and Pospiech, 2009). In the review article of Sailer and co-workers (2009b) it was concluded that survival rates seemed to be similar for ceramic and metal abutments. Abutment screw loosening was a frequent technical problem in the studies reviewed.

Only few studies have been conducted on zirconia oral implants. Kohal and Klaus (2004) presented a case report of an all-ceramic custom-made zirconia implant-crown system for replacing maxillary left central incisor. In the study of Mellinghoff (2006) the 1-year survival rate of zirconia implants was 93 %. Most of the failures occurred during the healing period and one implant fractured after prosthetic treatment. Oliva and co-workers (2007) reported a 1-year survival rate of 98 % for 100 zirconia implants. Only two implants were lost during the healing period. In the study of Pirker and Kocher (2009) the survival rate of one-piece zirconia implants placed immediately after extraction was

92 % during an observation period of up to 33 months. Although clinical studies have shown encouraging results, more long-term studies are needed before zirconia implants can be recommended for clinical use.

3. AIMS OF THE STUDY

The purpose of the present investigation was to evaluate whether certain treatments used in the manufacturing process of dental zirconia, such as sintering time, color shading or heat treatment affect the material properties. Another purpose was to evaluate the load bearing capacity and marginal fit of custom-made zirconia abutments. The working hypothesis of the study was that changing the sintering time or coloring the green-stage zirconia prior to the sintering process does not affect the mechanical properties. It was also hypothesized that heat treatment of the porcelain veneering process decreases the mechanical properties of the zirconia substructure. The third hypothesis of the investigation was that the load-bearing capacity of manually copy-milled custom-made zirconia abutments is similar to commercially available abutments.

The specific aims were:

1. To evaluate the effect of different sintering times and thermal cycling on the mechanical properties and phase transformation of zirconia material. (Study I)

2. To evaluate the effect of color shading on the mechanical properties of zirconia bulk framework material, fabricated in green-stage form. (Study II)

3. To determine the effect of heat treatment by the porcelain veneering process and the effect of coating the bulk framework material with a thin layer of glazing porcelain on the mechanical strength of zirconia, fabricated in green-stage form. (Study III)

4. To evaluate the load-bearing capacity and fit of custom-made versus commercially available zirconia implant abutments. (Study IV)

4. MATERIALS AND METHODS

This series of studies is based on laboratory *in vitro* studies. All of the studies aimed to evaluate mechanical properties of zirconia material after certain treatments. A universal testing machine (LRX, Lloyd Ltd, UK) was used for mechanical tests in all of the studies, I-IV. Because of the different specimen design, flexural strength testing was used in studies I-III and the off-axial loading test in study IV. The testing methods used in the different studies are summarized in Table 2.

Table 2. Summary of the testing methods and analysis used in the different studies

Study	I	II	III	IV
Flexural strength testing	x	x	x	
Vickers microhardness testing (VHN)	x	x	x	
Off-axial loading test				x
Thermal cycling	x			
Scanning electron microscopy	x	x	x	x
X-ray diffraction analysis	x	x	x	
Weibull analysis	x			

4.1 MATERIALS

4.1.1 Zirconia material

The material used in this study was yttrium partially stabilized (Y_2O_3 3 mol%) green – stage zirconium dioxide, zirconia (ICE Zirkon, Zirkonzahn GmbH, Gais, Italy). Green - stage zirconia powder is pressed to form a block and the powder contains binder (less than 1% of composite) that holds the powder together. The block is pre-sintered before the milling procedure. The binder is eliminated during the final sintering process. Milling of the pre-sintered zirconia is relatively easy as the material is soft. Material is milled dry and sintered after milling in a sintering furnace (Zirkonzahn). The material shrinkage during the sintering is about 20 % to 25 % and this has to be compensated by enlarging the original specimen model prior to the milling process.

4.1.2 Custom-made abutments (Study IV)

The custom-made abutments used in this study were copy-milled from Zirkonzahn green-stage zirconia blocks (ICE Zirkon, Zirkonzahn GmbH, Gais, Italy) with a specific manual copy-milling machine (Zirkonzahn). With a copy-milling machine, specimens are milled from green-stage zirconia block 20 % bigger than models used for milling. Commercially available zirconia abutments were used as controls and as models for manually copy-milled abutments. The pre-fabricated abutments were Astra ZirDesign 3.5/4.0 abutment

(Ø 5.5mm, gingival height 2 mm, AstraTech, Mölndahl, Sweden) and Xive Cercon 3.8/1 abutment (gingival height 1mm, Dentsply Friadent, Mannheim, Germany).

4.1.3 Specimen preparation

Sintering time (Study I)

In study I, 56 zirconia green stage disc shaped specimens (ICE Zirkon, Zirkonzahn GmbH, Gais, Italy) supplied by the manufacturer were divided into two groups. Different kinds of sintering programs were used. The disc shaped specimens of the first group were sintered according to the manufacturer's recommendations in a sintering furnace (Zirkonzahn) at 20 °C - 1500 °C using a rise time of 3 hours and kept at 1500 °C for 2 hours. The specimens of the second group were sintered at 20 °C - 1500 °C using a rise time of 1 hour 40 minutes and kept at 1500 °C for 1 hour (short sintering). Half of the specimens (n=14) from both groups were thermocycled (tc) in distilled water. Each cycle lasted 60 seconds: 20 s in 5 °C bath, 10 s to transfer samples to another bath, 20 s in 55 °C bath and 10 s to transfer samples back to 5 °C bath. A total of 20 000 cycles were performed. The treatments of zirconia specimens before mechanical testing are seen in Table 3. The thickness (1.6 mm) and the diameter (19.0 mm) of all sintered specimens were measured with a digital micrometer (Mitutoyo Ltd, Andover, England) before the mechanical tests.

Table 3. Treatments of zirconia discs before mechanical tests in study I.

	n	Time for temperature rising from 20ºC to 1500 ºC	Time for keeping temperature at 1500 ºC before cooling down	Thermocycling
Normal Sintering (Recommended by manufacturer)	14	3 hours	2 hours	Yes
Normal Sintering (Recommended by manufacturer)	14	3 hours	2 hours	No
Short Sintering	14	1 hour 40 minutes	1 hour	Yes
Short Sintering	14	1 hour 40 minutes	1 hour	No

Color shading (Study II)

In study II, 109 disc shaped specimens were cut from green-stage zirconia blocks (ICE Zirkon, ZirkonZahn GmbH, Gais, Italy) with a low speed diamond saw (Leitz 1600) without water cooling (Figure 3 a-b). The specimens were ground with 800 and 4000 grit (FEPA) silicon carbide grinding paper (Struers, Copenhagen, Denmark) and divided into 11 groups, n=10, except for the control group where there were 9 discs.

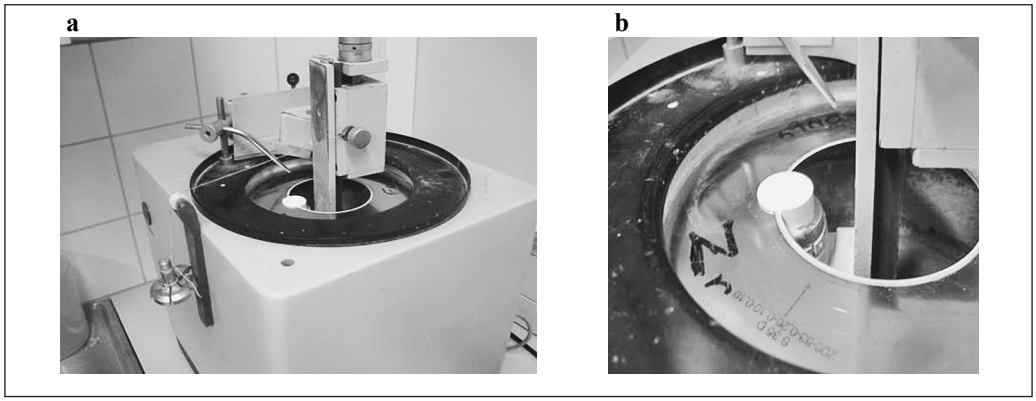

Figure 3 a-b. The disc shaped specimens were cut with low speed diamond saw.

Five different color liquid shades (Zirkonzahn) according to the Vita Classic scale (Vita, Zahnfabrik, Säckingen, Germany) were randomly chosen for coloring the specimens. Color shades A3, B1, C4, D2 and D4 were used. The control group was left un-colored. Two subgroups for each color shade were made: normal color shading for 3 s according to the manufacturer's instructions, and prolonged color shading for 1 min (Table 4). The specimens were dipped into the color liquid with plastic pincers, held there for the predetermined time (either 3 seconds or 1 minute), and dried under a warming lamp for 30 minutes. After coloring, all the specimens were sintered at 1500 °C in a sintering furnace (Zirkonzahn), using a temperature rise time of three hours and keeping the temperature at 1500 °C for two hours before cooling. The thickness (0.8 mm) and the diameter (19 mm) of the sintered specimens were measured with a digital micrometer (Mitutoyo Ltd, Andover, England) before the fracture test.

Table 4. Treatments of zirconia discs before mechanical tests in study II.

Group	n	Coloring for 3 s (manufacturer's instructions)	Coloring for 1 min (prolonged)
Control	9	-	-
A3 3s	10	X	-
B1 3s	10	X	-
C4 3s	10	X	-
D2 3s	10	X	-
D4 3s	10	X	-
A3 1min	10	-	X
B1 1min	10	-	X
C4 1min	10	-	X
D2 1min	10	-	X
D4 1min	10	-	X

Heat treatments (Study III)

In study III, 105 disc shaped specimens were cut from green – stage zirconia blocks (ICE Zirkon, Zirkonzahn GmbH, Gais, Italy) with a low speed diamond saw (Leitz 1600) without water-cooling. After cutting, the specimens were ground with 800 and 4000 grit (FEPA) silicon carbide grinding paper (Struers, Copenhagen, Denmark) to a thickness of 1.6 mm and were divided into seven groups (n=15/group). All the specimens were sintered at 1500 °C in a sintering furnace (Zirkonzahn) using a temperature rise time of 3 hours and keeping the temperature at 1500 °C for 2 hours before cooling down.

After sintering, the specimens in the study groups were treated in the following way: 1) control specimens were left as such, 2) one heat treatment in a porcelain firing furnace according to the porcelain firing process; 3) two repeated heat treatment cycles in a firing furnace according to the firing process; 4) one heat treatment with a thin coating of feldspathic glazing porcelain (ICE Zirkon keramik) fired on the specimens that were tested with the glazing on the tension side; 5) two heat treatments with an initial thin coating of feldspathic wash porcelain and a second thin coating of glazing fired on the specimens that were tested with the wash and glazing on the tension side; 6) one heat treatment with a thin coating of feldspathic glazing porcelain fired on the specimens that were tested with the glazing on the compression side; 7) two heat treatments with an initial thin coating of feldspathic wash porcelain and a second thin coating of glazing fired on the specimens that were tested with the wash and glazing on the compression side (Table 5).

Heat treatments for the study specimens were made in a porcelain furnace (Vacumat 200 Vita Zahnfabrik, Bad Säckingen, Germany). The heat treatment program started at 400 °C with 6 minutes preheating. After that, the temperature was raised at 55 °C per minute with a vacuum. The final temperature was 820 °C, where the specimens were kept for one minute before cooling started. Specimens in group 2 were heat treated at 820 °C without coating and the specimens in group 3 were heat treated twice at 820 °C with a heat treatment cycle without coating. Specimens in groups 4 and 6 were heat treated at 820 °C with a thin coating layer of the mixture of the glazing (ICE Zirkon Glaze, LOT: MA50001A, Zirkonzahn) and stain liquid (ICE Stain Liquid, LOT: MFAA13_01, Zirkonzahn) over the discs. Specimens in groups 5 and 7 were heat treated twice at 820 °C. The first heat treatment of groups 5 and 7 were done with a thin coating layer of the mixture of dentin porcelain (ICE Zirkon Keramik Dentin D4, LOT: KA50053A, Zirkonzahn) and modeling liquid (ICE Build Up Liquid, LOT: MFAA14_01, Zirkonzahn) over the discs. The second heat treatment was done with a thin coating layer of the mixture of glazing and stain liquid over the dentin porcelain. After the heat treatment cycles with or without coating, all the specimens were left as such and no grinding or polishing on the glazing surface was performed. The thickness (1.2 mm, SD 0.1 mm) and diameter (19 mm) of the sintered specimens was measured with a digital micrometer (Mitutoyo Ltd, Andover, UK) before the fracture test.

Table 5. Treatments of zirconia discs before mechanical tests in study III.

Group number and definition	n	First heat treatment and coating	Second heat treatment and coating	Note on biaxial flexural strength test
1) Control	15	---	---	---
2) Plain specimens with one heat treatment	15	820°C without feldspathic glazing	---	---
3) Plain specimens with two heat treatments	15	820°C without feldspathic glazing	820°C without feldspathic glazing	---
4) Specimens with glaze coating with one heat treatment	15	820°C with thin coating of feldspathic glazing	---	Coating on the tension side
5) Specimens with wash and glaze coating with two heat treatments	15	820°C with thin coating of feldspathic wash porcelain	820°C with thin coating of feldspathic glazing	Coating on the tension side
6) Specimens with glaze coating with one heat treatment	15	820°C with thin coating of feldspathic glazing	---	Coating on the compression side
7) Specimens with wash and glaze coating with two heat treatments	15	820°C with thin coating of feldspathic wash porcelain	820°C with thin coating of feldspathic glazing	Coating on the compression side

Preparation of custom-made abutments (Study IV)

In study IV, abutment shaped specimens were manually copy-milled from partially yttrium stabilized zirconium dioxide (Y_2O_3 3 mol%), zirconia green-stage blocks (ICE Zirkon, Zirkonzahn GmbH, Gais, Italy). The copy-milling was done with the Zirkonzahn machine (GmbH, Gais, Italy). Commercially available abutments were used as models and the abutments were divided into four groups (n=10/group) according to abutment design. The custom-made abutments were sintered at 1500 °C in the sintering oven (Zirkonzahn GmbH, Gais, Italy) at 20 °C - 1500 °C using a rise time of 3 hours and kept at 1500 °C for 2 hours (manufacturer's recommendation). Commercially available abutments were used as control (groups 1 and 4, n = 10/group). Abutments in the study groups were: 1) Astra ZirDesign 3.5/4.0 commercial abutment (Ø 5.5mm, gingival height 2 mm, AstraTech, Mölndahl, Sweden), 2) custom-made Zirkonzahn – Astra abutments, that were milled from a Zirkonzahn zirconia block using the Astra abutment as a model, 3) custom-made Zirkonzahn – Astra – short abutments, that were milled from a Zirkonzahn zirconia block using the Astra abutment as a model and the abutments were shortened to the same level as Xive - abutments, 4) Xive Cercon 3.8/1 prefabricated abutments (gingival

height 1 mm, Dentsply Friadent, Mannheim, Germany), 5) custom-made Zirkonzahn – Xive abutments that were milled from a Zirkonzahn zirconia block using the Xive Cercon abutment as a model, 6) custom-made Zirkonzahn – Xive – modified abutments, that were milled from Zirkonzahn zirconia block using the Xive Cercon abutment as a model, but the model was modified from the bottom of the abutment (gingival height 2 mm) and the upper part of the abutment was fully cylinder shaped (Figure 4 a-f).

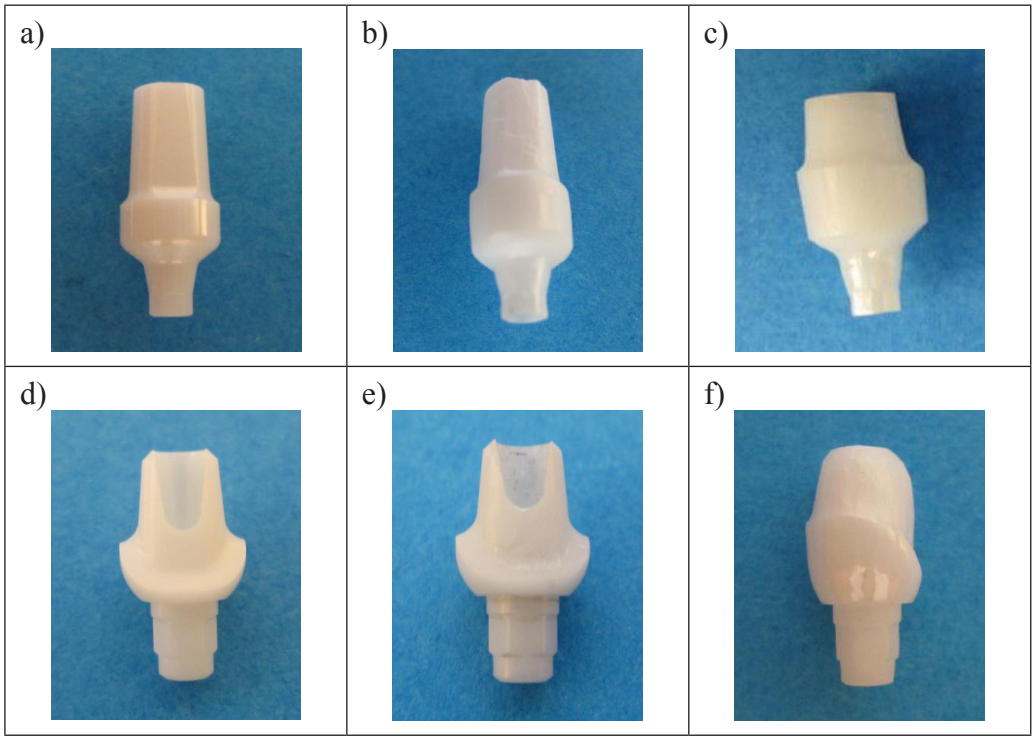

Figure 4 a-f. Abutments in the study groups: a) Astra, b) Zirkonzahn-Astra, c) Zirkonzahn-Astra-Short, d) Xive, e) Zirkonzahn-Xive, f) Zirkonzahn-Xive-Modified.

4.2 METHODS

4.2.1 **Flexural strength test** (Studies I-III)

The biaxial flexural strength test, according to the recommendations of ISO Standard 6872 was used for determining biaxial fracture strength values in studies I-III (ISO, 1995). The specimens were tested dry at room temperature with a universal testing machine (Model LRX, Lloyd Instruments Ltd) where they rested on three symmetrically based balls and the load was applied to the centre of the top surface by the piston (diameter 1.60 mm) until fracture occurred (Figure 5). The cross - head speed of the piston was 1.0 mm/min. Results were recorded with Nexygen (Lloyd Instruments Ltd, Fareham, England).

When zirconia substructure material is veneered with layer of porcelain it would lead to a bi-layered material and possibly hide the impact of actual heat treatment on the zirconia´s properties. Therefore, in order to get information on the possible heat treatment effect to the zirconia properties, instead of firing veneering porcelain a thin, less than 10 µm wash and glazing porcelain coating was used in study groups 4-7 of study III. Biaxial flexural strength was determined according to the recommendations of ISO Standard 6872 and the method for actual bi-layered discs recommended by Hsueh and co-workers (2006) was not justified.

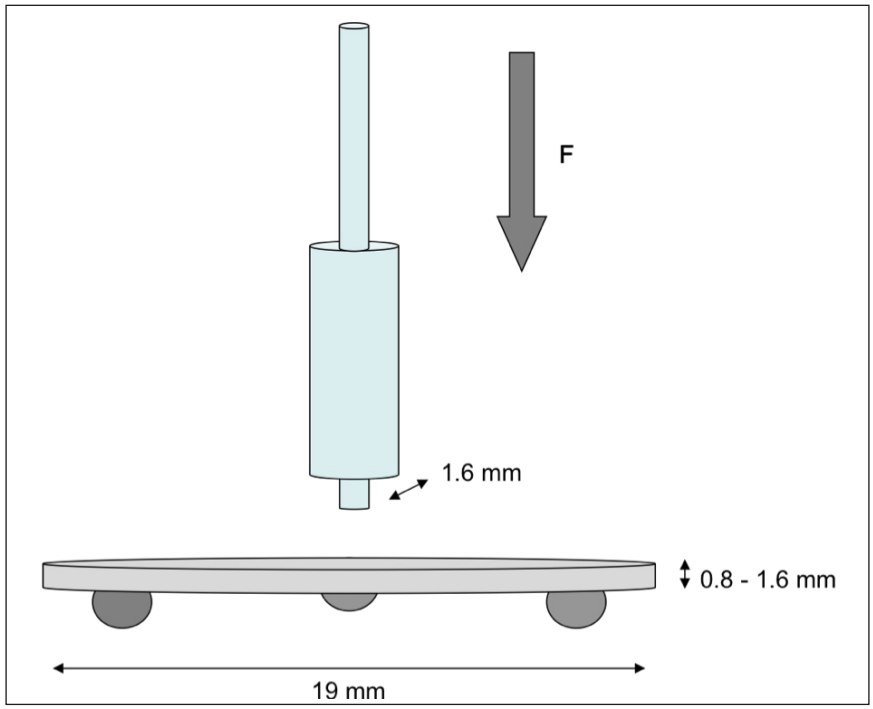

Figure 5. Illustration of the bi-axial flexural strength testing. The specimen rested on three symmetrically based balls, and the load (F) was applied to the center of the top surface by the piston (diameter 1.60 mm) until fracture occurred.

4.2.2 **Off-axial static loading test** (Study IV)

The seven abutment shaped specimens / group were screwed onto stainless steel implant replicas (size 3.5/4.0 AstraTech, 3.8 Dentsply Friadent) according to the manufacturer's instructions using their own torque devices. Replicas were embedded in the acrylic resin sample bases (Palapress vario: Heraeus Kulzer GmbH, Hanau, Germany) by light curing resin (50% Bis-GMA, 50% Teg-DMA). The specimens were loaded with a universal testing machine (Model LRX, Lloyd Ltd, UK) dry at room temperature. A testing angle of 45° was chosen as it represents mechanical loading conditions in the maxillary anterior area where tooth colored abutments are frequently used (Dixon et al., 1995; Strub and

Beschnidt, 1998; Strub and Gerds, 2003; Yildirim et al., 2003). The abutments were loaded at the upper end of the specimen with a flat piston until initial and final failures occurred (Figure 6). A thin layer of Mylar folio (0.1 mm) was placed between the piston and the abutment to prevent surface damage by the loading piston. The cross-head speed of the piston was 1 mm/minute and the final failure load and initial failure load were recorded. The fracture mode of the abutments was also evaluated visually.

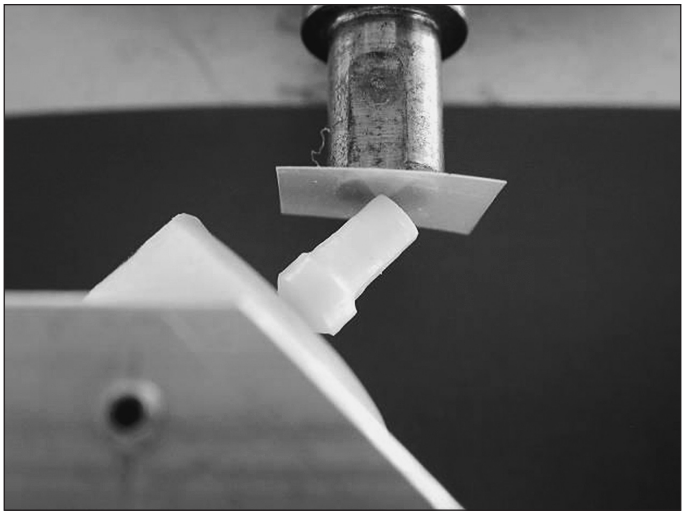

Figure 6. Illustration of off-axial loading off abutment shaped specimens in study IV.

4.2.3 **Surface microhardness test** (Studies I-III)

The surface microhardness (Vicker's hardness number, VHN) of the specimens in studies I-III was determined by the indentation technique (Callister, 2007). The indentations were performed after the flexural strength test to avoid introducing defects in the specimens that could influence the flexural strength results. A microhardness measuring device (Duramin -1, Sturers A/S, D-2610, Rødorve, Denmark) was used with a load of 9.81N and a loading time of 10 s. In study I, all the specimens tested were used and to some of them two indentations were made resulting in total of 20 indentations per group. In study II there were 15 randomly selected indentations per study group, and in study III 20 randomly selected indentations per study group were made to the non-coated surface of the specimens.

4.2.4 **Determination of dimensional changes** (Study II)

In study II, in addition to the earlier mentioned specimens, 7 discs (thickness 1 mm) per five groups were prepared using the same procedure as described previously. The weakest and strongest color shade in the mechanical tests was chosen in the determination of dimensional changes. The specimens were color shaded as described earlier; shading

times were 3 seconds and 1 minute for the groups. One group was used as a control. All the specimens were weighted using balance (Mettler Toledo AB54-S, Switzerland) and the diameter was measured using micrometer screw (Mitutoyo, Japan) before and after the color shading and after sintering.

4.2.5 **Scanning electron microscopy** (Studies I-IV)

A scanning electron microscope (SEM) (JSM 5500, Jeol Ltd, Tokyo, Japan) was used for visual examination of the specimen surfaces after certain surface treatments and for measuring the marginal fit of custom-made and commercially available abutments on implant replicas. The specimens were prepared for imaging by cleaning them ultrasonically with distilled water and ethanol. All the specimens were coated either with carbon or gold (Bal-Tec SCD 050, Sputter coater) to get a signal from the specimen surface.

In study I, one disc from each group was cleaned ultrasonically. In order to inspect the grain structure, thermal etching was performed in the sintering oven at 20°C-1500°C using a rise time of 3 hours and kept at 1500°C for 30 minutes. The grain size determination of zirconia for each group was made on a scanning electron microscope SEM (Princeton Gamma-tech x-ray microanalysis) with a magnification of 6000x using semiautomatic image analysis for calculation. Five specimens from each group in study III with a coating on the surface (4-7) were ultrasonically cleaned and covered with carbon (Bal-Tec SCD 050, Sputter coater) before the imaging of the fracture surfaces with a scanning electron microscope (SEM) (Princeton Gamma-tech x-ray microanalysis). Visual inspection of the fractured surfaces was carried out with magnifications of x60, x120, x500 and x5000. Thickness of the coating layer of wash and glazing were measured from images.

After ultrasonic cleaning three abutments from each group in study IV were screwed onto stainless steel implant replicas (size 3.5/4.0 Astra, 3.8 Dentsply Friadent) according to the manufacturer's recommendations and covered with gold (Bal-Tec SCD 050, Sputter coater) before the imaging of the implant / abutment interface with a scanning electron microscope SEM (Princeton Gamma-tech x-ray microanalysis). The distance between the implant and the abutment was evaluated with a magnification of x1000. Six measurements per abutment were performed from the images with MeasureIT.

In study II, for determining the elemental composition of the shaded ceramics and the color liquids energy-dispersive x-ray analysis (EDX, Princeton Gamma-tech x-ray microanalysis) was performed by scanning electron microscope (SEM, JEOL 5500). After mechanical tests, the fractured discs were ultrasonically cleaned and covered with carbon (Bal-Tec SCD 050, Sputter coater) before analysis. Additionally, four sample bases with a diameter of 2 cm and a thickness of 1 cm were cut from the PMMA tube with a saw (Fox) and small holes for color liquids were drilled into each sample base with a carborundum drill. A small drop of the tested color liquids (Zirkonzahn) A3, B1, C4, D2, and D4, was put into the hole in the sample base with a clean pipette (Figure 7)

and the drops were allowed to dry at room temperature for two days. The sample bases were covered with carbon and the EDX analysis was carried out using an acceleration voltage of 20 kV and a magnification of 50x. A spectra collection time of 120 seconds was used to determine the elemental composition of the solidified substructure from the color liquid. One recording for each color liquid sample was done. The weight% of the elements of color liquids was analyzed with EDX-computer-software (Spirit, PGT, Princeton Gamma-tech x-ray microanalysis, USA).

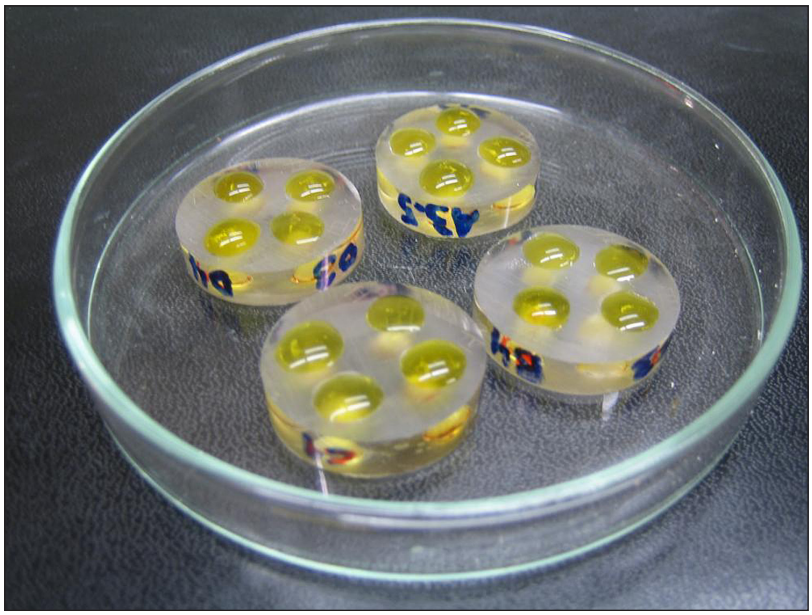

Figure 7. Sample bases with drops of different color liquids for determining the elemental composition of the liquids in study II.

4.2.6 X-ray diffraction analysis (Studies I-III)

The phase diagram of zirconia material studied was determined by X-ray diffraction (XRD) analysis (Philips PW 1830 Generator) using 40kV and 30mA and Cu Kα -1 radiation. The relative amount of the monoclinic phase was calculated according to the polymorph method recommended by Garvie and Nicholson from the integral intensities of two monoclinic peaks M(III) and M(II$\bar{\text{I}}$) and one tetragonal peak T(III) (Garvie and Nicholson, 1972). The equation for the monoclinic phase is:

$$X_m = \frac{\mathrm{I_m(III) + I_m(II\hat{I})}}{\mathrm{I_m\,(III) + I_m(II\hat{I}) + I_t\,(III)}}.$$

In study I, one specimen that was not yet mechanically tested, from both (short and long sintering) thermocycled groups, was stored in distilled water for 7 months. Additionally, two mechanically tested discs from the thermocycled groups (short and long sintering) were stored dry at room temperature for 7 months. The relative amount of the monoclinic phase after thermocycling, short/long sintering time and dry/wet storage was determined. The relative amount of the monoclinic phase in the thermocycled and water stored groups was also measured after 13 months. In addition, two disc shaped control specimens were cut with a saw (Leitz 1600) from the green stage zirconia block, sintered in Zirkonzahn sintering furnace at 20°C-1500 °C using a rise time of 3 hours and kept at 1500°C for 2 hours. One of the control specimens was left as such and the other was polished with diamond paste. XRD- analysis of the control discs was performed after sintering.

To discover the possible effect of color shading on phase stability, XRD-analysis in study II was performed on shaded and sintered disc shaped specimens that were not yet mechanically tested. Un-shaded zirconia specimen was used as a control.

In study III, the effect of heat treatment and glazing coating on phase transformations in zirconia specimens was performed on sintered and heat treated specimens (with and without a thin coating of wash and glazing on the opposite side of the specimen) and to sintered and twice heat treated specimens that were not yet mechanically tested. A sintered disc shaped zirconia specimen was used as a control.

4.2.7 Statistical methods

In studies I, II, III and IV statistical analyses were performed with SPSS (SPSS Inc., Chicago, USA) software for Windows using analysis of variance (ANOVA). Subsequent comparisons between different groups and treatment types were performed with Tukey's Post Hoc analysis. The level of statistical significance was set at $p < 0.05$. Additionally in study I, the reliability of the study groups was calculated. Because of the brittle nature of zirconia ceramic and uneven distribution of the flaws inside the material, the probability of failure can be determined (Ritter, 1995). Variability of the flexural strength values was determined by Weibull-analysis (Weibull, 1951). A higher value of Weibull modulus (m) indicated the homogeneity of the group.

5. RESULTS

5.1 FLEXURAL STRENGTH (Studes I-III)

In study I, the biaxial flexural strength of thermocycled and non-thermocycled specimens was evaluated. There were no statistically significant differences between the groups ($p>0.05$). Neither thermocycling nor different sintering time influenced the mechanical properties of zirconia ($p>0.05$) (Figure 8). Weibull-analysis revealed high ρ-values showing the reliability and homogeneity of the groups (Figure 9). The Weibull-modulus was lower (7.95) on the first group (sintered at 20° C - 1500 °C using a rise time of 3 hours and kept at 1500 °C for 2 hours, no thermocycling, number 2 in Figure 9) compared to other groups (11.07 – 14.33).

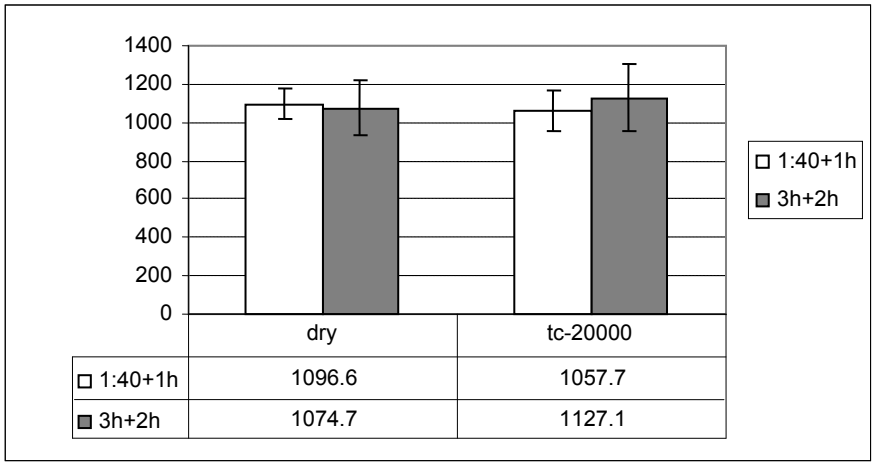

Figure 8. Biaxial flexural strength (MPa) of the groups in study I: Short sintering (1:40h+1h) dry and thermocycled (tc-20 000), normal sintering (3h+2h) dry and thermocycled.

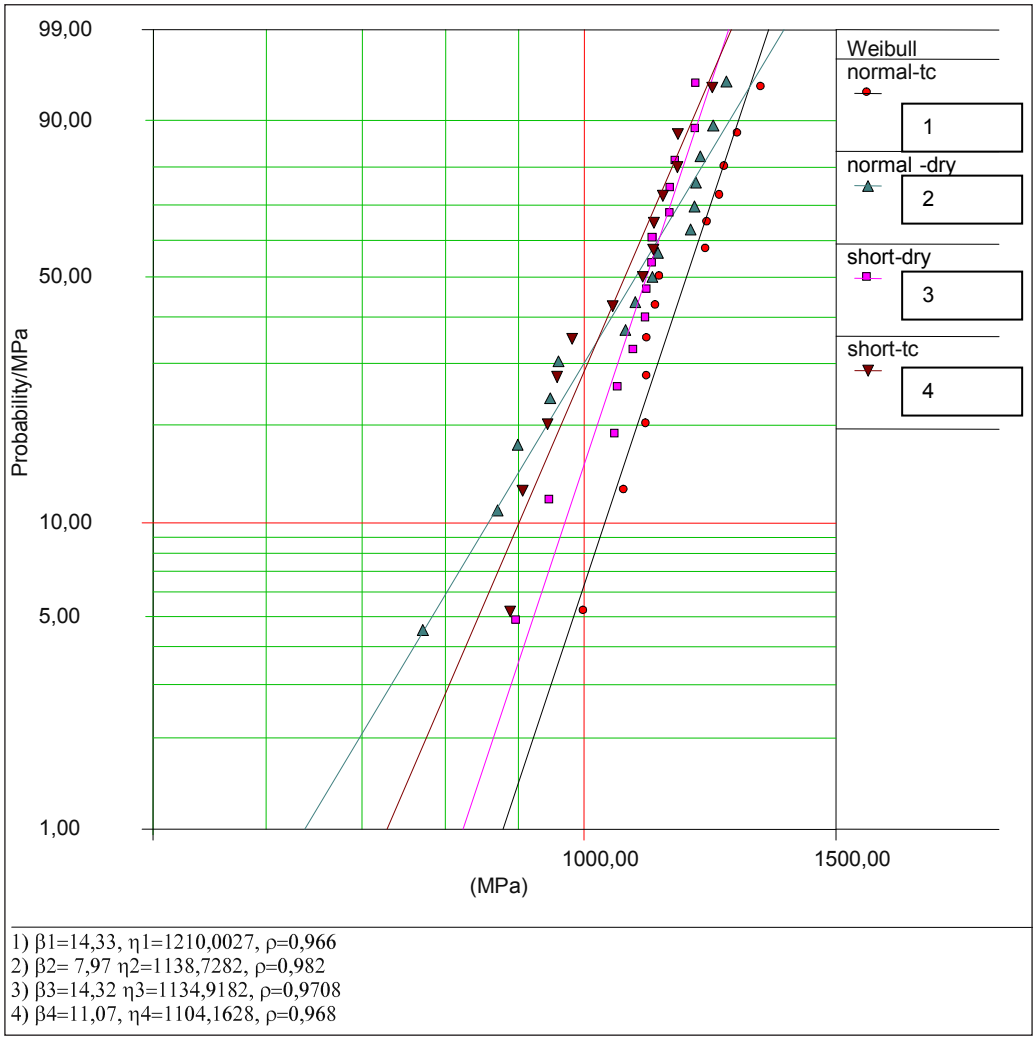

Figure 9 Weibull- distribution of the study groups 1) Normal sintering (1500 ºC 3h) thermocycling (tc), 2) Normal sintering dry storage, 3) Short sintering (1500 ºC 1h 40 min) dry storage, 4) Short sintering thermocycling (tc).

In study II, the ANOVA analysis revealed a statistically significant difference ($p<0.05$) in biaxial flexural strength between the groups with different color shading (Table 6). Specimens colored with shade D4 revealed the highest strength of the shaded specimens, but it did not differ statistically from the control group. The specimens shaded for three seconds were statistically significantly weaker than the un-shaded specimens in the control group. Prolonged color shading time (1 min) further decreased the strength of the specimens ($p<0.05$). However, group D4, shaded for one minute, had bi-axial flexural strength on the same level as the three-second-shaded specimens (A3, B1, C4, D2).

Table 6. Biaxial flexural strength (MPa) of zirconia specimens in study II according to different color shades and shading times. Statistical differences are counted from the relation between certain color shade and flexural strength.

Parameters	Flexural strength MPa (SD)	Stat. diff.
Control	1132 (162)	a
D2, 3 s	897 (95)	b,c
D4, 3 s	1007 (121)	b
B1, 3 s	918 (81)	b,c
C4, 3 s	885 (91)	c
A3, 3 s	898 (116)	c
D2, 1 min	812 (106)	b,c
D4, 1 min	934 (89)	b
B1, 1 min	809 (88)	b,c
C4, 1 min	793 (159)	c
A3, 1 min	798 (84)	c

*Different letters show the statistical difference in results. Values with the same letter do not have a statistical difference.

Biaxial flexural strength in study III varied between 553.0 MPa and 1019.4 MPa (Figure 10) and one-way ANOVA- analysis revealed statistically significant differences between the groups ($p<0.05$). Repetitive heat treatment increased the biaxial flexural strength slightly, but the difference was not statistically significant ($p>0.05$). A thin coating of feldspatic wash and glazing decreased the strength of the specimens when the coating layer was positioned on the tension side ($p<0.05$). When the specimens were tested with a coating of glazing or wash and glazing positioned on the compression side, the bi-axial flexural strength was at the same level as control group ($p>0.05$). Loading curves shown by Nexygen software did not demostrate any signs of existing pre-cracks in the material.

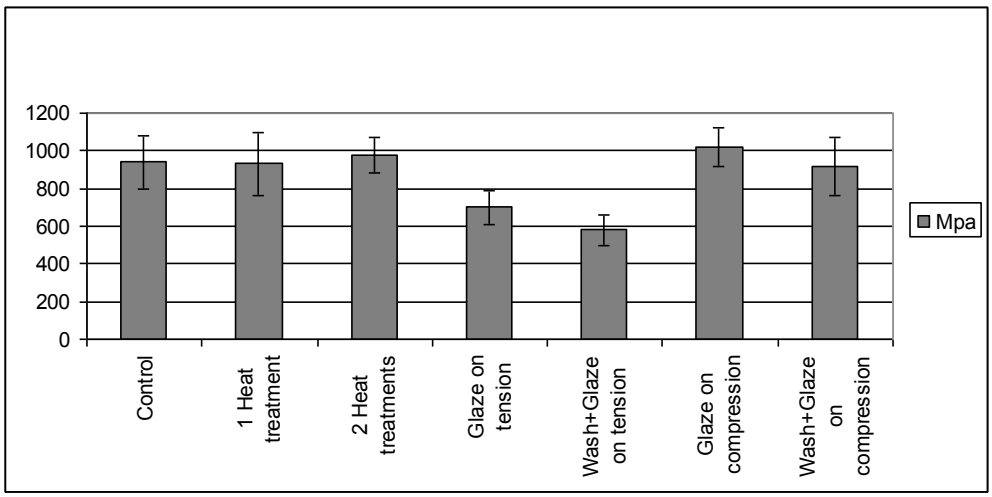

Figure 10. Biaxial flexural strength (MPa) of the groups in study III; control, one heat treatment, two heat treatments, thin coating of glaze on tension side, thin coating of wash and glaze on tension side, thin coating of glaze on compression side, thin coating of wash and glaze on compression side.

5.2 LOAD-BEARING CAPACITY OF ZIRCONIA ABUTMENTS (Study IV)

In study IV, the load-bearing capacity of custom-made and commercially available zirconia abutments was determined by the off-axial static loading test. The custom-made abutments showed comparable failure load values to prefabricated commercially available abutments as the final failure loads varied from 412 N to 624 N in groups 1-5 ($p>0.05$) (Table 7). Copy-milled Zirkonzahn – Xive - modified abutments (group 6) were statistically significantly stronger (1099 N) compared to other groups ($p<0.05$). The initial failure was recorded when the strength curve notched. With some samples, bending of the implant screw happened at the time of initial failure and most of the groups showed initial failure before final failure. The initial failure was not detected in the copy-milled Zirkonzahn - Xive group (5) (Figure 11).

Table 7. Initial failure loads (N) and final failure loads of custom-made and prefabricated commercially available zirconia abutments in study IV.

Abutment type (Group)	Initial failure load N (SD)	Stat. diff	Final failure load N (SD)	Stat. diff*
Astra (1)	534 (137)	a	606 (113)	a
Zirkonzahn – Astra (2)	461 (180)	a	511 (156)	a
Zirkonzahn – Astra – Short (3)	523 (162)	a	624 (103)	a
Xive (4)	369 (31)	a	412 (79)	a
Zirkonzahn – Xive (5)	412 (111)	a	412 (111)	a
Zirkonzahn – Xive-Modified (6)	1092 (212)	b	1099 (207)	b

*Different letters show the statistical difference in results. Values with the same letter do not have a statistical difference.

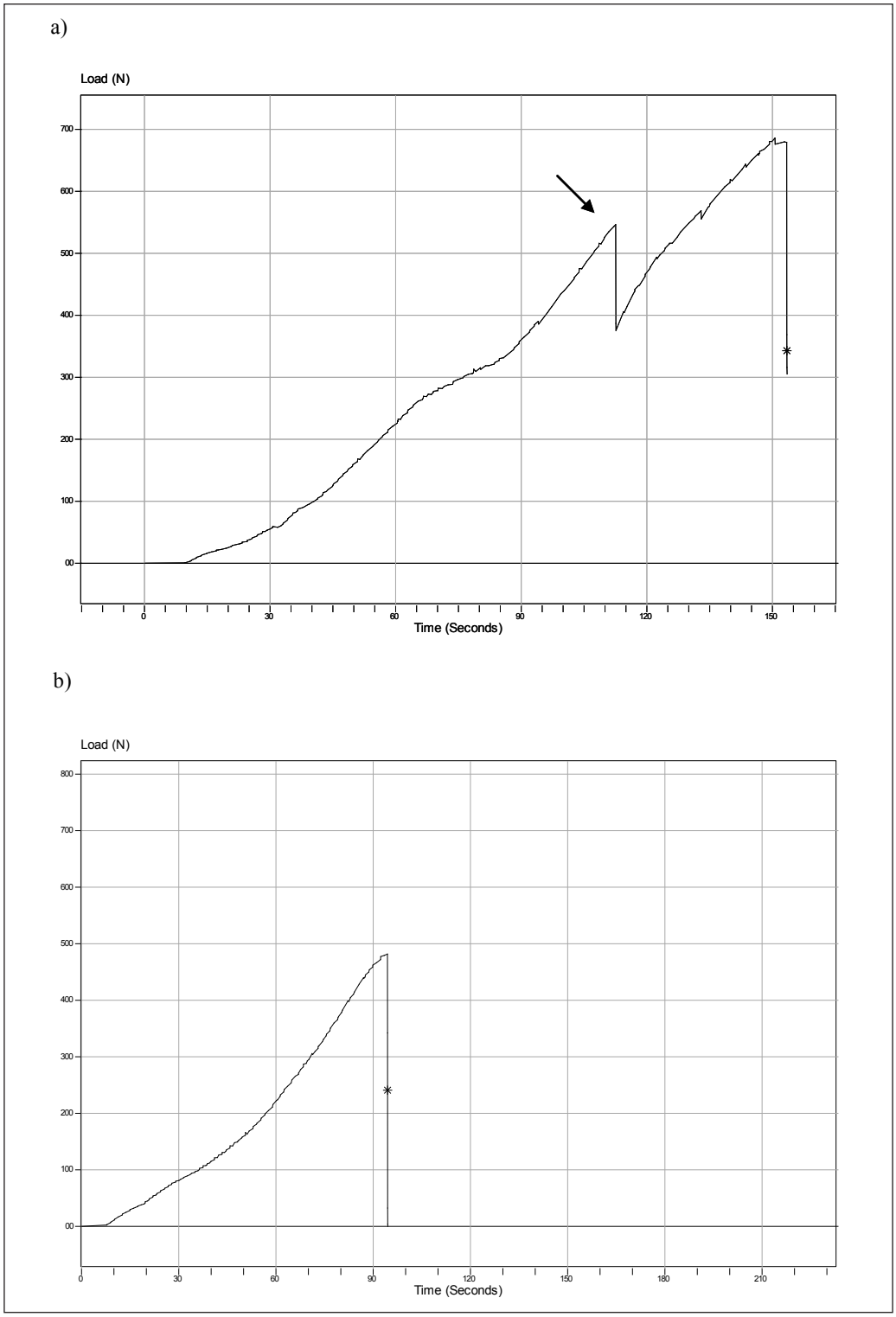

Figure 11. Failure graphs of Zirkonzahn - Astra (a) and Zirkonzahn - Xive (b) abutments, showing initial failure (black arrow) in Figure a, but not in Figure b.

5.3 SURFACE MICROHARDNESS TEST (Studies I-III)

In general, the different treatments did not affect the surface microhardness of the zirconia specimens. In study I, Vicker's Hardness varied between 1478 and 1532 and there were no statistical differences between groups of different sintering time or thermocycling treatment ($p>0.05$). In study II, surface Vicker's microhardness varied between 1352 and 1481. There were some differences between the groups of different color shades but the color shading time did not influence the surface microhardness. Discs shaded with A3 and D4 had lower microhardness than discs in the other shaded groups ($p<0.05$). In study III, surface Vicker's microhardness measured from the zirconia side of the specimens varied between 1383 and 1526 and there was no statistical difference between the groups of different heat treatments ($p>0.05$).

5.4 FAILURE MODES OF ZIRCONIA ABUTMENTS (Study IV)

In study IV, the failure mode of the abutments was visually analyzed. The Xive-model resulted in catastrophic failure. The Astra-design showed visual bending supported by the implant screw and minor cracks on the bottom of the abutment (Figure 12 a-f).

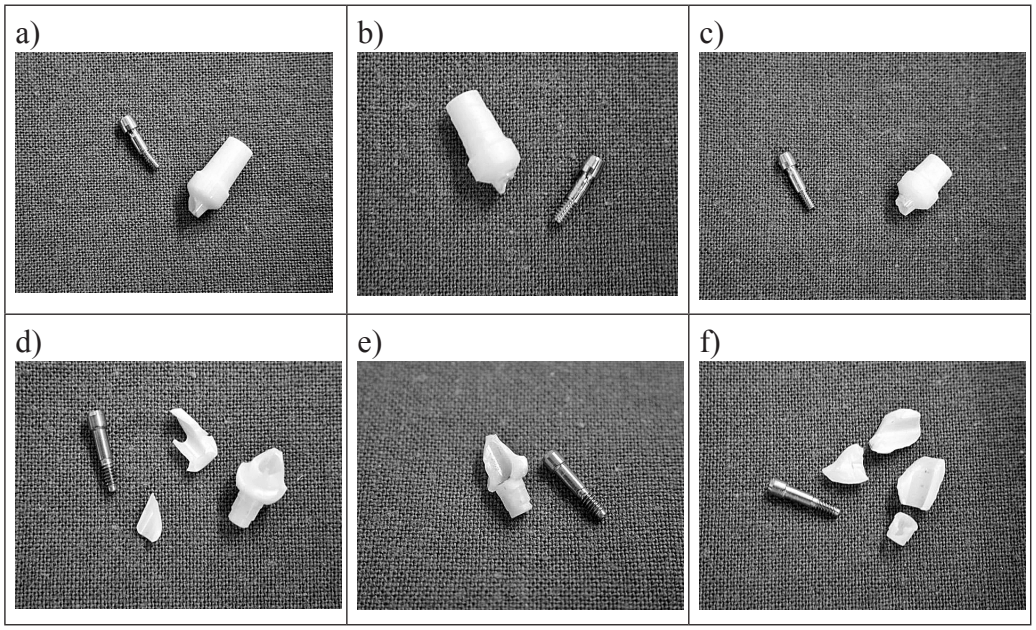

Figure 12. Failure modes of the abutments in study IV: Astra (a), Zirkonzahn-Astra (b), Zirkonzahn-Astra-Short (c), Xive (d), Zirkonzahn-Xive (e), Zirkonzahn-Xive-modified (f).

5.5 DIMENSIONAL CHANGES OF ZIRCONIA SPECIMENS AFTER COLOR SHADING (Study II)

The dimensional changes of zirconia specimens were determined in study II based on the results of mechanical tests. Groups D4 and C4 were chosen, as they were found to be the strongest and the weakest color shade group according to mechanical tests. Sintering shrinkage in the diameter of the un-shaded specimen was 19.8%, whereas the sintering shrinkage of shaded specimens was lower and varied between 19.4-19.5%; the difference was statistically significant ($p<0.05$) (Figure 13). As an absolute value in millimeters the average difference in diameter was 0.08 mm between control and shaded specimens. All the shaded specimens revealed 15% higher weight after dipping in color liquid. After sintering, the weight of the control specimens had decreased 0.12 wt% more than the weight of the shaded specimens (Figure 14), which is wt% of color pigment at zirconia. The difference was statistically significant ($p<0.05$).

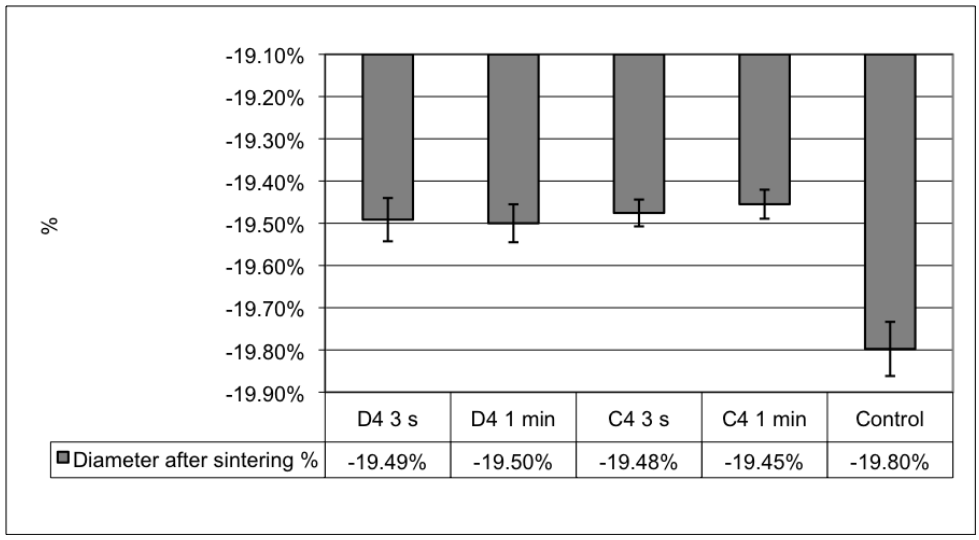

Figure 13 Sintering shrinkage in diameter (%) after sintering of shaded zirconia specimens in study II. Control discs were un-shaded.

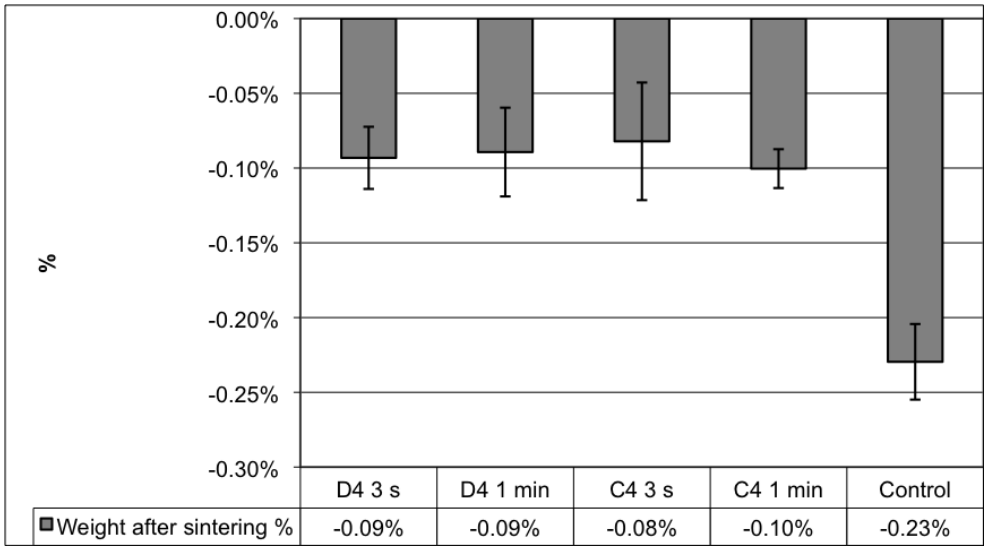

Figure 14. Change in weight (%) after sintering of shaded zirconia specimens in study II. Control discs were un-shaded

5.6 SEM ANALYSIS OF ZIRCONIA SPECIMENS (Studies I-IV)

Scanning electron microscopy was used in study I for determining the grain size of different groups. Thermal etching was used and a minor difference on the grain size of the groups could be seen. The mean grain size values are seen in Table 8. Specimens with shorter sintering time had slightly smaller grain size but the difference was not statistically significant ($p>0.05$).

Table 8. Mean grain size of the specimens with different sintering times and with or without thermocycling in study I.

Group	1500°C 3hrs dry	1500°C 3hrs tc	1500°C 1h40min dry	1500°C 1h40min tc
Mean grain size µm (SD)	1.05 (0.39)	0.98 (0.32)	0.77 (0.22)	0.83 (0.24)

In study II, the analysis of the surface elemental composition of the colored specimens demonstrated that the specimens mainly consisted of zirconium (Zr), yttrium (Y) and hafnium (Hf), with no clear signs of the elements of color liquids being seen. When the plain color liquids were analyzed with EDX, predominant elements of the dried liquids were oxygen, chlorine and iron. Small quantities (< 1.0 %) of chromium, erbium, aluminum, cobalt and sulfur were detected, but those quantities were close to the detection limit. Only with shade D4 was a minor quantity of calcium seen.

The thickness of the coating layers in study III was measured from SEM images. The thickness of the glazing coating in groups 4 and 6 was 4.3 µm and the thickness of the coating layer of wash and glazing in groups 5 and 7 was 7.6 µm (Figure 14 a-b). In the SEM images, after mechanical testing some of the specimens showed minor de-lamination of the coating layer and the de-lamination was seen regardless of whether the coating was on the tension or the compression side of the specimens.

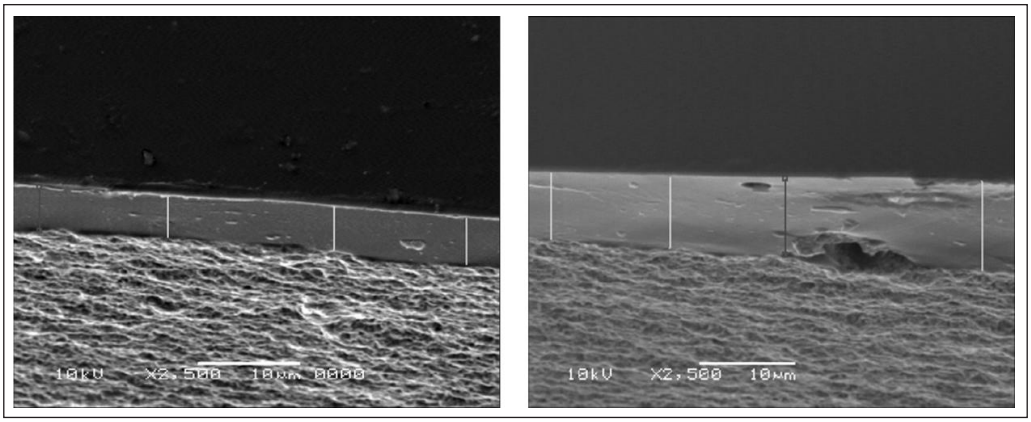

Figure 14 Scanning electron microscope images with a magnification of 2500 in study III: thickness of glaze coating layer (a), thickness of wash and glaze coating layer (b)

In study IV, SEM-analysis was used to determine the marginal fit between the zirconia abutment and the implant replica. Magnification of x1000 was used and the measurements were made with MeasureIT. The horizontal distances varied between 4.9 µm (SD 2 µm) (Group 1), 7.2 µm (SD 5.2 µm) (Group 2) and 10.7 µm (SD 11.1 µm) (Group 3) in the Astra-groups. In the manually copy-milled Zirkonzahn-Astra-short group (3) the distance between the abutment and implant replica was statistically significantly ($p<0.05$) wider than in groups 1 and 2 (Figure 15 a-c). The vertical distances varied between 1.5 µm (SD 0.5 µm) (Group 4), 2.5 µm (SD 1.5 µm) (Group 5) and 7.5 µm (SD 5.8 µm) (Group 6) in the Xive-groups. In the manually copy-milled Zirkonzahn-Xive-modified group (6) the distance was statistically significantly ($p<0.5$) wider than in groups 4 and 5 (Figure 15 d-f).

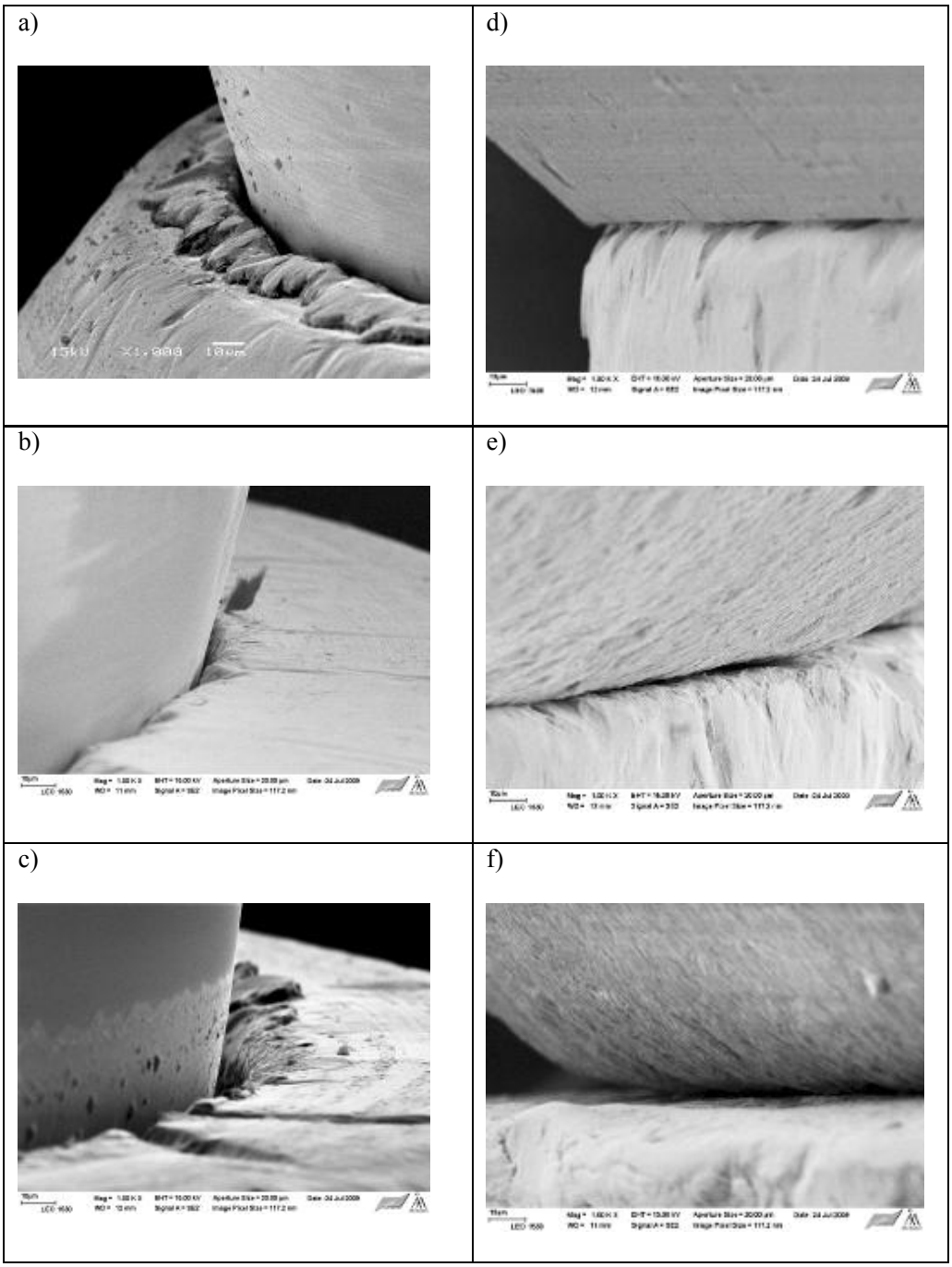

Figure 15. SEM - images of the horizontal distance between Astra prefabricated commercially available / custom-made zirconia abutment and implant replica and vertical distance between Xive prefabricated commercially available / custom-made zirconia abutment and implant replica in study IV: Astra (a), Zirkonzahn-Astra (b), Zirkonzahn-Astra-Short (c), Xive (d), Zirkonzahn-Xive (e), Zirkonzahn-Xive-modified (f).

5.7 X-RAY DIFFRACTION ANALYSIS (Studies I-III)

X-ray diffraction analysis, XRD, was performed to determine the relative amounts of monoclinic zirconia after certain treatments. In study I, the sintered control specimens did not have any monoclinic zirconia. Control specimens were sintered according to the manufacturer's instructions at 20°C-1500 °C using a rise time of 3 hours and kept at 1500°C for 2 hours and the shorter sintering was not performed to control specimens. When the disc shaped control specimen was stored in distilled water for 6 months the relative amount of the monoclinic phase was slightly increased (0.7%). Biaxial flexural strength testing also increased slightly the amount of monoclinic zirconia on the surface of the specimen (2.2%). The highest amount of the monoclinic phase was seen on the thermocycled specimens and the relative amount rose from 4.0% to 6.0% after storage in distilled water for 13 months compared to the specimens stored in distilled water for 7 months. Specimens with short sintering times had less monoclinic phase than the specimens sintered for a longer period of time (Figure 16).

In study II, XRD analysis did not reveal any changes from the tetragonal to the monoclinic phase in zirconia discs after color shading and the prolonged shading time did not affect phase change either.

The relative amounts of monoclinic zirconia in study III were determined by one or two heat treatments, with and without coating. The amount of the monoclinic zirconia in the heat treated and coated groups were 1.2% (one heat treatment with glazing coating) and 1.7% (two heat treatments with wash and glazing coating). No monoclinic zirconia was found on the surface of sintered control specimens or discs heat treated without coating.

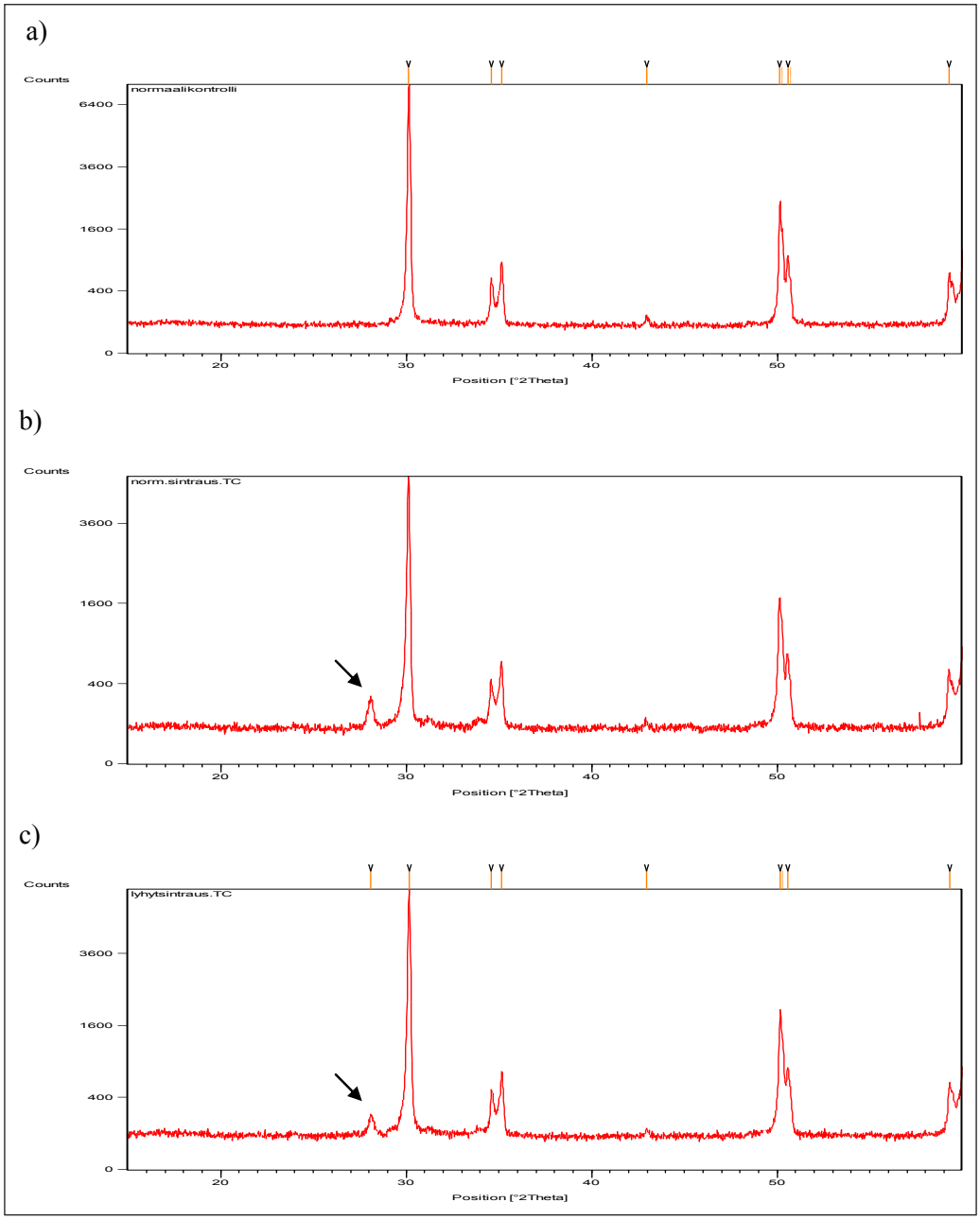

Figure 16. Relative amounts of monoclinic zirconia in study I: a) normal control (X_M 0%), b) normal sintering time, thermocycled and stored in water for 7months (X_M 4.0%), c) short sintering time, thermocycled and stored in water for 7 months (X_M 2.2%). Black arrow shows the peak of monoclinic zirconia.

6. DISCUSSION

6.1 General discussion

This series of *in vitro* studies aimed of evaluating whether certain treatments used in the manufacturing process, such as sintering time, color shading or heat treatments of the zirconia material affect the material's properties. Another aim was to evaluate the load-bearing capacity and marginal fit of custom-made manually copy-milled zirconia abutments. These aims were of interest because zirconia has rapidly become one of the most often utilized ceramic materials in prosthetic dentistry. Despite the popularity of zirconia as a dental material some aspects still remain to be clarified and this series of studies attempted to answer some of these questions.

The thickness of the test specimens in this series of studies varied from 0.8 mm (study II) to 1.2 mm (study III) and 1.6 mm (study I). The thickness of the test specimens was chosen in each study according to the technical requirements and this can be acknowledged as a shortcoming in respect to methodology. Even if the thickness of the specimens is taken into account when calculating the bi-axial flexural strength, the thickness of the specimen might affect the results (Kelly, 1995). The thicker specimens do not bend as much as thinner ones and more shear stress is formed instead of tensile stresses.

It has been shown that static and monotonic uni-axial mechanical loading might give higher strength values compared to cyclic fatigue loading (Jung et al., 2000; Sobrinho et al., 1998; Zhou et al., 2007). Itinoche and co-workers (2006) have shown that there can be differences in the results between cyclic and static loading tests, although in their study, the differences were not statistically significant. However, the failure modes of the specimens are different depending on the testing method. In cyclic loading, the failure starts from cone cracks on the surface. In uni-axial single loading predominant radial cracks are seen (Kelly et al., 1989; Rekow et al., 2007; Zhou et al., 2007). Radial cracks lead to degradation in mechanical properties. In this series of studies uni-axial static loading was used, as the aim was to get information about the effect of different treatments on disc shaped zirconia specimens and to compare the different groups. The abutment shaped specimens were also tested with a static single loading test but the fatigue resistance was not evaluated. One future research topic might be testing the abutments in water under cyclic loading.

Another aspect for measuring the bi-axial flexural strength of the zirconia specimens in this series of studies (I-III) is that when the piston-on-three-ball technique is used contact stress is induced between the loading piston and the specimen. In the ring-on-ring technique such compressive stress does not affect the centre surface of the specimen. However, the compressive stress has not been shown to considerably affect the tensile stress of the specimen (Hsueh et al., 2006). In the study of Guazzato and co-workers

(2004a) it was shown that when the load is increased, the crushing of the porcelain on the top surface occurs before the fracture of the core material. In study III, the piston-on-three-ball technique was used and no pre-cracks were observed during the loading process, as the glazing coating layer was thin.

In the study of Hsueh and co-workers (2006) a different method for calculating the bi-axial flexural strength for bi-layered zirconia/porcelain specimens was introduced. In their study, the ratio of zirconia and veneering porcelain was about 2:1. In study III, a thin coating of wash and glaze porcelain was used to demonstrate the veneering procedure and the heat treatment cycle. The coating was less than 10 μm thick and since the thickness of the specimens was about 1.2 mm, the ratio for zirconia and coating would be approximately 120:1. In study II, the color liquid penetrated the whole specimen regardless of the shading time and the specimens could be treated as a uniform material. In both studies II and III testing the specimens according to ISO prefabricated commercially available nr. 6872 was justified (ISO, 1995).

Several studies show that when milling or grinding zirconia material in fully sintered form it affects the material properties by causing some pre-cracks and flaws on the material surface (Guazzato et al., 2005; Kosmac et al., 1999; Luthardt et al., 2002). In the present studies, the negative effect of grinding fully sintered zirconia could be eliminated when the specimens were milled in green-stage form.

In study I, the grain size was measured after short and normal sintering time. The grain size was slightly smaller with shorter sintering time and this is in accordance with previous studies. Swain has shown that the grain size of zirconia increases after longer sintering time (Swain, 1986).

6.2 Mechanical properties

The thermocycling or shorter sintering time did not affect the bi-axial flexural strength of zirconia material. Similar results on the effect of water have been seen in the study of Curtis and co-workers (2006) with zirconia material was tested after water storage for 24 hours. In study II, the results revealed that shading influences the bi-axial flexural strength of zirconia specimens. Similar results are suggested by Ardlin and co-workers (2002), who found a higher strength with a yellowish shade. However, there is also a report about LAVA zirconia material where no changes were observed between the groups of material shaded with different color shades (Pittayachawan et al., 2007). In the present, an interesting aspect was seen: the shade D4 did not result in a major reduction in strength unlike other color shades. Elemental analysis with SEM-EDX of the shaded and sintered specimens did not provide a clear explanation for this. Apparently, the detection limit of the SEM-EDX system is not high enough, and the components of the color liquids were not observed from the sintered specimens. On the other hand, the elemental analysis of solidification remnants of the color liquid itself provided some information on the composition of coloring agents. Shade D4 liquid contained some calcium (Ca),

which was not found in any other color liquids. It can be speculated that the color shading oxides of the shade D4 did not affect the grain structure of zirconia, which might have been the case with the oxides used in other shades of the coloring agents. The other color shade liquids might have caused swelling of the material structure during liquid immersion. This could have caused more porosities and lower density in the material during the sintering process. However, possible changes in crystal structure could not be determined with the methods used and require further investigation.

In study III, the results showed a decrease in strength when zirconia material was tested with an additional thin coating of wash and glazing on the tension side. Similar results are seen in previous studies with bi-layered zirconia/porcelain specimens (Guazzato et al., 2004a; White et al., 2005). In the present study, one or multiple heat treatments as such did not affect material strength. The influence of heat treatment on the properties of zirconia has also been reported in other studies. The heat treatment of zirconia specimens after air-particle abrasion, grinding or polishing decreased the flexural strength of the material (Guazzato et al., 2005; Sato et al., 2008). The decrease was explained by the release of compressive stresses, which were caused by surface treatment such as sandblasting. In the study of Øilo and co-workers (2008) it was shown that heat treatment of the veneering process lowered the flexural strength of zirconia, but multiple firing cycles did not further lower the strength. These materials were machined into restorations after final sintering, whereas in the present study, the zirconia was milled in an pre-sintered green-stage form. The effects of the firing procedure may depend on the form of manufacturing and the results of study III support manufacturing substructures of fixed partial dentures and crowns from green-stage material.

The surface microhardness (VHN) in studies I-III was in the range of 1352–1532. In general, there were no differences between the groups in certain studies, but some shaded specimens represented lower VHN values. Theoretically, the phase change from tetragonal to monoclinic of thermocycled specimens could cause some compressive stresses to the surface of the specimens. This might have increased the surface microhardness. However, no difference in microhardness was seen in study I. In general, the results of studies I-III are in accordance with previous studies (Luthardt et al., 2002; Piconi and Maccauro, 1999; Pittayachawan et al., 2007).

6.3 Failure modes of zirconia abutments

The final failure loads of zirconia abutments in study IV varied from 412 N to 1099 N. Group 6 (Zirkonzahn–Xive-Modified) showed higher load values. In groups 1-5 the loads varied from 412 N to 624 N. This seemed to be lower than values reported in a previous study, where the mean failure load for Atlantis abutments and Nobel Biocare Procera AllZirkon abutments was 831N and 740N, respectively (Kerstein and Radke, 2008). This is probably related to the differences in the loading conditions and the abutment design used in the present study. In the study of Kerstein and Radke the implants were

loaded in a vertical direction through the abutment body, while in the present study the load was directed at a 45º angle. Vertical loading in the anterior region can be achieved only in edge-to-edge occlusion. This is clinically rare as most patients have a few millimeters vertical and horizontal overbite, which results in abutment loading in an oblique direction. It is apparent that the abutments in study IV would have shown higher failure loads under axial loading.

In study IV some differences between the groups could be seen as the Zirkonzahn–Xive-Modified (group 6) abutments had a higher mechanical strength than the abutments in the other study groups. This was probably due the abutment design, as the abutments of group 6 were relatively short and had more zirconia in volume than the abutments in the other groups.

The results showed that the failure modes of the abutment were dependent on the implant design. The abutments of groups 1-3 had more material in volume compared to groups 4-6 and they fractured from the bottom of the abutment, whereas abutments in groups 4-6 fractured from the upper part of the abutment. Bending the implant screw has been reported to be a typical failure when loading ceramic abutments (Adatia et al., 2009; Tripodakis et al., 1995) and it could be also seen the in present study, especially in groups 1-3.

In a study of zirconia abutments the fracture of some of the tested titanium fixation screws was seen during chewing simulation (Kolbeck et al., 2008). Further, all the screws became loose during testing procedures. In other studies, bending of the abutment screw during loading of ceramic abutments has been reported (Adatia et al., 2009; Tripodakis et al., 1995). The screw seems to be the weakest link of the implant-abutment combination. In a clinical study some loosening of the screws has been reported (Glauser et al., 2004). Some studies show that using gold screws and a controlled torque the rate of failure might be reduced compared to titanium screws (Butz et al., 2005; Strub and Gerds, 2003). In the study of Butz and co-workers (2005), the zirconia abutments were titanium-reinforced with a titanium insert, which could have resulted in better results in terms of screw loosening compared to all-zirconia abutments (Adatia et al., 2009).

A stainless steel replica was used instead of titanium implant in study IV. This might cause some difference in test results with titanium implants *in vitro*, as a stainless steel replica might have behaved differently than titanium. When comparing titanium implants and stainless steel analogs, Sundh and Sjögren (2008) found that there was no statistical difference between the bending resistances of the titanium or steel implants. However, titanium implants undergo more deformation, such as bending, during mechanical testing because of the different elastic modulus of stainless steel and titanium implant 200 GPa and 100 GPa, respectively. Another possible drawback worth mentioning is the fact that the acrylic resin sample base in the present study also does not fully imitate the resilience and elasticity of bone and can give some difference to results compared to an *in vivo*

situation. However, within the limitations of this study, it was still possible to compare the differences between standard and custom-made abutments.

6.4 Dimensional changes after coloring

In study II, the interesting observation was the change in dimensions after coloring the specimens in green-stage form. The weight of the specimens increased directly after coloring but during the drying and sintering processes the major parts of the color shading liquids had evaporated. Un-shaded specimens lost more weight after sintering than the shaded. This indicated that colorant particles stay in the crystal structure of zirconia material. Additionally, shading diminished the shrinkage of zirconia specimens during sintering. This can have clinical effects as the marginal accuracy, fit and cement thickness of shaded substructures is different to the un-shaded. The difference in shrinkage is larger when the substructure is bigger.

6.5 Feldspathic coating of zirconia specimens

Thin coating of feldspathic wash and glazing was used in study III to demonstrate the heat treatment cycles in the veneering process when manufacturing fixed partial dentures and crowns using zirconia as a substructure material. According to the manufacturer of the material used in this study, the coefficient of thermal expansion (CTE) for ICE Zirconia is 10 $x10^{-6}$ K^{-1} and ICE wash and glazing 9.6 $x10^{-6}$ K^{-1}. When porcelain is fused to the bulk substructure material attention must be paid to the matching of the CTE values as a large mismatch between the porcelain veneer and core materials can cause residual stresses and result in chipping of the veneer (Hermann et al., 2007; Taskonak et al., 2005). In the present study, no large chippings were seen. Instead, some de-lamination of the wash or glaze coating was seen through the scanning electron microscope after mechanical testing although the coating layer was relatively thin. This supports the findings that the bonding between the zirconia substructure and the veneering porcelain might be insufficient and that the crack has a tendency to run along the porcelain/zirconia interface, causing de-lamination, especially on disc shaped specimens (Aboushelib et al., 2005; Guazzato et al., 2004b). However, the cohesive fracture in veneering porcelain and porcelain chipping has been seen when veneered zirconia crowns have been tested with mouth-motion sliding-contact fatigue (Coelho et al., 2009a). Similar cohesive porcelain chipping from the substructure has also been seen as a failure in recent clinical studies (Sailer et al., 2009a; Tinschert et al., 2008).

The thin coating on the specimens in study III caused only minor change of the dimensions of specimens compared to the situation where a thicker porcelain layer would have been used in veneering. In mechanical testing the coated samples revealed lower biaxial flexural strength on tension. The bulk zirconia substructure was ground with 800 and 4000 grit grinding paper before sintering. The grinding may have left some

flaws on the surface of the specimens. Melt wash or glaze behaved as a visco-elastic liquid and probably penetrated into flaws and microcracks during the firing the glazing or wash coating on zirconia. Cooling increases the viscosity and when bonded to another material with different thermal dimensional behavior the glass matrix of the wash or glaze liquid started to retain stresses when it became solid (Bertolotti, 1983). The stress in the glazing and wash porcelain which filled the microcracks may have predisposed the material to crack and result in an increased probability of fracture during loading of the restoration (Anusavice et al., 1983; Mora and O´Brien, 1994).

6.6 Marginal fit of zirconia abutments

Even though the marginal gap between the implant replica and abutment was larger in the custom-made copy-milled abutments it did not seem to affect the mechanical strength of the abutment-implant system. It is known that zirconia has a low bacterial colonization potential (Rimondini et al., 2002; Scarano et al., 2004), yet a large gap between the implant and the abutment offers a suitable niche for plaque accumulation and may cause some clinical problems such as peri-implant inflammation (Jansen et al., 1997). The long-term effect of a large marginal gap on the mechanical properties of an implant abutment is unclear. However, there is a growing concern that with poor fit there might be more wear over time on both the titanium implant and the zirconia abutment.

When measuring the marginal fit of the abutment, six measurements per abutment were made. The information of the marginal fit was used in addition to mechanical testing to discover the differences between the groups. More measurements would have been needed if the goal of the study would have been the marginal discrepancies between the groups (Groten et al., 2000). One idea for future study might be more systematic measurement of the marginal fit of zirconia abutments comparing the fit to that of titanium abutments.

6.7 X-ray diffraction analysis

Thermocycling and water storage increased the amount of the monoclinic phase on the surface of zirconia specimens. It has been shown that annealing the zirconia material in water of 65-120 °C tetragonal to monoclinic phase change occurs only on the surface of zirconia (Sato and Shimada, 1985). It is likely that the monoclinic grains were only found on the surface of zirconia in study I, as the phase change did not affect material strength. The monoclinic peaks were not seen in the XRD-chart of unexposed specimens, which confirms the results of previous studies (Ardlin, 2002; Kosmac et al., 2000). In study I, the specimens with shorter sintering time and thermocycling / water storage had a lower ratio of the monoclinic zirconia than specimens that were sintered according to the manufacturer's instructions with thermocycling / water storage. This is due to differences in grain size, as it is known that the bigger the grain size, the more prone the grains are

for transformation (Kosmac et al., 2000; Munoz-Saldana et al., 2003; Tsukuma et al., 1984). Specimens with shorter sintering time had a slightly smaller grain size.

In study II, XRD analysis did not reveal any phase change after coloring of zirconia specimens and no coloring agents were seen on the surface of the zirconia specimens. This, together with EDX analysis of the specimens showed that the color liquids were dispersed as nano-particles inside of the zirconia grain structure.

XRD-analysis was performed to see the possible phase change on the surface of the specimens in study III. Small monoclinic peaks were seen on the surface of the heat treated specimens with coating on the opposite side of the specimen. This might have been due to different thermal expansion co-efficients between zirconia and feldspatic glazing coating. The coating might have caused some residual stresses to the zirconia surface and that might have been the reason for the phase change of the surface grains.

6.8 Future studies and clinical considerations

The results of this series of studies showed that some methods of production, such as coloring, affect the strength of the zirconia. Testing with crown shaped specimens with cyclic loading may have mimicked the clinical situation better and might have given different results. The copy-milling of custom-made zirconia abutments and the shrinkage of zirconia FDPs during coloring in green-stage form might affect the marginal fit of zirconia abutments and FDPs. The marginal misfit of the zirconia abutments was relatively small but increased up to 22 μm with some copy-milled specimens. For disc shaped specimens the difference in shrinkage was 80 μm between control and shaded specimens. The relevance of these differences can only be evaluated under clinical conditions in a long-term study. The diameter of a microbe is on average < 2.0 μm (Callan et al., 2005). The microbial leakage and subsequent bacterial colonization to the marginal gap area can be assumed to happen in all implant-abutment configurations. It would be advisable to keep the gap as small as possible and the same conclusion can be drawn concerning the accuracy of zirconia FDPs. It has to be kept in mind that many of the failures of zirconia FDPs have been shown to be related to porcelain chipping but also failures related to secondary caries caused possibly by marginal discrepancies have been seen (Sailer et al., 2007; Sailer et al., 2006; Tinschert et al., 2008). However, means to decrease the clinical failures of zirconia restorations include clear instructions to clinicians and dental laboratory technicians on the use, cementation and preparation of zirconia structures. Careful treatment planning and handling the material gives better results.

Zhang *et al.* recently introduced a new functionally graded glass/zirconia/glass structure that had improved damage resistance, aesthetics and potentially cementation properties compared to homogenous Y-TZP (Zhang and Kim, 2009). The glass was infiltrated to the surface of pre-sintered zirconia during final sintering. This new material might have potential to solve some of the existing problems with zirconia fixed partial dentures and

crowns and may lead to the development of ultra strong ceramic material for inlays, onlays, crowns and fixed partial dentures.

Another solution for the porcelain chipping problem is the development of monolithic zirconia material. Guess and co-workers (2010) showed that in fatigue IPS e-max lithium-disilicate crowns were more durable than veneered zirconia crowns since the veneering porcelain caused the early failure of zirconia restorations. The zirconia substructure itself is durable but veneering porcelain is the weakest link. Monolithic zirconia material will be the next topic of interest. Zirkonzahn has already developed Zirconia Prettau material that can be used for FDPs without veneering porcelain. The natural color shade and outcome of the crowns can be achieved by painting the crown before sintering.

The long-term effects of possible microbiological leakage and poor marginal fit of zirconia abutments calls for closer attention. In general, more long-term clinical studies are needed to determine whether the phase transformation of zirconia affects material reliability. Within the next 10-15 years we will know how useful and durable zirconia is in the long run.

7. CONCLUSIONS AND SUMMARY

The main findings and conclusions are:

1. Thermocycling or shorter sintering time does not affect the bi-axial flexural strength of zirconia specimens. However, thermocycling and water storage increase the amount of monoclinic phase on the surface of zirconia

2. Some reduction in bi-axial flexural strength is seen when coloring zirconia specimens in green-stage form. Color shading of green-stage material also causes some dimensional changes.

3. Repeated heat treatment does not affect the strength of the zirconia bulk material which is milled in green-stage form but causes some transformation from the tetragonal to the monoclinic phase of zirconia when coating of feldspathic wash or glaze coating is fired on zirconia specimens.

4. Custom-made manually copy-milled zirconia abutments have comparable failure loads to commercially available abutments. The marginal fit of the custom-made abutments is not necessarily as satisfactory as with standard abutments.

These studies suggest that neither different sintering time nor heat treatment affect the strength of zirconia material that has been milled in green-stage form, but coloring the green-stage material affects the strength. They also indicate that the heat treatment process does not affect material strength but even a thin glazing coating on the tension side reduces the strength of the zirconia material. Custom-made zirconia abutments proved to be as durable as commercially available ceramic abutments. Therefore, the hypothesis of these studies was partly verified.

According to the results in these studies, zirconia is a strong dental restorative material and some of the normal treatments in the fabricating procedure do not affect the material properties. However, coloring induced dimensional changes in zirconia, which needs to be taken into account when coloring the substructures made in green-stage form. It is also worth noticing that the marginal fit of the custom-made abutments might not be as satisfactory as the fit of commercially available abutments. Within these limitations, zirconia can still be recommended as a ceramic material for fixed dental prostheses.

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