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CHAPTER 1

Introduction:

Overview on zirconia – basic properties and results on FPDs.

Keywords: zirconia, CAD/CAM, properties, transformation toughening, corrosion, aging, cementation, colour, core treatment, clinical results

The application of zirconia ceramics for the fabrication of fixed partial dentures (FPDs) has expanded rapidly in the last years. The CAD/CAM technology, which is required for the processing of zirconia, has been significantly improved, leading to the achievement of high quality restorations. The number of CAD/CAM manufacturers had increased to about 100 exhibitors at the last Cologne International Dental Show (IDS)[1]. The high diversity in this field warrants an overview of the properties of the different zirconia ceramics and their dental applications.

1.1 General

Zirconia's raw materials are the minerals zircon ($ZrSiO_4$) and baddeleyite ($\beta-ZrO_2$), which are mined in Australia, South Africa, and the USA. Worldwide suppliers are Metoxit (Switzerland) and Tosoh (Japan). The term zirconium refers to the metal, while zirconia ceramic ("zirconia") refers to zirconia-dioxide-ceramic (ZrO_2). Zirconia was identified by the German chemist Martin Heinrich Klaproth in 1789. A first application in orthopedics was described in 1988 [2]. The first dental applications were post systems [3] and fixed partial dentures [4].

1.2 Zirconia Properties

Zirconia has a high temperature stability and melting point ($2680^\circ C$), low thermal conductivity ($<1 \text{ W/mK}$), high thermal expansion ($>10 \times 10^{-6} \text{ 1/K}$), high hardness (1200-1350 HVN), and a good thermo-shock resistance ($\Delta T=400-500^\circ C$). Zirconia is chemically synthesized, for example in a sol-gel process by mixing zirconyl-chloride and yttria tri-chloride. The different stages of polymorph zirconia are temperature dependent: between room temperature and $1170^\circ C$, pure zirconia is stable in a monoclinic (m) phase. Over $1170^\circ C$ it transforms into a tetragonal (t) phase and over $2370^\circ C$ it transforms into a cubic (c) phase. The ceramic shows a hysteretic martensitic $t \rightarrow m$ transformation during heating and cooling. A stress-induced reorientation of the elastic dipoles has been reported, which causes a decrease of the elastic modulus between $100^\circ C$ and $200^\circ C$ [5].

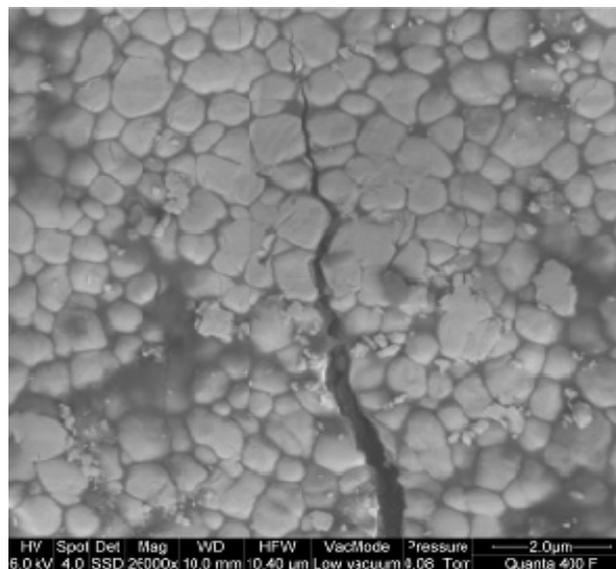
1.3 Transformation toughening

The $t \rightarrow m$ transformation is a diffusionless shear process with a speed near to that of sound. The transformation is associated with a volume change of about 3-5%. In pure zirconia, the volume change leads to cracks and disintegration of monolithic zirconia because the elastic limit and yield strength of the materials are exceeded. The addition of yttria, calcia, or

magnesia (PSZ) causes a delay of the $t \rightarrow m$ transformation, which results in a high strength material. Tangential stress during crack propagation (**Fig. 1.1**) causes a local phase transformation from $t \rightarrow m$, which is combined with a volume increase of about 5%. This pressure results in a local stop of the crack propagation. The process is called transformation toughening, and the resistance against crack propagation increases with the length of the crack (so-called R-curve behaviour) [6]. The type of stabilization allows for the differentiation of three systems:

- Fully stabilized zirconia (FSZ): The cubic phase is stabilized to room temperature by the use of different oxides.
- Partly stabilized zirconia (PSZ): The amount of oxides is reduced, and in addition to the cubic phase, a transformable tetragonal phase is available. Its microstructure at room temperature is mostly cubic with portions of monoclinic and tetragonal phases.
- Tetragonal Zirconia Polycrystals (TZP): The ultra-fine, nanometre-scaled structure allows for the transformation during cooling from the cubic to the tetragonal phase, but not to the monoclinic phase.

Fig. 1.1: Zirconia surface: grain size and crack propagation (magnification 26000x).

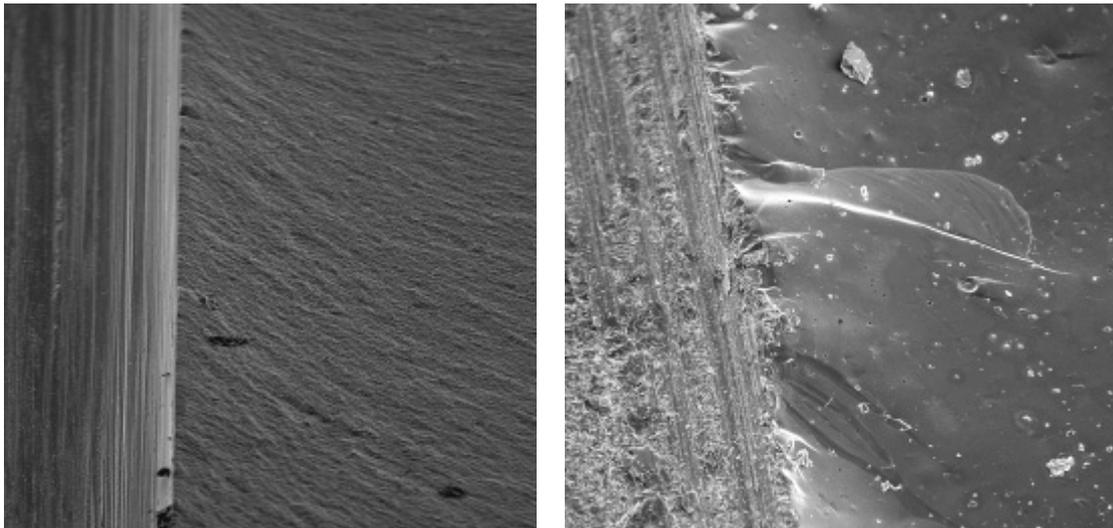


1.4 Mechanical Properties

For the application of materials in medical systems, high toughness (K_{Ic}) and fracture threshold values (K_{I0}) are required [7, 8]. In comparison to glass-ceramics, zirconia materials provide a 10-fold higher strength and fracture toughness [9]. Besides fracture (**Fig. 1.2**),

ceramics fail due to sub-critical crack-growth (SCCG), which is a water-assisted break-down of metal-oxide bonds at the crack tip under applied stress [10]. The flaw size distribution of the ceramic depends on the time and material. Cyclic loading can cause a degradation of the toughening mechanisms [11] and a toughened core material is more susceptible [12-16]. Cracks originate on or close to the veneer-core interface and propagate to the interface [11]. An aqueous environment supports the degradation process [11, 17]. Microscopic cracks can develop without stress in systems if a critical middle grain size is reached: cracks may develop in single phase ceramics because of the anisotropic thermal expansion or in multi-phase systems because of different thermal expansion [18]. The influence of the superficial properties is visible: glossy ceramic does not favour crack growth under cyclic loading [19, 20].

Fig. 1.2: Fracture surface of a notched bar; left side: zirconia, right side: glass-ceramic (magnification 100x).



1.5 Biological factors

Biocompatibility problems, which occurred in the 1990s due to impurities of radioactive Uranium and Thorium [21], are not an issue today. It has been reported that zirconia is not cytotoxic [22-25] and shows no mutagenicity [26-28]. Dust from milling zirconia, in contrast to that of asbestos, may not cause medical problems as the relationship between the length and thickness of the particles is not dangerous, but the published results remain inconclusive [29]. Recycling of the milling dust may be possible.

Besides toxicity, bacterial adhesion is a biological issue because plaque and bacteria layers may be a reason for gingival inflammation and secondary caries. In laboratory tests, the

bacterial adhesion of *S. mutans* and *S. sanguis*, *A. viscosus*, *A. naeslundii* and *P. gingivalis* on zirconia is comparable to that on titanium or even lower [30]. In-vivo, fewer bacteria accumulated on zirconia than on titanium (implant materials) [31], but glazed zirconia showed a higher tendency to accumulate bacteria [32].

1.6 Corrosion and aging

Zirconia is a chemically stable ceramic [33]. The critical chemical solubility of dental ceramics (ISO 6872) is located at a maximum of 100 $\mu\text{g}/\text{cm}^2$, but the available ceramics, including zirconia, reach only about 70% of this value. It has been described that Y-TZP does not suffer from low-temperature degradation [34]. Under different corrosive conditions [19, 35, 36], zirconia has shown reduced strength due to water or moisture, where contamination with SiO_2 may play a role. Yashimura [37] described the stress corrosion reaction between ZrO_2 and water that results in cracks and structural changes. Even autoclaving may cause a decrease of strength of zirconia [38]. Superficial phase transformation due to aging has been reported [33], and the fraction of cubic phases is thought to be responsible for the aging effects [39]. Water that enters into existing cracks may cause internal stress which further results in a crack increase (Rebinder-Effect). Stress corrosion causes a reduction of the energy that is necessary for crack growth. Attachment and interaction of water molecules with the crystalline structure provide the mechanism underlying this reduction [40]. This behaviour is supported by mechanical loadings [41]. Zirconia may be further degraded by the insertion of hydroxyl ions into vacant oxygen areas. These ions induce a phase transformation from t->m, a volume increase, and micro-cracking [42-44]. Nevertheless, after a steep degradation, a further decrease is decelerated [45].

It has been shown that zirconia loses about 10-50% of its strength due to aging and permanent loading [46-48]. After aging, strength results for zirconia were still found to be higher than the strength of conventional glass-ceramics or Alumina-infiltrated ceramics without aging.

1.7 Configuration

For easier fabrication, zirconia is milled in a soft, chalk-like, pre-sintered “green” or “white” configuration. During sintering, the materials undergo an individual volume shrinkage of about 25%. The exact shrinkage information is required for the individual zirconia blank to guarantee optimized fitting of the restoration. Hipped („hot iso-static pressed“) zirconia is an industrially sintered material, which is CAD-milled at its final high strength. Hipped zirconia has a constant grading and thus a more homogeneous quality. As expected, milling time and wear of the milling tools is higher in comparison to the pre-sintered variants. High pressure

during milling of these high strength materials may cause superficial defects or micro-crack development and therefore reduce the above-mentioned advantages. Below are some materials that are fabricated in the different stages:

Milling in white stage: Cercon, Lava, Hint-Els TZP-G, ZirkonZahn, Xavex.

Pre-sintered: YZ-Cubes, ZS-Blanks, Hint-Els TZP-W, DC-Schrink.

Sintered: DC-Zirkon, Z-Blanks, Zirkon TM, Pro 50, Hint-Els TZP-HIP, HIP Zirkon.

Pure zirconia ceramic should not be confounded with zirconia reinforced ceramic (Vita Zirconia), which is an alumina-zirconia infiltrated glass ceramic [49].

1.8 Materials for dental applications

For dental applications, zirconia is stabilized at room temperature with the addition of 3-5 mol% yttria. This configurations reach high strength (800-1200 MPa) and good fracture toughness ($6-15 \text{ MPa} \times \text{m}^{1/2}$) combined with a high reliability (Weibull modulus $m = 10-20$). Different manufacturers provide materials with different amounts of yttria and sizes of the oxides, but the mechanical properties show only small variations. In contrast to metals with equally distributed strength results, ceramic materials show a Weibull distribution of the strength values. This means that the distribution of the values starts at low values, increases to a maximum, and finally shows a steep decrease [50]. The fracture behaviour is strongly influenced not only by fabrication (density, severity, flaws, voids, or cracks), but also by the surface design of the restoration [51].

1.9 The fabrication process: computer aided design and manufacturing (CAD/CAM)

In contrast to that of porcelain fused to metal (PFM), the fabrication of the zirconia framework requires rapid prototyping procedures such as milling or electrophoretic deposition [52]. The different systems use milling-machines in dental laboratories or centralized production centres. The fabrication process starts with optically digitizing the clinical situation with a camera (Cerec) or with 3D-scanning devices using gypsum models or wax-models. In a second step, the framework is designed on the computer (CAD). The construction of simple cores as well as anatomically shaped frameworks that support the later veneering is possible. Due to the geometry of the milling bur, it is actually not possible to mill an anatomic occlusal design with fissures. The design may be reserved for rapid prototyping, such as electrophoretic manufacturing, laser processing [53], or ceramic plotting [54]. Some manufactures (e.g. Amman-Girrbach, Zirkonzahn) provide manual copy-cutting from a model (comparable to key-copying), which is easy to handle and which requires only small investments for the equipment.

1.10 *Influence of manufacturing and design*

The properties of the zirconia cores may be influenced by the manufacturing process. The use of soiled or time-worn burs, as well as insufficient preparations, parallel or divergent design, or even caps with imprecise dimensions / thickness reduce the integrity of zirconia restorations. Pre-application damage may be induced by the false application of fixing devices and canting of the restoration during sintering, not to mention dust or impurities before sintering [55-67]. An effect describes the influence of the number of defects in a single ceramic part: based on the assumption that the number of failures is regularly distributed in a component, a bigger part is assumed to have a higher number of defects, which can cause failure of the whole part. This explains the higher failure probability of a bigger part. The design of the core, whether it is a simple cap or an occlusal supporting design, has a strong influence on the lifetime of the veneering [68-70]. The dimensions and design of FPDs, especially in the connector areas, determine the quality of the all-ceramic restoration [71-78]. Computational methods predict an increased lifetime of FPDs using an optimized bridge design [71, 73, 74, 79]. For the quality of the marginal fit, besides the well-known clinical parameters, the CAD/CAM fabrication process may play a decisive role. Different milling devices, milling strategies, and software capabilities may contribute to the results even more than the different types of ceramic materials. Based on the assumption that the clinically acceptable marginal fit extends to 200 μ m, CAD/CAM fabricated restorations with values between 64-83 μ m and 245 μ m [80-88] are in most cases good to acceptable. The results for the marginal fit are in the range of porcelain-fused-to-metal (PFM) restorations or press-ceramics [89] and vary widely depending on the abilities of the dental technician.

1.11 *Veneering*

The opaque zirconia frameworks are veneered for aesthetic reasons and for the protection of the zirconia against the oral environment. The veneering of the zirconia ceramic may be performed with ceramics using a layering technique, or a press technique, or combination of these techniques. Veneering ceramics in general are glass-ceramic systems used for the veneering of metal supported restorations. Their thermal expansion coefficient (TEC) and firing temperature (FT) must be adapted on the zirconia framework. The TEC of the core is slightly greater than that of the veneering, which causes a compression of the veneering in the core due to cooling contraction. Cut back or press over techniques and combinations contribute to the large variety of veneering possibilities. Further on, zirconia may even be veneered with composite [90]. Insufficient veneering design as well as impurities or inclusions between the framework and the veneering may cause defects or crack propagation,

which may result in chipping of the veneer. Tensile investigations have shown good bonding properties between the framework and veneering [91] that are comparable to the bonding properties between veneering ceramic and metal framework. The thickness of the veneering influences the strength of the FPDs [92] for which a constant veneering thickness helps to create an equal distribution of the chewing force [93]. An optimal veneering has been shown to improve the strength of the whole FPD [94]. Contradictory results have been reported by Beuer [95] and Flemming [96], who reported no influence of the veneering thickness on the fracture force. Repeated firing of the veneering may lead to an increase of the TEC (due to increased concentration of leucite) and changes in the crack formation [97, 98].

In-vitro bond strength investigations [99-101] between the core and veneering have demonstrated the influence of the thermal expansion coefficient, zirconia transformation, and sintering temperature, respectively. The influence of veneer thickness [68], the pre-treatment of the core [63, 102], and the roughness of the veneering [103] have been discussed. The failure mode between the zirconia core and veneering is thought to be predominantly interfacial [100, 104], but exceptions have been found on FPDs [105]. During the mechanical loading, local occlusal stress may superpose with global compressive residual stress resulting in lateral cracks and chipping [106]. Veneering ceramic with a small reliability (m about $1 \text{ MPa} \times m^{1/2}$) may be affected especially with pre-existing bulk or surface defects [58, 107]. The high strength of the core material may be offset by veneering with weaker glass-ceramic materials [108]. Detailed failure models of dental layer structures have been described previously [109-113].

1.12 Core treatment

The pre-treatment of the core before veneering or insertion has been widely discussed. In general, the framework should be free from grease and dust. A chemical bonding between the core and glass-ceramic veneering may not be achieved. In contrast to glass ceramics, no surface roughing is provided by etching the zirconia surface. While some manufacturers recommend roughening with sandblasting (Aluminiumoxide $110 \mu\text{m}$; DeguDent) or tribochemical (silicating and silanizing) treatment (3M Espe) [114], some manufacturers report that it is unnecessary to treat the core (Vita Zahnfabrik). A superficial treatment like sandblasting may cause a short term strength increase [62, 64], but strength reduction in combination with cyclic loading is thought to develop in the long term [60, 61, 115]. When high pressure or coarse grained particles are used for sandblasting, the zirconia surface is damaged. Cracks are induced by toughening effects during sandblasting [58]. Sandblasting causes compression stress into the damage layer ($t \rightarrow m$ transition) [116] and additional micro-cracks [117, 118]. Later on, flaws may have the nature of micro-cracks [57, 64]. The

resulting damage is dependent on the severity of the sandblasting. It was concluded that slow crack growth degenerated zirconia by about 10-30%. Earlier studies reported an approximately 2-4 times reduction [119]. Grinding caused a $t \rightarrow m$ transition and an increase in strength as well as hardness [34, 57, 63, 64, 120], with rhombohedral and tetragonal zirconia on the surface. However, grinding and polishing also resulted in superficial damage, which is associated with long-term fatigue behaviour [120]. It has been suggested that the framework should be annealed by baking at 1000°C for one hour [120], but this treatment may also reduce an earlier induced strength increase due to sandblasting [63]. A selective infiltration etching technique [121] and thin superficial glass-layers have been proposed to improve the bonding between the core and veneering.

1.13 Colour

Pure zirconia is translucent, but additives such as oxides (rare earth) result in yellow or black colours after a reduction baking. The atmosphere during sintering (HIP) generates black or greyish ceramics: a subsequent annealing in an air atmosphere reduces these colour effects. Small amounts of trace elements are responsible for the colour of zirconia, but stabilization reduces these effects [122]. Metallic oxides [33] have been used for staining the zirconia frameworks directly by the manufacturer (Cercon Base) or individually by the technician (Lava), but ferric components can lower the sintering temperature of a ceramic. It has been reported that the coloured blanks in some cases showed higher strength values than the comparable white blanks [33, 123]. The opacity of zirconia prevents a highly aesthetic appearance like that of glass ceramics, but it may allow for masking of dichromatic abutment teeth [27]. The light transmission of zirconia is lower compared to glass-ceramic systems [124]. The opacity of zirconia rises from 65% at a thickness of 0.5 mm to 85% at a thickness of 1.5 mm [125].

1.14 Cementation

The high strength of the zirconia framework may allow for adhesive bonding or conventional cementation. The bonding between zirconia and adhesive resin cements have been discussed in detail. The core treatment before cementation follows the same requirements as the treatment before veneering. The rough surface due to the manufacturing process may promote an additional micromechanical interlocking of the luting agent [114]. In some cases, for the application of silicating / silanization, good bonding results have been reported [126], but this bond fails with increasing storage time due to hydrolysis [127-129]. Other pre-treatment methods are plasma spray treatment, addition of low fusing porcelain layers [130],

tribochemical silica coating (Rocatec, 3M-Espe) [114, 128], or the use of phosphate acid ester monomers [129, 131]. Nevertheless, sufficient bonding after long term storage was found only for cements that contain phosphate-groups [131, 132]. In-vitro tests showed advantages of adhesive bonding [127, 132, 133] even in combination with an insufficient preparation height or low preparation angle [134]. The application of self-adhesive cements is promising. The opaque core may hinder the application of light-curing systems: therefore, dual or chemical curing systems should be preferred [132]. Contamination during try-in may reduce bond strength [135].

1.15 Fracture resistance on in-vitro restorations

A large number of laboratory investigations were performed to determine the strength of different FPDs under varying laboratory conditions. The failure pattern of 3- to 4-unit FPDs has been described in various investigations [74, 76, 136].

4-unit FPDs were investigated with and without crack initiation. Most of the failures that occurred were due to cracking of the veneering ceramic, in some cases the failures were due to the framework [137]. Significantly different results were found for a green-sintered zirconia (Cercon (904-921 N)) in comparison with a hipped material (Digizon (1132-1263 N) [137]. Tinschert [94] determined a fracture force of 1382 N for a plain zirconia 4-unit framework (DC Zirkon) and an increase of the fracture force to 1607 N for veneered FPDs, when the tests were performed without aging. They compared the fracture resistance of different types of all-ceramic systems. Rountree [138] reported a force of about 930-979 N for 4-unit FPDs after laboratory aging of the restorations.

Rosentritt investigated 3-unit Lava FPDs [139] and found fracture values of 1000 N. Stiesch-Scholz [140] reported values between 1266 N and 927 N for Lava FPDs. Lüthy [141] tested Cercon FPDs with a reduced framework of 7.3 mm² and reported fracture values of about 706 N. High fracture values were found with mechanical loading without any resilience of the abutment teeth (2237 N for Denzir [142]; 1900 N Vita YZ; 1450 N Denzir M [143]). Stamouli [144] found fracture values for restorations with/without aging: 1256/1522 N (Procera), 1618/1683 N (DC Zirkon), and 1556/1702 N (Vita YZ). Filser investigated 3-unit DCM frameworks and found fracture values of about 1000 N [4]. Att *et al.* reported median values between 1394 N and 2131 N, without significant differences before and after aging [145, 146].

Ceramic crowns in generally fail due to cracks beginning in the occlusal and cementation surfaces [60, 61, 93, 111, 112, 115, 147]. Cementation areas were reported to be especially sensitive, because the cracks can propagate to the margins and split the crowns. Flexure of the crown may occur due to the relatively docile dentin. Thus, the crown's inner surface is under

tension and flaws can start from the cementation surface [119, 148]. Fractographic analysis was used to compare clinical and laboratory failure behaviour of all-ceramic systems [74, 149, 150]. It has been found that superficial occlusal wear was one reason for chipping. Scherrer and Quinn performed some fractographic investigations in order to understand the cause of clinical failure of crowns. De Jager provided some finite element analyses to improve the design of all-ceramic crowns [68, 69], and Rekow *et al.* reported on variables that influence the strength of crowns [151]. Sundh underlined the necessity of an anatomical coping for supporting the veneering ceramic [105]. For the crown application, zirconia showed a fracture resistance that is comparable to porcelain-fused-to metal or adhesively bonded all-ceramics.

1.16 Clinical results

Clinical data are currently available over a period of about five years (**Table 1.1**) with survival rates between 89% and 100%. Nevertheless, the published data showed small variation in identical studies but after different periods of reporting. Compared to survival rates of PFM restorations of 96% (5 years) and of 87% (10 years), zirconia restorations had only somewhat higher failure rates. The high strength core exhibited no fractures or failures. Only in individual cases, which were under the dimension requirements or which did not meet the indications, were a few rare failures found. Especially in the beginning, when the first zirconia restorations were launched on the market, high chipping rates were reported with these early and maybe not well-adapted veneering ceramics. Beyond this, a reason for chipping is the core design: although connector areas of about 9mm² may be sufficient to withstand the oral loadings [141], only an occlusal supporting core design may help for avoiding chipping of the relatively weak veneering ceramic. Early in-vivo data [152] was reported concerning about 22 adhesively luted three-unit FPDs (DCM) without any failures after a short observation period of only one year. Von Steyern [153] provided data about 23 three-unit FPDs with 15% smaller chippings of an experimental veneering ceramic after two years. Pospiech *et al.* [154] investigated 38 three-unit FPDs made of Lava zirconia (3M Espe) and found only one chipping after one year. They found no further chipping after three years with the remaining 35 restorations. Fifty-nine Cercon FPDs, in these cases with an early veneering ceramic, showed survival rates between 96-100%. The FPDs were affected only by some minor chippings [155]. Zembic [156] investigated 58 adhesively luted zirconia FPDs, which replaced 1-3 posterior teeth. After two years, 29 FPDs had no fractures of the framework, but 10% showed chipping and 8% had biological complications. After 3 years, 18 FPDs were investigated with one biological consequence, two cementation problems, and five chippings. In both cases, 18% marginal discrepancies were found. Raigrowski [157]

investigated 20 three-unit FPDs over a period of 31.2 months and showed five chippings. Tinschert *et al.* [158] investigated 20 three-unit and 6 four-unit FPDs (DCS) with Zinc oxide phosphate cementation and found no failures after one year. The same authors [159] published data after 15.5 months on 36 posterior and 10 anterior FPDs (with GIC) and found 2.5% of the FPDs with chipping. After three years, the chipping rate increased to 6% on 33 three-unit, 14 four-unit, and three 5-unit FPDs. Sailer *et al.* [160, 161] investigated 58 three- to five-unit DCM FPDs over a period up to five years and found 11% chipping after three years. After five years, they found a survival rate of 93.3%. Molin [162] provided results of the in-vivo investigation of 18 posterior and 1 anterior restoration after two years (Denzir) and found a survival rate of only 67%. In contrast to pure zirconia FPDs, zirconia infiltrated ceramic restorations did not provide sufficient strength for application in posterior areas: in a study by Suarez [163], 18 restorations failed after three years because of fracture.

Table 1.2: Clinical survival rates of different zirconia restorations.

Author	Material	Type of Restoration	Observation Time	Survival Rate
Sturzenegger [152]	DCM	3-unit FPDs	1 Year	100%
Tinschert [158]	DCS	3-unit FPDs 4-unit FPDs	1 Year	100%
Tinschert [159]	DC Zirkon, DCS	3-5-unit FPDs	3 Years	94%
Pospiech [154]	Lava	Divers Restorations	3 Years	100%
Zembic [156]	Cercon	3-5-unit FPDs	2 Years	93%
Sailer [160]	Cercon	3-5-unit FPDs	3 Years	83%
Sailer [161]	Cercon	Divers restorations	3 Years	87%
Bornemann [155]	Cercon	3-4-unit FPDs	½ Year	96,5%
Molin [162]	Denzir	18 posterior/ 1 anterior restorations	2 Years	67%
v. Steyern [153]	DC Zirkon	3-unit FPDs	1 Year	85%

1.17 Outlook and Summary

Alternative and minimally-invasive restorations have been investigated and may be promising PFM alternatives, assuming the bonding is improved [164]. Some authors have reported good results with single unit cantilever bridges [165-167]. Monaco [168] published results regarding inlay-retained FPDs. Pre-fabricated slot-bridges [90] were clinically described. There were some basic investigations about removable dentures with zirconia abutments [69, 170]. The high strength of zirconia allows for the fabrication of implants [171-175] and implant abutments [176], which may, however, be sensitive to fracture because of their angular design. In-vitro and in-vivo results indicate that fixed partial dentures made of zirconia may be an alternative for metal-supported restorations. The majority of clinical failures, which involve chipping of the veneering, may be avoided with adequate occlusal supported core design and optimized adaptation of the veneering.

1.18 Scope and content of this thesis

As described, zirconia and CAD/CAM manufacturing have gained increasing interest in dental society for the fabrication of metal-free restorations. The commercially available CAD/CAM devices up to now have not allowed for the fabrication of the zirconia restorations with a final occlusal design. This is one reason why the cores are veneered with glass-ceramics, which provide further protection and good aesthetics for the restoration.

The idea of this thesis is based on the observations of various clinical studies [152-163] that describe a high prevalence of veneer chipping on restorations with a zirconia framework. Three different scenarios for failure are possible: cracks, which evolve in the glass-ceramic, may run in between the border core-veneering (interfacial chipping), may remain in a superficial layer of the veneering (chipping), or may even jump over into the core (fracture). Based on these ideas, the veneering surface, the interface and interaction veneer-core, and the core itself may contribute to the performance of the restorations.

The combination of a “weak” glass ceramic ($E < 100 \text{ GPa}$) with the high strength zirconia ($E \approx 200 \text{ GPa}$) may especially influence the stability of the FPD [99]. Therefore, the core material and veneering had to be adapted, for example, in the thermal expansion coefficient and firing temperature to achieve optimal bonding. During baking of the veneering, small differences between the expansion coefficients cause tensile stress on the ceramic, which contributes to the bond between the glass-ceramic and core. The application of opaquer as a stress-brake is reported to improve the bonding between zirconia and layering glass ceramic, but the combination of opaquer and press veneering has been reported as detrimental to bonding results [99]. In the two-layer system core-veneering, tensile or compressive stress

may develop further due to different relaxation mechanisms [113]. Overall, in-vitro investigations showed good to sufficient bonding between zirconia and glass-ceramic [99, 100, 102], but thermal treatment during veneering may cause stress in the ceramic compound. Although temperature loadings up to 250°C [177] do not have any influence the structure of zirconia, the heat treatment during veneering may have an influence on the stress distribution. Sandblasting before veneering or cementation, which reduces superficial defects or milling traces, may be assumed to be responsible for further internal stress due to surface damage and microcracks. A moist environment supports the degradation [11, 17], and the crack increase may be further accelerated. Stress may finally result in chipping of the veneering.

In addition to the bonding factors concerning the interface between the core and veneering, the design of a restoration may influence the performance of a fixed partial denture. The thickness of the core especially determines the strength of the whole restoration, and its shape defines the support of the “weak” veneering. A consistent thickness of the veneering is a result of an optimized core design and may help to reduce chipping. Ceramic materials are susceptible to tensile and bending stress, and therefore, the location in which different thick veneer layers are placed (on top means under pressure and on the bottom means under tensile stress) may have a of significant influence on the strength of the restoration [108]. In contrast to crowns, bridges may be especially exposed to bending stress due to the individual mobility of the abutments. Considering a dental restoration, superficial wear or local disruption may be an additional reason for chipping. This repeated occlusal loading in the contact areas can be simulated with oral environments. This underlines why structural testing on dental restorations may be of further interest in materials research. In this context, the influence of cementation on the failure behaviour and marginal performance of zirconia restorations, which, in contrast to glass-ceramic restorations, require no adhesive bonding, must also be investigated.

The above factors emphasize the scope of this thesis for further investigations on zirconia, the improvement of all-ceramic zirconia restorations, and especially the interaction of zirconia and veneering and its influence on the performance of the whole restoration.

The introduction, **chapter 1**, gave a literature overview on zirconia ceramics.

In **chapter 2**, details about the interplay between high strength zirconia and comparable low strength glass-ceramic veneer were investigated. The influence of veneering in press- and layering techniques was studied. In this context, the influence of treatment and aging of zirconia on the dynamic modulus was investigated. All tests were performed with dynamic mechanical analysis.

Chapter 3 is based on the idea that the results on laboratory specimens like bars may not be translated directly to clinical restorations. The failure behaviour of zirconia restorations was investigated in a clinical simulation, and the failure rates were compared to clinical data. The fracture resistance after simulation was used to estimate the influence of artificial aging.

Based on the results of chapter 3, the influence of different types of veneering on the fracture resistance of three-unit fixed partial dentures (FPDs) was investigated in **chapter 4**. The restorations were fabricated with different veneering ceramics, which varied especially in firing temperature and thermal expansion coefficients.

Chapter 5 develops this topic further by investigating the influence of a special framework design, which improves the occlusal support of the ceramic veneering and which is thought to reduce chipping problems. Alternative veneering in the press-technique was compared to conventional layering methods. Special zirconia surface treatments were tested, which should allow for the replacement of ceramic veneering by composite material.

Whereas the earlier investigations were performed on only one zirconia material, **chapter 6** deals with the comparison of the fracture resistance of various available zirconia systems. It should be evaluated whether there is an influence of the type of zirconia on the survival rate or fracture resistance of three-unit FPDs. The effect of adhesive bonding and conventional cementation on the fracture resistance was included.

Chapter 7 expanded the idea of investigating zirconia FPDs on the examination of various crown systems with different cementation. Crowns instead of FPDs were investigated because they factor out torsion as a reason for chipping or failure of FPDs, therefore supporting the suggestion of ceramic wear and damage as a reason for failure. Therefore, aspects of fractography in relation to crown size were tested.

Based on the earlier results, where it was found that both types of cementation (adhesive and conventional) result in comparably good fracture resistance, **chapter 8** dealt with the investigation of the bonding strength between zirconia and different cements, especially so-called self-adhesive cements. Bond strength was determined even after a long-term storage.

Chapter 9 revives the proposal of minimizing failures due to chipping by omitting the veneering on the zirconia framework. The framework may be deliberately exposed, for example, in the connector area in order to increase the zirconia connector cross section. On the other hand, grinding, which is applied for adjusting the occlusal fit, may accidentally expose the underlying zirconia framework. The question of whether an exposed zirconia framework is more susceptible to bacterial adhesion than a veneering ceramic was addressed.

All chapters can be read independently because they have been written in a form which suited for publication in international scientific journals.

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