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# Influence of the surface and heat treatment on the flexural strength and reliability of Y-TZP dental ceramic

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To my beloved parents and brother for their constant support and understanding

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## 1. Introduction

Since many decades metal-ceramic restorations represent the most popular and successful solution for restoring extensively damaged teeth or replacing missing ones. Clinical studies show a survival rate of metal-ceramic restorations of about 90% after a period of 10 years (Creugers *et al.*, 1994; Scurria *et al.*, 1998; Lang *et al.*, 2004). On the other hand, metal frameworks have inherent disadvantages, such as material corrosion and discoloration of gingival tissues adjacent to the crown margins (Riley EJ, 1977).

The last two decades all-ceramic restorations have been increasingly gaining acceptance. Ceramic materials can successfully replicate the esthetic qualities of natural teeth (Webber *et al.*, 2003). Furthermore they show better biocompatibility and low plaque accumulation (Campbell and Sozio, 1988) and have low thermal conductivity (Tinschert *et al.*, 2001a). However, despite their strength under compression, they are brittle materials with limited tensile strength, which limits their indications (Pröbster and Diehl, 1992; Piconi *et al.*, 1998; Lawn *et al.*, 2001).

At first all-ceramic restorations were used for inlays and later the indications were expanded to onlays, partial crowns and veneers and single front crowns. Later stronger materials like silicium-dioxide glass-ceramic (IPS Empress® 2, Ivoclar Vivadent, Lichtenstein), or glass-infiltrated alumina In-Ceram® Alumina (Vita, D-Bad-Säckingen) were introduced to the market, which were also appropriate for small front teeth bridges.

Today different materials are available for all-ceramic restorations. The mechanical properties of recently developed high-strength ceramics make them appropriate as core materials for all-ceramic restorations (Tinschert *et al.*, 2001b) and together with the constant development of CAD/CAM technologies promise a new era in restorative dentistry.

Zirconia holds a unique place amongst oxide ceramics due to its excellent mechanical properties (Denry and Kelly, 2008), which are attributed to the transformation toughening mechanism, similar to that exploited in quenched steel (Kosmac *et al.*, 1999). The interest in the material zirconia is increasing because of its strength and recent improvements in CAD/CAM technologies. Today, zirconia is being manufactured under optimized industrial conditions and can be designed for its processing by computer-aided design/manufacturing (CAD/CAM) technologies (Tinschert et al. 2001b) so that high quality all-ceramic restorations can be produced for teeth and implants (Meyenberg *et al.*, 1995; Luthardt *et al.*, 1998). However, it is essential, that its properties, the effect of different treatments and the long-term behavior of the material are first evaluated in-vitro and in clinical conditions, in order to optimize the fabrication procedures and be able to use zirconia with safety in the daily practice.

## 2. Literature Review

### 2.1 History/ Evolution of dental ceramics

At all times people have tried to fabricate tooth restorations using tooth colored minerals, but it was the control of the porcelain manufacturing in Europe at the beginning of the 18th century, which accelerated the use of ceramics in dentistry and dental technology (Kelly *et al.*, 1996). Traditional porcelain is a blend of three minerals: quartz, feldspar and pure white clay ($Al_2O_3 \cdot 2SiO_2 \cdot xH_2O$). In order to produce various shades and translucencies, pigments and opacifying agents are added to porcelain. After baking, the material contains small leucite crystals and/or alumino-silicate crystals embedded in a silicate glass (a non-crystalline, amorphous matrix). Leucite, a reaction product of potassium feldspar and glass, is responsible for the optical properties, thermal expansion, strength and hardness of porcelain (Rosenblum and Schulman, 1997).

In 1723, Piere Fauchard was credited with recognizing the potential of porcelain enamels and initiating research with porcelains to imitate the color of teeth and gingival tissues (Jones, 1985). In 1774, Alexis Duchateau and Nicholas Dubois de Chemant fabricated the first successful porcelain dentures. Dubois de Chemant, who improved porcelain formulations continually during his scientific career, was awarded both French and British patents. In 1808, in Paris, Giuseppangelo Fonzi introduced individually-formed porcelain teeth that contained embedded platinum pins. Their esthetic and mechanical versatility provided a major advance in prosthetic dentistry.

At the beginning of the nineteenth century Charles Henry Land developed the porcelain jacket crown, based on a feldspathic composition, which is still used today in a slightly modified form. Jacket crowns were the only fixed esthetic restorations available at that time (Freese, 1959). Despite their esthetic advantages, the restorations failed to gain widespread popularity because of their high probability of fracture, low strength and poor marginal seal. This technique went out of fashion once the metal-ceramic era began (Jones, 1985). Several attempts were undertaken throughout time to improve porcelains. In the late 1940's firing of porcelain under vacuum reduced porosities and improved the esthetic appearance of ceramic restorations (Jones, 1985). The introduction of gap-graded finer porcelain powders with better packing densities made carving and layering of green porcelain easier and improved the esthetics. A noteworthy development occurred in the 1950s, with the addition of leucite to porcelain formulations that elevated the coefficient of thermal expansion to allow their fusion to certain gold alloys to form complete crowns and fixed partial dentures (FPDs)  (McLean, 2001).

Refinements in metal-ceramic systems dominated dental ceramics research during the past 35 years and resulted in improved alloys, porcelain-metal bonding and porcelains (Kelly *et al.*, 1996). In the 1960's, following the era of plastic restorations, a return by the dental profession was made to the use of ceramics for crown and bridge fabrications (McLean and Hughes, 1965). Porcelain crowns and pontics were constructed from copings of gold with cemented porcelain facings or from gold alloys veneered with low-fusing porcelain. The unsightly appearance of gold margins was considered a shortcoming (McLean and Hughes, 1965).

In 1965, McLean and Hughes performed a study on the reinforcement of dental porcelain with ceramic oxides. They found that the use of alumina crystals as a reinforcing phase (40-50%vol) in a glass matrix provides a substantial improvement in the mechanical properties of fired specimens that reach a flexural strength of 130 MPa. In their study, various techniques of reinforcement of porcelain were used. The most significant effect was achieved by the use of an already sintered alumina core (97% consistency in alumina crystals) veneered with enamel porcelain. The maximum breaking stress value was five times higher than that of conventional dental porcelains. The authors stated that this principle could be adapted for the fabrication of pontics (McLean and Hughes, 1965). Prefabricated alumina backings, veneered with aluminous porcelain (Vitadur-N) and cemented onto the gold framework of the FPDs, were used for the fabrication of pontics (McLean, 1967). In 1968, MacCulloch was the first to use glass ceramics in dentistry (McLean, 2001). The interest in esthetic all-ceramic restorations was renewed with the introduction of a castable glass ceramic (Dicor, Dentsply/York Division, York, Penn., USA). The material contained tetrasilic fluormica crystals that increased the strength and the resistance to crack propagation. Despite the enhanced mechanical properties, the material was not strong enough for the fabrication of posterior all-ceramic FPDs (Schwickerath, 1986b).

In the mid-1970s, special shoulder porcelain masses were developed and applied in collarless metal-ceramic restorations to overcome the esthetic problems of metal-ceramic restorations (Riley EJ, 1977; McLean, 2001).

In 1982, McLean introduced the platinum foil-reinforced alumina FPD, in order to reduce the frequent problem of fracture at the connector area. Oxidation of the tin coating provided a mechanism for bonding of porcelain and the traditional cast-metal framework was eliminated. Its application was recommended only for the replacement of single anterior teeth (McLean, 2001). Because of the high failure rate at the connector sites, this restorative option was not feasible for the fabrication of bridges and was limited to the fabrication of jacket crowns (Rosenblum and Schulman, 1997).

In the past two decades, several approaches have been suggested to enhance the strength of ceramics. These approaches have generated toughened ceramics with microstructure that substantially differs from that of conventional feldspathic porcelains. Their common feature is a considerable crystalline phase in the glassy matrix that contributes to their physical, mechanical and optical properties. Particle size and distribution, nature and amount of the crystalline phase affect the fracture behavior of these ceramics. In addition, mismatches in thermal expansion coefficients among various phases can cause localized stresses at phase boundaries improving the overall toughness (Seghi and Sorensen, 1995).

In 1989, In-Ceram Alumina glass-infiltrated ceramics (Vita Zahnfabrik, Bad Sackingen, Germany) were introduced. The material has a 70% crystalline content in its mass. This made it possible to fabricate frameworks for three-unit anterior FPDs (Kappert and Krah, 2001). In 1991 IPS-Empress® (Ivoclar-Vivadent, Schaan, Liechtenstein), which uses the principle of leucite crystal dispersion, was brought to the market. The later developed IPS Empress® 2 (Ivoclar-Vivadent, Schaan, Liechtenstein), a lithium disilicate glass ceramic with 66% crystalline content, showed a flexural strength 3 times greater than that of Empress® 1. The sintered, high alumina-content glass-infiltrated ceramic core material (In-CeramAlumina) and the recently developed lithium disilicate glass-ceramic (Empress 2), respectively are recommended for anterior fixed partial dentures (FPDs) (Scotti *et al.*, 1995; Sorensen *et al.*, 1998) and three-unit FPDs replacing the first premolar (Sorensen *et al.*, 1998; Edelhoff *et al.*, 1999).

Further efforts to enhance the strength of ceramic cores were made by adding leucite (Optec HSP, Jeneric/Pentron, Wallingford, USA), aluminium oxide (Hi-Ceram, Vita Zahnfabrik), or zirconium dioxide crystals (Mirage II, Mirage Dental Systems, Chameleon Dental) to conventional feldspathic porcelains. However, the resultant ceramic did not meet the requirements for the fabrication of posterior FPDs (Tinschert *et al.*, 2001b).

Alumina- and Zirconia-based ceramics are the most recent core materials for all-ceramic crowns and FPDs. Because of their outstanding loading capacity, these materials seem to be promising in their potential applications (Luthardt *et al.*, 1998; Tinschert *et al.*, 2000a; Tinschert *et al.*, 2000b; Tinschert *et al.*, 2001a; Luthardt *et al.*, 2001a).

## 2.2 Composition and properties of dental ceramics

Dental ceramics consist of a compound of metals (aluminium, calcium, lithium, magnesium, potassium, sodium, tin, titanium, and zirconium) and nonmetals (silicon, boron, fluorine, and oxygen) that may be used as a single structural component, such as when used for a CAD-CAM inlay, or as one of several layers used for the fabrication of a ceramic-based restoration.

Conventional dental porcelain is a vitreous ceramic based on a silica ($SiO_2$) network and potash feldspar ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$), soda feldspar ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$) or both. Pigments, opacifiers and glasses are added to control the fusion temperature, sintering temperature, thermal contraction coefficient, and solubility. The feldspars used for dental porcelains are relatively pure and colorless. Therefore, pigments must be added to produce the shades of natural teeth (Anusavice, 2003). Most of the ceramics are characterized by their refractory nature, hardness, and chemical inertness. A hardness of a ceramic similar to that of the enamel is desirable to minimize the wear of the ceramic restoration as well as of the enamel. These materials are abrasion-resistant and relatively chemically inert and insoluble and thus fully biocompatible and neutral to other restoration materials in the mouth. The mineral building-blocks of the ceramics can be selected and adjusted in such a way, that ideal optical properties are achieved in order to reproduce in a restoration the full range of natural tooth shades (Kunzelmann *et al.*, 2006), making thus great esthetics the most attractive property of ceramics (Anusavice, 2003). Furthermore, ceramics demonstrate excellent insulating properties, such as low thermal conductivity, low thermal diffusivity, and low electrical conductivity.

On the other hand, a characteristic property of ceramics is their brittleness and the lower fracture toughness and flexural strength compared to metals, especially when flaws and tensile stresses coexist in the same region of the restoration (Kunzelmann *et al.*, 2006). This flaw may be a surface microcrack created by occlusal adjustments or a subsurface porosity by a processing mistake during the fabrication of the restauration. (Rosenblum and Schulman, 1997).

When tension stress is applied, small flaws tend to open up and propagate cracks (crack propagation theory) (O' Brian W.J., 2002). Irregularities in a bulk of the material, such as discontinuities and/or abrupt changes in shape or thickness in the ceramic contour, act as stress raisers, making the restoration more prone to failure. Stress around a stress raiser is higher than the average stress in the body of the material. Because of the stress concentration at surface scratches and other defects (brittleness), ceramics tend to fail at stress levels that are much lower than the theoretical strength to be tolerated.

Compared to metals, which can yield to high stress by deforming plastically, ceramics tend to have no mechanism for yielding to stress without fracture (O' Brian W.J., 2002). Therefore, cracks may propagate through a ceramic material at low average stress levels. As a result, ceramics and glasses have lower tensile strengths than compressive strengths (O' Brian W.J., 2002).

## 2.3 Mechanisms of increasing the fracture resistance of ceramics

i) Development of residual compressive stresses:

The thermal expansion coefficient (CTE) of the core ceramic is slightly greater than that of the veneering ceramic. This mismatch allows the core material to contract slightly more upon cooling from the firing temperature to room temperature, and leave the veneering ceramic in residual compression while offering additional strength (Mackert, 1988).

ii) Minimize the number of firing cycles:

Firing procedures sinter the particles densely together and produce a relatively smooth surface. In addition, they increase the concentration of leucites in the porcelain, which in turn leads to an increase of the TEC and a further mismatch between core/veneering porcelain. This mismatch will cause immediate or delayed crack formation in the porcelain (Mackert, 1988; Mackert and Evans, 1991; Fairhurst *et al.*, 1992).

iii) Minimize tensile stress through optimal design of ceramic restorations:

Dental restorations containing ceramics should be designed in a way to overcome their weaknesses. The design should avoid exposure of the ceramic to high tensile stresses (Anusavice, 2003). In the case of a crown, tensile stresses can be reduced by using strong core materials with appropriate thickness, since these stresses are distributed on the inner surface (the core material is in tension) (Kelly, 1995; Zeng *et al.*, 1996; Lawn *et al.*, 2001).

iv) Ion Exchange (or chemical tempering):

This process involves the exchange of larger potassium ions for the smaller sodium ions (a common constituent of a variety of glasses) (Anusavice *et al.*, 1992). If a sodium-containing glass article is placed in a bath of molten potassium nitrate, potassium ions in the bath exchange places with some of the sodium ions on the surface of the glass particles. The potassium ion is about 35% larger than the sodium ion. Squeezing of the potassium ion into the place formerly occupied by the sodium ion creates large residual compressive stresses in the surfaces of the glasses subjected to this treatment. However, the depth of the compression zone is less than 100 µm, so that this effect would be easily worn out after long–term exposure to certain inorganic acids (Anusavice *et al.*, 1992; Seghi *et al.*, 1995).

### v) Thermal Tempering:

This is a process of creating residual surface compressive stresses by rapidly cooling the surface of the object while it is hot and in the softened (molten) state. This rapid cooling produces a skin of rigid glass surrounding a soft (molten) core. As the molten core solidifies˜ it tends to shrink, but the outer skin remains rigid. The pull of the solidifying molten core, as it shrinks, creates residual tensile stresses in the core and residual compressive stresses within the outer surface, inhibiting the initiation and the growth of cracks (Anusavice, 1991; De Hoff, 1992).

### vi) Dispersion strengthening:

This involves the reinforcement of ceramics with a dispersed phase of a different material that is capable of hindering a crack from propagating. Dental ceramics containing primarily a glass phase can be strengthened by increasing the crystal content of leucite, lithium disilicate, alumina, magnesia-alumina spinell, zirconia and other types of crystals (McLean and Hughes, 1965).

When a tough, crystalline material such as alumina ($Al_2O_3$) is added to a glass, the glass is toughened and strengthened, because the crack cannot pass through the alumina particles as easily as it can pass through the glass matrix (McLean and Hughes, 1965; Jones, 1983).

The amount of toughening depends on the crystal type, its size, its volume fraction, the interparticle spacing, and its relative thermal expansion coefficient to the glass matrix. In most instances, the use of a dispersed crystalline phase to disrupt crack propagation requires a close match between the thermal contraction coefficients of the crystalline material and the surrounding glass matrix (Jones, 1983).

### vii) Transformation toughening:

The dispersion strengthening process relies on the toughness of the particle to absorb energy from the crack and deplete its driving force for propagation. The transformation toughening process relies on a crystal structural change of a material under stress to absorb energy from the crack (Morena, 1986). Zirconia ($ZrO_2$) ceramic is a good example for this mechanism. The material is polymorph occurring in three forms: monoclinic (M), tetragonal (T) and cubic (C). Pure zirconia is monoclinic in room temperature. This phase is stable up to 1170°C. Above this temperature it transforms into tetragonal and then into a cubic phase at 2370°C. When $ZrO_2$ is heated above 1170°C, the transformation from the monoclinic to the tetragonal phase is associated with a 5% volume decrease. Reversely, during cooling, the transformation from the tetragonal to the monoclinic phase is associated with a 3% volume expansion. These phase transformations, however, induce stresses which result in crack formations. The inhibition of these transformations can be achieved by adding stabilizing oxides

(CaO, MgO, $Y_2O_3$), which allow the existence of tetragonal-phase particles at room temperature. When sufficient stress develops in the tetragonal structure and a crack in the area begins to propagate, the tetragonal grains transform to monoclinic grains. The associated volume expansion results in compressive stresses at the edge of the crack front and extra energy is required for the crack to propagate further (Tateishi and Yunoki, 1987).

## 2.4 Classification of high-strength all-ceramic systems

From a chemical perspective, a ceramic is an inorganic, non-metallic material, whose interatomic bonding is covalent or ionic. The material characteristics of a ceramic are determined by:

a) the chemical compound of which it consists ($SiO_2$, $ZrO_2$, $Al_2O_3$ etc.)

b) its atomic 3D structure, amorphous or crystalline. An amorphous

structure has no long range order, whereas in a crystalline structure, every atom takes an exactly defined place within a 3D network.(3M Espe, 2008). All-ceramic dental materials can be very different in their chemical composition as well as in

their structure and therefore demonstrate very different material properties. Veneer ceramics are feldspathic porcelains which consist almost entirely of an amorphous glass phase and therefore deliver ideal optical characteristics for the veneering.

The high strength core ceramic materials in dentistry can be classified in three major different groups according to their chemical structure (Figure 2.1-3): glass ceramics, glass infiltrated ceramics and polycrystalline ceramics (Kelly *et al.*, 1996; Raigrodski, 2005; Kunzelmann *et al.*, 2006).

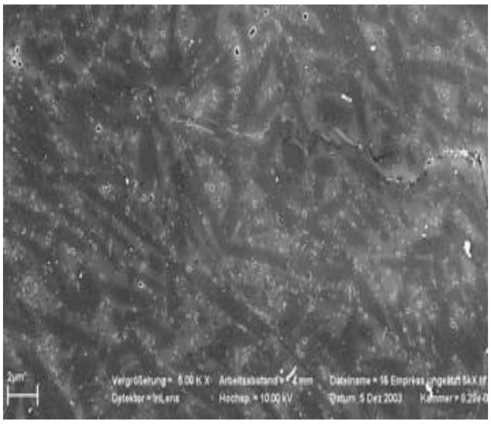

Fig. 2.1. Glass ceramic (contains glass), e.g. Empress® I/II.

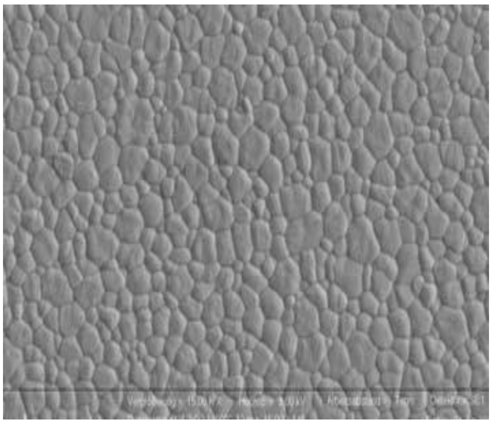

Fig. 2.3. Polycrystalline ceramic (glassfree), e.g. Lava™.

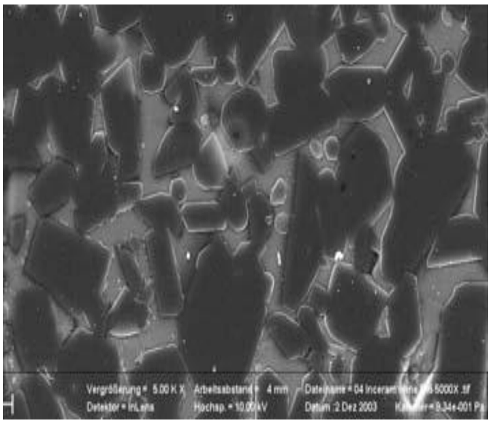

Fig. 2.2. Infiltrated ceramic (contains glass), e.g. In-Ceram®.

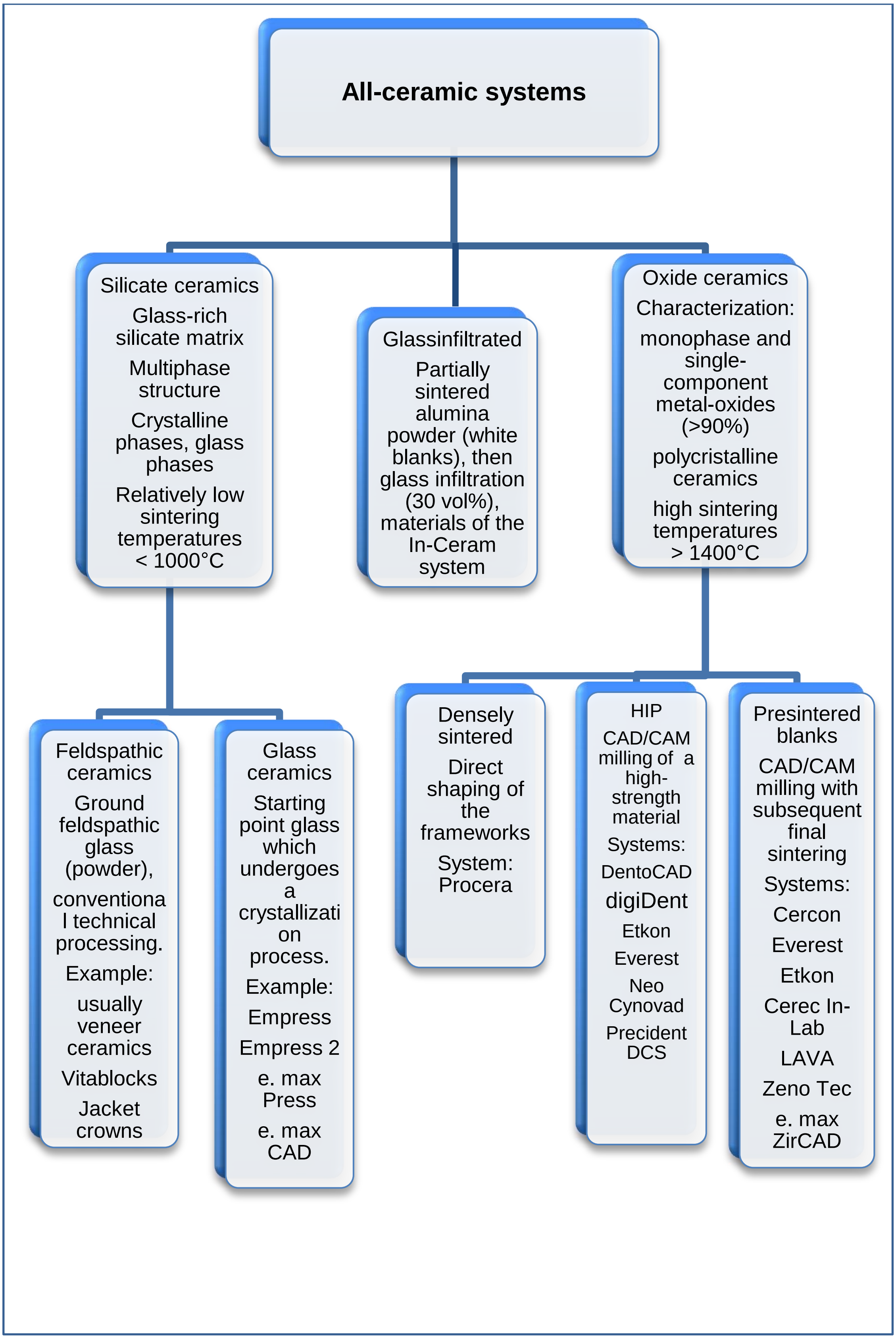

Fig. 2.4. All-ceramic systems.

### 2.4.1 Glass-ceramics

Glass-ceramics are multi-phase materials and contain crystalline constituents in addition to an amorphous glass phase.

#### 2.4.1.1 Silicate ceramics

Silicate ceramic such as feldspathic and glass ceramic is manufactured from quartz, kaolin and feldspar in a vitreous melt. The glass or silicate ceramic is formed through heat treatment and crystal-forming additives (Kunzelmann *et al.*, 2006). The main representatives of this category are the IPS Empress® (Ivoclar Vivadent, Schaan, Lichtenstein) and the Optec® OPC (Jeneric Pentron, Kusterdingen, Germany). In such glass ceramics the hardening of the ceramic is achieved by finely dispersed leucite and feldspar crystals.

The restorations are highly translucent providing the potential for a highly esthetic restoration (Heffernan *et al.*, 2002a; Heffernan *et al.*, 2002b). Therefore, they are not recommended for cases where the underlying abutment is a discolored tooth, a metallic-core built up, or a metal implant abutment. However the reported flexural strength of this core material ranges between 105-120 MPa and the fracture toughness from 1.5 to 1.7 MPa x √m (Seghi and Sorensen, 1995; Seghi *et al.*, 1995). The strength of these restorations depends on a successful bond to the tooth structure and therefore they must be adhesively cemented. Their indication is restricted only for veneers or crowns at the front region giving survival rates up to 95% after 11 years of clinical service (Fradeani and Redemagni, 2002).

### 2.4.1.2 Lithium Disilicate and Fluorapatite glass ceramics

By adding lithium or other materials, the physical properties of glass ceramics are additionally improved and reach strengths up to 450 MPa (Kunzelmann *et al.*, 2006). The main representatives of this category are the Empress II® (Ivoclar, Schaan, Liechtenstein) (lithium disilicate) and the IPS e.max® (Ivoclar, Schaan, Liechtenstein) (fluorapatite glass ceramic) core materials. Empress II® is composed of densely arranged lithium disilicate crystals (over 60% volume) uniformly bonded in an amorphous glassy matrix. The framework can be fabricated either with the lost-wax and heat-pressure technique, or can be milled out of prefabricated blanks (Raigrodski, 2004a). The interlocking structure of the ceramic hinders crack propagation and elevates flexural strength to 300-400MPa (Quinn *et al.*, 2003; Raigrodski, 2004b).

Adhesive luting is recommended for these restorations to initiate a stable bond to the tooth and enhance their strength and longevity (Edelhoff *et al.*, 1999; Kunzelmann *et al.*, 2006). The material is indicated not only for the fabrication of anterior FPDs, but also for short-span posterior FPDs (pontic not wider than a premolar) extending up to the second premolar (Sorensen *et al.*, 1998; Edelhoff *et al.*, 1999). Esquivel-Upshaw et al. reported a survival rate of 93% for posterior Empress II® FPDs after 2 years (Esquivel-Upshaw *et al.*, 2004), whereas Marquardt reported a survival rate of 100% for single crowns and 70% for FPDs extending up to the second premolar after 5 years of function (Marquardt and Strub, 2006).

### 2.4.2 Glass-infiltrated oxide ceramics

Glass-infiltrated oxide ceramics consist of framework materials based on aluminium oxide (alumina) infiltrated with glass (lanthanum glass) to increase strength.

The main representatives of this category are In-Ceram Alumina®, In-Ceram Spinell® and In-Ceram Zirconia® (Vita, Bad Säckingen, Germany).

### 2.4.2.1 In-Ceram Alumina® (Vita, Bad Säckingen, Germany)

The material is composed of a highly sintered-alumina glass-infiltrated core and the veneering porcelain. The fabrication of the core/framework can be carried out either with the slip-cast technique, by electrophoretic depositing (EPD), by copy milling or by the milling out of prefabricated partially sintered blanks through CAD-CAM technology (Tinschert *et al.*, 2001b; Pröbster and Groten, 2006), which are described later.

For the slip-casting technique an aqueous suspension of aluminium oxide powder, called a slip, is applied to a refractory die and the restoration is modeled. The slip is porously sintered at 1120˚C for 10 hours in a ceramic furnace. The porous sintered framework is then infiltrated with lanthanum glass during a second firing process at 1100˚C, which gives the material its final strength (Kunzelmann *et al.*, 2006; Pröbster and Groten, 2006).

Similar to the galvanoplating technique, electrophoresis involves the migration of charged particles in a liquid and highly homogeneous, electrical field. Electrophoretic depositing includes two different partial processes:

1. The electrophoretic migration of charged particles in the electrical field, which are dispersed in a liquid and

2. the deposition of the particles on a membrane (membrane deposition).

Compared to the manual application of the slip, very high density and homogeneity of the particles is achieved. After electrophoretic depositing, the framework features high precision of fit and is sintered porously (shrinkage-free) and subsequently infiltrated with the special glass in accordance with the VITA In-Ceram® technique (Pröbster and Groten, 2006).

The flexural strength of the material ranges between 236 and 600 MPa (Giordano *et al.*, 1995; Guazzato *et al.*, 2002) and the fracture toughness between 3.1 and 4.61 MPa x √m (Seghi *et al.*, 1995; Wagner and Chu, 1996). The increased toughness and strength of In-Ceram Alumina is explained through the crack-bridging mechanism. The crack propagation is deflected along the grain boundaries, causing friction between the separated fragments. The longer path of the crack and the friction between the parts are responsible for dissipating the initial energy (Guazzato *et al.*, 2002).

The material is recommended for anterior and posterior crowns, as well as for 3-unit anterior FPDs (Sorensen *et al.*, 1998; McLaren, 1998).

#### 2.4.2.2 In-Ceram Spinell® (Vita, Bad Säckingen, Germany)

The In-Ceram Spinell® consists of a $MgAl_2O_4$ core infiltrated with glass. Its flexural strength is lower than that of In Ceram Alumina® ranging between 283 and 377 MPa (Magne and Belser, 1997; McLaren, 1998), but its translucency is twice as high. Therefore, it is indicated for anterior crowns, where esthetic demands are higher (Fradeani and Redemagni, 2002).

#### 2.4.2.3 In-Ceram Zirconia® (Vita, Bad Säckingen, Germany)

The In-Ceram Zirconia® core consists of glass-infiltrated alumina with 35% partially stabilized zirconia. The fabrication may be carried out with the same methods as for In-Ceram Alumina®. Its flexural strength ranges from 421 to 800 MPa and its fracture toughness from 6 to 8 MPa x √m (Seghi and Sorensen, 1995; Guazzato *et al.*, 2002). The high strength of In-Ceram Zirconia is attributed to the phase transformation toughening mechanism that takes place in the material (McLaren and White, 1999), which is described later.

In a biaxial flexural strength test, no statistically significant difference was found between the strength of In-Ceram Zirconia and In-Ceram Alumina discs (Guazzato *et al.*, 2002; Guazzato *et al.*, 2004a). The authors attributed this to little particle transformation and the effect of pores in the mass of In-Ceram Zirconia. Other in vitro studies reported that the fracture strength value of three-unit all-ceramic FPDs, fabricated with the CAD/CAM technology using In-Ceram Zirconia blanks, was between 1000-2000 N (Tinschert *et al.*, 2000a; Tinschert *et al.*, 2001a).

### 2.4.3 Polycrystalline ceramics

Polycrystalline ceramics are monophase materials with densely packed particles and no glassy components. Pure polycrystalline oxide ceramics have only been in clinical use for about 15 years (e.g. Procera®) For the first time they displayed a type of material that possesses sufficient stability for posterior applications, whereas pressed ceramics, such as Empress have been used successfully only for anterior applications for more than 10 years, however, the latter was not being used for fixed partial dentures for posterior applications. Alumina and zirconia are the only two polycrystalline ceramics suitable for use in dentistry as framework materials able to withstand large stresses. A dental material needs to adjust to the different influences and conditions of the oral environment. It should have high stability in order to spontaneously withstand extreme stresses and high fracture toughness in order to show the optimal tolerance level towards defects. Various examinations prove higher stability of infiltrated ceramics than of glass ceramics (Wagner and Chu, 1996; Tinschert *et al.*, 1999b; Tinschert *et al.*, 2000a; Tinschert *et al.*, 2000b).

The highest stability, however, has been measured in polycrystalline ceramics (Wagner and Chu, 1996; Tinschert *et al.*, 1999a; Tinschert *et al.*, 2000b; Marx *et al.*, 2002; Curtis *et al.*, 2006a). These materials are shown to provide both necessary esthetics and material properties required of a modern tooth restoration (Marx *et al.*, 2002). Today, polycrystalline oxide ceramics are mainly processed by applying Computer-Assisted-Design/Computer-Assisted-Machining (CAD/CAM) technologies using industrial pre-fabricated ceramic blocks which possess a very high micro-structure quality due to a standardized manufacturing procedure.

### 2.4.3.1 Aluminium oxide ceramics

- **The Procera® AllCeram System (Nobel Biocare, Göteborg, Sweden)**

This system creates high-precision crown copings, frameworks for fixed partial dentures, abutments of densely sintered pure alumina consisting of more than 99.9% aluminium oxide particles of 5µm grain size with a dry pressing technique against the enlarged die of a prepared tooth (Kunzelmann *et al.*, 2006).

The frameworks are fabricated with the help of the Procera system, which consists of a computer-controlled scanning and design station located in a dental laboratory. Tooth models are tactile scanned in 3D using either the Procera® Piccolo or the more advanced Procera® Forte. Designs are sent via the Internet to the manufacturing center of Nobel Biocare (Göteborg, Sweden) where the system mills a 20% enlarged metal refractory die on the basis of the 3-D data. This enlargement is made in order to compensate the sintering shrinkage of the high purity alumina powder, that is pressed against the stump (White *et al.*, 1996). The alumina cores of copings and pontic are milled individually and fully sintered at 1600°C to their correct size.

The flexural strength of the material ranges between 464 and 687MPa (Wagner and Chu, 1996; Esquivel-Upshaw *et al.*, 2001; Itinoche *et al.*, 2006).

For the fabrication of FPDs, the minimal recommended dimensions for the connectors are 3 mm in height and 2 mm in width (Raigrodski, 2004b).

### 2.4.3.2 Zirconium dioxide ceramics ($ZrO_2$)

Zirconia-based materials were initially introduced for biomedical use in orthopedics for total hip replacement, because of their excellent mechanical properties and biocompatibility (Piconi *et al.*, 1998; Piconi and Maccauro, 1999). Zirconia ceramics have been used in dentistry for orthodontic brackets (Keith *et al.*, 1994), post-and-core systems (Meyenberg *et al.*, 1995; Kern and Wegner, 1998), implant abutments (Wohlwend *et al.*, 1997; Glauser *et al.*, 2004) and implants (Kohal *et al.*, 2004; Kohal and Klaus, 2004).

Zirconium (Zr) is a metal with the atomic number 40, which was discovered in 1789 by the German chemist Martin Klaproth. The material has a density of 6.49 g/cm$^3$, a melting point of 1852°C and a boiling point of 3580°C. It has a hexagonal crystal structure and a grayish color. Zirconium does not occur in nature in a pure state. It can be found as zircon sand in conjunction with silicate oxide ($Zr_2SiO_4$ , alvite) or as a free oxide $ZrO_2$ (baddeleyite, brasilite) (Piconi and Maccauro, 1999; Kunzelmann *et al.*, 2006).

In order to produce pure zirconia powders, complex and time-consuming processes that result in an effective separation of such elements are used. The material can be used after purifying as a ceramic biomaterial (Piconi and Maccauro, 1999).

Pure Zirconia ($ZrO_2$) has a high melting point (2680°C) and low thermal conductivity. However, its polymorphism restricts its widespread use in the ceramics industry. $ZrO_2$ occurs in three crystallographic forms: monoclinic (M), tetragonal (T) and cubic (C). At ambient pressure, unalloyed zirconia can have three crystallographic forms depending on the temperature: the monoclinic phase, which is stable up to 1170°C, where it transforms to the more dense tetragonal phase with a 5% volume decrease, which in turn converts to the cubic phase over 2370°C up to its melting point (2680 °C) (Subbarao, 1981; Rauchs *et al.*, 2001; Denry and Kelly, 2008). Reversely, while cooling, a tetragonal to monoclinic transformation takes place in a temperature range of about 100°C below 1070°C and a volume increase of approximately 3-4% (Figure 2.5) which can lead to stresses and subsequent crack formation in the structure (Christel *et al.*, 1989; Piconi and Maccauro, 1999).

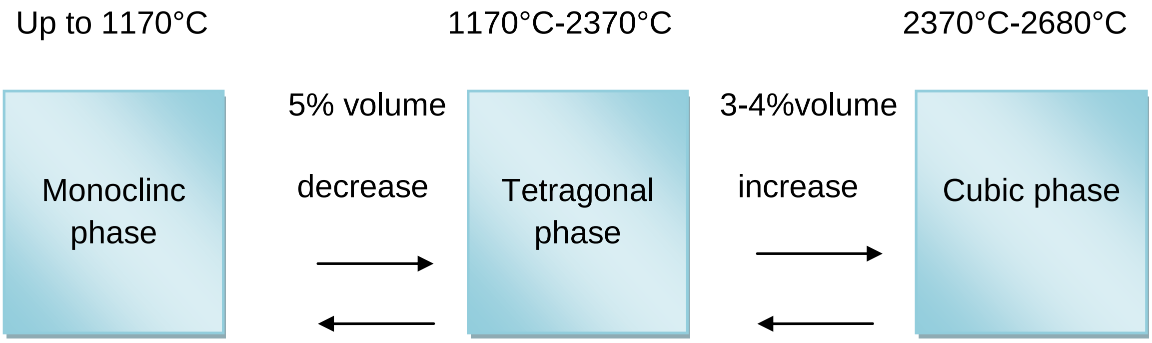

Fig.2.5. The transformation of the $ZrO_2$ crystalline phase depending on the temperature.

### 2.4.3.2.1 Stabilized Zirconia

The addition of stabilizing oxides to pure zirconia, such as calcia (CaO), magnesia (MgO), ceria ($CeO_2$) or yttria ($Y_2O_3$) can inhibit the phase transformations of the material in room temperature resulting in a multiphase material named stabilized zirconia (Christel *et al.*, 1989; Piconi and Maccauro, 1999).

The most useful mechanical properties can be obtained when zirconia is in a multiphase form known as Partially Stabilized Zirconia (PSZ) (Garvie *et al.*, 1975). PSZ can be obtained with the addition of smaller amounts of stabilizing oxides in pure zirconia, compared to that for obtaining fully stabilized zirconia. Several PSZ have been tested as ceramic biomaterials. Mg-PSZ is one of the most commonly used zirconia-based engineering ceramics (Sundh and Sjögren, 2006), but a rather coarse grain size (30-40 μm) and residual porosity of the material reduce the interest for biomedical use (Piconi and Maccauro, 1999).

#### 2.4.3.2.2 Y-TZP (Yttrium-Tetragonal Zirconia Polycrystalline)

The addition of approximately 2-3% mol yttria can stabilize zirconia ceramics in room temperature resulting in the formation of yttria-stabilized tetragonal zirconia polycrystalline (Y-TZP) (Swain *et al.*, 1983; Masaki T., 1986), which is made of almost 100% small metastable tetragonal grains (Christel *et al.*, 1989).

The amount of the tetragonal phase as well as the mechanical properties depend on the yttrium content, the size of the matrix and the processing temperature (Piconi and Maccauro, 1999).

Addition of $Y_2O_3$ in higher concentrations produces a fully stabilized zirconia ceramic with a cubic phase only and lower fracture strength (Sato and Shimada, 1985a).

To obtain a metastable tetragonal structure at room temperature (3mol% $Y_2O_3$-doped tetragonal $ZrO_2$), the ceramic grain size must be less than 0.8μm (Theunissen *et al.*, 1992). A critical grain size exists, linked to the yttria concentration, above which spontaneous T→M transformation of grains takes place, whereas this transformation would be inhibited in an overly fine-grained structure (Theunissen *et al.*, 1992).

The T→M transition in TZP materials depends not only on the $Y_2O_3$ content, but also on its distribution. The stabilizing oxide is introduced in $ZrO_2$ during the early stages of the ceramic powder manufacturing process. $Y_2O_3$ can either be co-precipitated with $ZrO_2$ salts or coated on the $ZrO_2$-grains for the production of ceramic powders (Piconi and Maccauro, 1999).

### 2.4.3.3 Transformation-toughening mechanism

Significant for its mechanical properties is the toughening mechanism due to transformation from the tetragonal phase to the monoclinic that occurs by a diffusionless shear process at near sonic velocities similar to those of martensite formation of quenched steel (Wolten, 1963). The tetragonal grains may transform into monoclinic as a result of external stresses generated by procedures like grinding, sandblasting or impact. This phenomenon can be explained through the lower surface energy of the tetragonal $ZrO_2$ particles and the constraint of the rigid matrix on them that opposes their transformation to the less dense monoclinic form. The tetragonal $ZrO_2$ grains can transform into the monoclinic phase when the constraint exerted on them by the matrix is relieved, i.e. by a crack advancing in the material (Reed and Lejus, 1977; Piconi and Maccauro, 1999). This transformation produces a 4% expansion which induces localized compressive stresses at the tip of a propagating crack (Figure 2.6) (Green, 1983; Swain and Hannink, 1989; Chevalier *et al.*, 1999; Luthardt *et al.*, 2004) which counteract the external stresses on the crack tip and extra energy is required for the crack to propagate further (Tateishi and Yunoki, 1987), thus counteracting strength degradation.

This transformation corresponds the martensite transformation of steel which led Garvie to call zirconium dioxide “ceramic steel” (Garvie *et al.*, 1975). The result is a high initial strength and fracture toughness (Kappert and Krah, 2001) and, in combination with a low susceptibility to stress fatigue, an excellent life-time expectancy for zirconia frameworks.

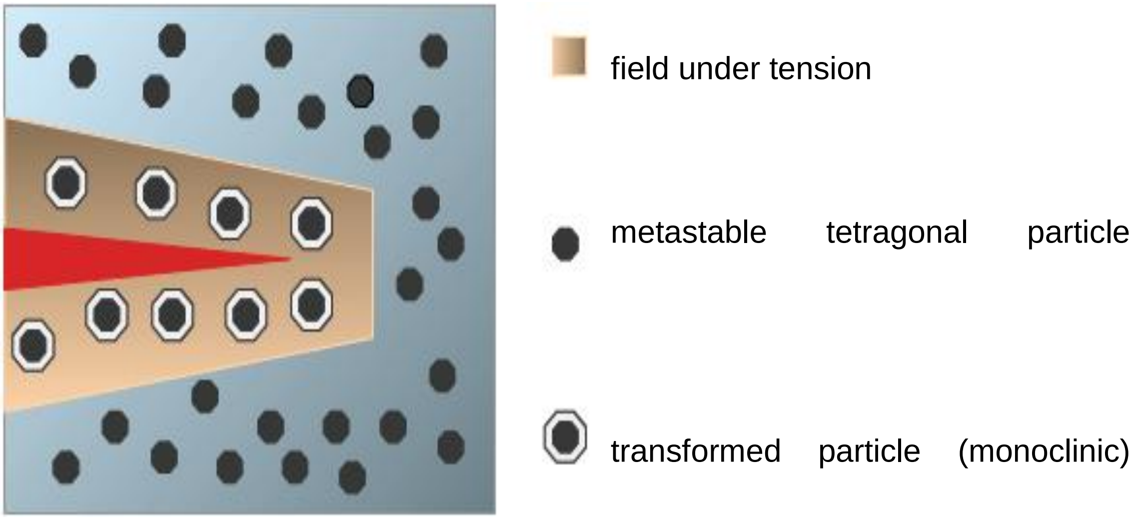

Fig. 2.6. Representation of stress-induced transformation toughening process (Pospiech P., DGZPW annual congress, Wuppertal. Germany). Energy of the advancing crack is dissipated in phase transformation and in overcoming the matrix constraint by transforming grains.

### 2.4.3.4 Physical and chemical properties of Y-TZP

Table 2.1 shows that zirconia ceramic exhibits higher bending strength and fracture toughness than alumina ceramics (Wagner and Chu, 1996). Additionally, its Young's modulus is much lower than that of alumina, in the same order of magnitude of stainless steel alloys (CoCr alloy 230 GPa), pointing out its interesting elastic deformation capability. Fracture toughness is a very important physical property since it represents the ability of a material to resist crack growth. Clinically, lots of subcritical loads are applied on the materials by chewing, leading to the growth of subcritical cracks. Therefore, materials with higher fracture toughness are more ideal clinically, since more energy is required to cause crack growth (McLaren and Terry, 2002).

**Table 0. Physical and chemical properties of zirconia.**

| **Property** | **Units** | **Alumina** | **Mg-PSZ** | **TZP** |
|---|---|---|---|---|
| Chemical composition | | 99.9% $Al_2O_3$+MgO | $ZrO_2$+ 8-10% mol MgO | $ZrO_2$ 3% mol $Y_2O_3$ |
| Density | g $cm^{-3}$ | ≥3.97 | 5.74- 6 | >6 |
| Porosity | % | <0.1 | — | <0.1 |
| Bending strength | MPa | >500 | 450-700 | 900-1200 |
| Compression strengrth | MPa | 4100 | 2000 | 2000 |
| Young‘s modulus | GPa | 380 | 200 | 210 |
| Fracture toughness $K_{IC}$ | Mpa √m | 4 | 7-15 | 7-10 |
| Thermal expansion coeff. | $K^{-1}$ | $8x10^{-6}$ | 7-10 $x10^{-6}$ | $11x10^{-6}$ |
| Thermal conductivity | W $m^{-1}$ $K^{-1}$ | 30 | 2 | 2 |
| Hardness | HV | 2200 | 1200 | 1200 |

### 2.4.3.5 Mechanical Properties

#### 2.4.3.5.1 Flexural strength

By flexural strength one understands the critical bending tension, at which a fracture occurs by crack formation. It is the limit of the elastic strain of a dental ceramic or the yieldable mechanical strain (Kappert and Krah, 2001). It is measured as the resistance (limit value) against forces, which act perpendicular to the longtidunal axis of a body (bar or disc). On the side, on which pressure is applied during bending, prevails tensile stress.

Zirconiumdioxide shows the highest flexural strength and at the same time the highest fracture toughness of all the ceramics (Kappert and Krah, 2001). The flexure strength of $ZrO_2$ is equivalent to that of CoCr alloys. Figure 2.7 shows the flexural strength of different all ceramic materials used in dentistry.

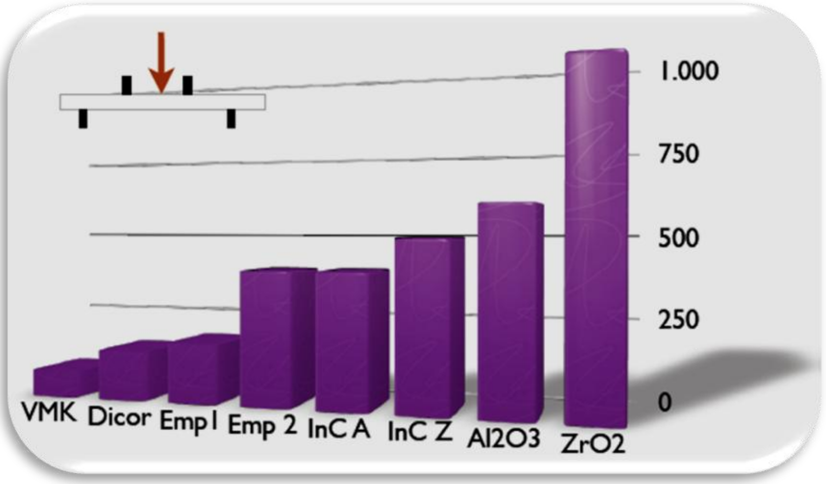

Fig. 2.7. Flexural strength of different all ceramic dental materials in MPa (Pospiech P., DGZPW annual congress, Wuppertal, Germany).

### 2.4.3.5.2 Modulus of elasticity (Young's modulus)

The modulus of elasticity describes the resistance of the material against flexible deformation and it is with the flexure strength one of the most important characteristics of a dental ceramic (Seghi *et al.*, 1995; Kappert and Krah, 2001). For zirconium dioxide the young's modulus amounts to approximately 200-300 GPa (fig. 2.8).

Other full-ceramic systems reach approximately 100 GPa while metal-ceramic systems reach values between 100 (for noble metal alloys) and 200 GPa (for non-noble metal alloys) (Baltzer and Kaufmann-Jionian, 2003).

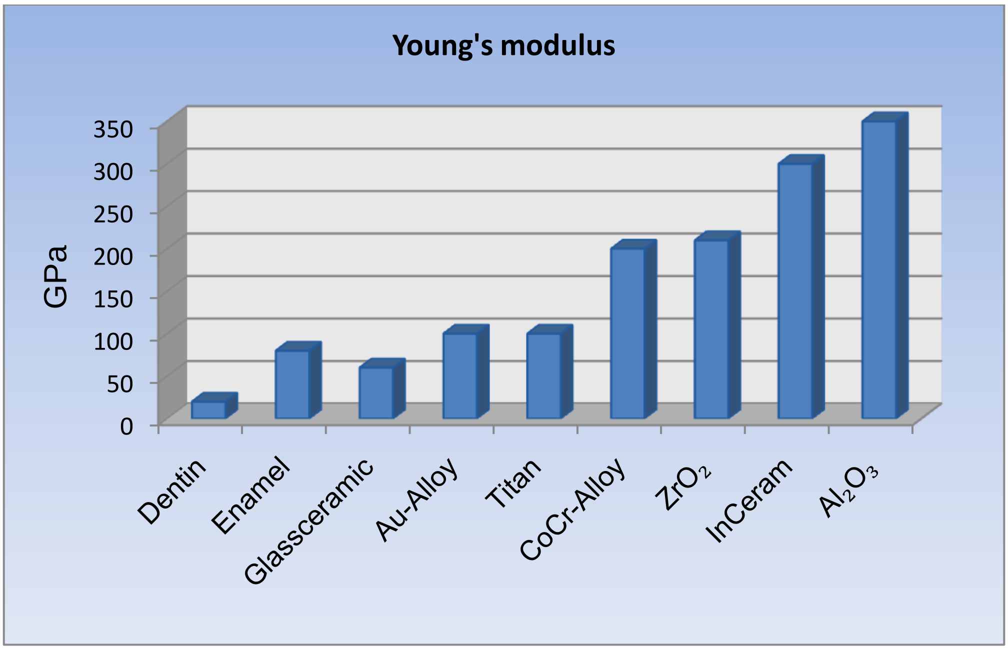

Fig. 2.8. E-modulus of different dental materials (Kappert, 2000).

### 2.4.3.5.3 Fracture toughness

Fracture toughness describes the ability of a material containing a crack to resist crack propagation and thus the fracture (Kappert and Krah, 2001). It is denoted $K_{Ic}$ and has the units of MPa × √m. Fracture toughness is an expression of the reliability of the material. The value $K_{Ic}$ shows the critical stress intensity factor for the fracture toughness. When the tension exceeds the fracture toughness, the crack becomes unstable. This results in crack propagation in supersonic velocity, which ends with the fracture of the ceramic.

The $K_{Ic}$ value is an experimentally determinable material characteristic frequently used for brittle materials as measure for their ability to absorb deformation energies. For Zirconium dioxide ceramic values of 10 Mpa × √m can be obtained (Strub *et al.*, 2005). The fracture toughness of some dental materials is shown on figure 2.9.

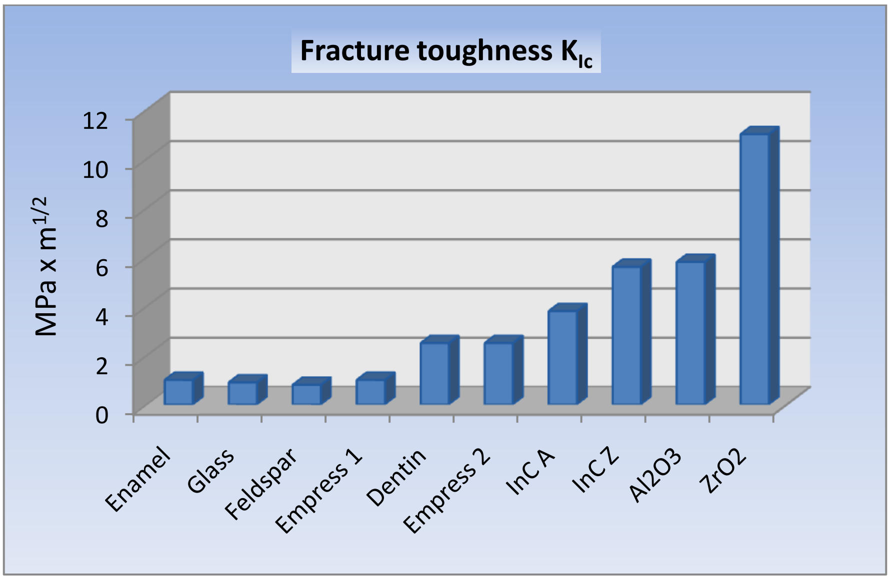

Fig. 2.9. Fracture toughness of different dental materials (Pospiech P., DGZPW annual congress, Wuppertal, Germany).

Statements about the fracture toughness are not sufficient for the evaluation of the fatigue strength of ceramics, because they do not take into consideration the long-term behaviour in different environment conditions.

Other tear parameters play here an important role (Marx *et al.*, 2001). One of these parameters describes the resistance of a ceramic against the subcritical crack growth ($K_{I0}$). Tensions higher than the threshold value ($K \geq K_{I0}$), but smaller than the fracture toughness

($K \leq K_{IC}$) cause the development of a subcritical crack growth. It degrades slowly but continuously the strength of a ceramic, which can lead to failure of a ceramic restoration far below the flexure strength of the material (Marx *et al.*, 2004).

#### 2.4.3.5.4 Weibull modulus

Large dispersions and an asymmetrical distribution of the breaking loads are characteristic for ceramic materials. The description of the strength behavior of dental ceramics with average values and standard deviations is inaccurate, because the measured values do not follow a normal distribution and can be described correctly with the Weibull distribution (Tietz, 1994). For ceramics the material-specific characteristic value is often indicated as Weibull characteristic strength ($\sigma_0$). It designates the stress at which 63.2% of all tested specimens would fail. The distribution of the strength values is described as correlative to the standard deviation with the Weibull modulus (m). Thus from a series of measurements a forecast can be made over the strength behavior of construction units. The higher the Weibull-modulus m the closer the measured values lie to each other. The Weibull module is an expression of the mechanical reliability. As material-specific characteristic value it is an additional measure for the homogeneity of the failure distribution including manufacturing technical influences. For dental ceramics manufactured by dental technicians the Weibull module lies between 5 and 15 (Tinschert *et al.*, 1999a; Tinschert *et al.*, 2000b). For industrially manufactured ceramics the Weibull module can be between 15 and 25, which shows high mechanical reliability (Baltzer and Kaufmann-Jionian, 2003).

#### 2.4.3.5.5 Fatigue strength

Fatigue strength is the stress limit which a material can resist in the long term in the given environment (corrosive influences of the oral cavity, dynamic chewing load) in the long term. For ceramics it is usually equivalent to approximately the half of the flexural strength and it is directly related to the fracture strength (Schwickerath, 1986a; Schwickerath, 1994). Geis-Gerstorfer and Fässler subjected Y-TZP bridges to dynamic loading whereby the fatigue strength of

480 MPa was less than 50% of the initial flexure strength of 1016 MPa (Geis-Gerstorfer and Fässler, 1999).

The chewing forces during normal chewing amount from 50 N to 250 N, in case of parafunctions (bruxism) values between 500 and 1000 N are measured (depending on the measuring method, measuring point and measuring instrument) (Körber and Ludwig, 1983). The chewing forces at the posterior region are up to four times higher than those at the anterior. Therefore prosthetics restorations at the molar regions should have a safety margin of 200 N a fatigue strength of approximately 500 N (Körber and Ludwig, 1983). Accordingly an initial strength of at least 1000 N should be expected in order to ensure a favorable clinical prognosis at the posterior region (Tinschert *et al.*, 1999a; Tinschert *et al.*, 2001a).

#### 2.4.3.5.6 Coefficient of thermal expansion

The coefficient of thermal expansion (CTE) describes the degree of expansion of a material during a change of temperature of 1K.

The CTE of framework and veneering materials are coordinated, whereby the CTE of the veneering material should be approximately 10-15% lower. Thereby a good adhesion of the ceramics during the cooling phase after the firing cycles as well as during thermocycling in the oral cavity can be guaranteed (Kappert and Krah, 2001).

### 2.4.3.6 Biological safety of Y-TZP

In vitro and in vivo studies have confirmed the high biocompatibility of Y-TZP when high purity zirconia-powders are used and have reported no local or systemic adverse reactions to the material (Christel *et al.*, 1989; Ichikawa *et al.*, 1992; Richter *et al.*, 1994; Piconi and Maccauro, 1999; Covacci *et al.*, 1999). Recent studies have demonstrated that fewer bacteria accumulate around Y-TZP than titanium (Rimondini *et al.*, 2002; Scarano *et al.*, 2004). These findings have lead to the suggestion that zirconium oxide may be a suitable material for manufacturing implant abutments with a low colonization potential (Scarano *et al.*, 2004).

### 2.4.3.7 Aging of zirconia

The mechanical performance of $ZrO_2$ as a function of time is of particular concern in Y-TZP for biomedical applications. $ZrO_2$-ceramics are prone to age in the wet environment, showing degradation of their mechanical properties. Low temperature degradation (LTD) of zirconia known as "aging", which leads to mechanical property degradation happens due to the progressive spontaneous transformation of the metastable tetragonal phase into the monoclinic phase (Piconi and Maccauro, 1999). This behavior is well known at a temperature range above 200°C and in the presence of water or vapor (Sato and Shimada, 1985a; Sato and Shimada, 1985b; Papanagiotou *et al.*, 2006). The aging of zirconia was described in steps by Swab (Swab, 1991):

1. The most critical temperature range is 200-300°C.

2. Aging reduces strength, toughness and density of the material, and increases the monoclinic phase content.

3. Degradation of mechanical properties is due to the T→M transition, which takes place with micro and macro cracking of the material.

4. T→M transition starts on the surface and progresses into the bulk of the material.

5. Reduction in grain size and/or increase in concentration of stabilizing oxide reduce the transformation rate.

6. T→M transformation is enhanced in water or in vapor.

The models proposed to explain the spontaneous phase transformation in TZP are based on the formation of zirconium hydroxides at the tip of the crack, which accelerates crack growth of pre-existing flaws and promotes the T→M phase transformation (Sato and Shimada, 1985a; Sato and Shimada, 1985b).

The degradation resulting from aging is characterized by surface roughening and microcracking at the surface (Chevalier, 2006).

The variability in aging behavior among different zirconia materials is related to the differences in equilibrium of the microstructural parameters, such as size, concentration and distribution of the grains as well as size and distribution of flaws (Lilley , 1990).

The LTD rate of Y-TZP is related to several factors, such as chemical composition, duration of exposure to aging medium, loading of the ceramic restoration and manufacturing processes, all of which affect the microstructure of the material (Ardlin, 2002; Chevalier, 2006).

Another relevant aspect for the stability of the material in a biological environment is the presence of glassy phases formed by $SiO_2$, $Al_2O_3$, $TiO_2$ or CaO impurities in grain boundaries. These impurities may come from the chemical precursors, from the milling bodies used in powder processing, they may be added to powders as sintering aids (Piconi and Maccauro, 1999) or may be components added for different purposes such as shade adjustment (Ardlin, 2002). Their presence leads to a loss of stability of the tetragonal phase, as it was demonstrated that aluminosilicate glassy phases in grain boundaries are able to scavenge yttrium ions from TZP grains (Lin *et al.*, 1990).

The aging sensitivity of Y-TZP is directly linked to the type (compressive or tensile) and amount of residual stresses. Rough polishing produces a compressive surface stress layer beneficial for the aging resistance, while smooth polishing produces preferential transformation nucleation around scratches, due to elastic/plastic damage and the tensile residual stresses occurred (Deville *et al.*, 2006).

Stable performances of Y-TZP ceramics in a wet environment were reported by several authors (Swab, 1991; Chevalier *et al.*, 1997; Geis-Gerstorfer and Fässler, 1999), which indicates that TZP stability can be controlled acting on parameters, such as stabilizing oxide concentration, distribution, grain size and residual stresses in the ceramics (Lepistö and Mäntylä, 1992), or the presence of the cubic phase (Chevalier *et al.*, 2004).

#### 2.4.3.8 Zirconia as material for dental restorations

Zirconium dioxide ceramics are being used in dentistry as framework materials for the fabrication of crowns and fixed partial dentures (Luthardt *et al.*, 1998), as well as for implant abutments (Wohlwend *et al.*, 1997) and orthodontic brackets (Keith *et al.*, 1994). Today, polycrystalline oxide ceramics are mainly processed by applying CAD/CAM technology in means of milling industrial pre-fabricated ceramic blocks which possess a very high micro-structure quality due to a standardized manufacturing procedure.

Frames can either be fabricated by grinding already sintered blanks (e.g. DCS®, Celay®), which is both time-consuming and leads to a high mechanical wear on tools, or by processing nonsintered (“green”) or pre-sintered (“white”) zirconia blanks (e.g. Lava™). In the latter, restorations are milled from pre-sintered zirconia and are subsequently sintered to their full density. Thereby, the milling times are considerably shortened and the mechanical wear on the tools decreased. The restoration must, however, be milled in a larger size in order to compensate for the shrinkage during the sintering process (Raigrodski, 2004b).

Green stage $ZrO_2$-blocks can be milled using dry carbide burs, pre-sintered $ZrO_2$-blocks can be milled using carbide burs under cooling liquid and milling of completely sintered $ZrO_2$-blocks requires the use of diamonds under cooling liquid (Witkowski, 2005).

Apart from CAD/CAM technology new innovative techniques have lately been presented for the production of $ZrO_2$-frameworks. Some of them have already been used in industry:

The Sono-erosion technique makes use of ultrasound vibrations that act on fully sintered $ZrO_2$-blocks to produce the framework of the restoration or the complete restoration with occlusal surfaces (Tinschert *et al.*, 2001b).

The electrophoresis technique is analogue to the galvanic technique and can be used for the fabrication of $ZrO_2$-frameworks.

In the so-called Electro-Deposited Ceramics-Technology (EDC), a model of the prepared teeth is made out of a mixture from wax and ceramic. Then, the wax is burnt out and the model is expanded to compensate for subsequent sintering shrinkage. A duplicate model is made and coated with silver lacquer (Rudolph *et al.*, 2003). Ceramic particles are applied on the die to form the framework through electrophoretic deposition (Tinschert *et al.*, 2001b). The framework is finally sintered to become stronger (Rudolph *et al.*, 2003).

The new fabrication techniques are very promising, as the damaging of ceramic material by milling and grinding is avoided.

## 2.5 CAD/CAM

### 2.5.1 Definition/Historical Background

The term CAD/CAM, which comes from machine-tool technology and stands for “Computer-Aided-Design / Computer-Aided-Manufacturing”, designates the three-dimensional planning of a workpiece on the screen of a computer with subsequent automated production by a computer controlled machine tool

(Tinschert *et al.*, 2004). Francois Duret is viewed as the founder of CAD/CAM technology in dental medicine (Duret *et al.*, 1988). His idea was based upon the assumption that the technologies established in industry could be easily transferred to dentistry. The industrial use of CAD-CAM allows the production of any number of similar workpieces automatically, while saving time and manual effort. In dental medicine, however, this philosophy cannot be applied due to the demands of the individual adaptation of the restoration design (one-of-a-kind production) to the patient (Tinschert *et al.*, 2004). The manufacturing of zirconia crowns and bridges by direct sintering on suitable stumps or the application of conventional pressing or casting technologies is not possible due to the high processing temperatures of zirconia. Besides the extraordinary hardness of Zirconium dioxide ceramics prevents a simple and economical treatment. Therefore zirconium dioxide restorations can be manufactured mainly with CAD/CAM technologies (Luthardt *et al.*, 1998).

While thermal processing is necessary to shape the restoration in the pressable-ceramic and slip-casting techniques, subtractive procedures with CAD/CAM technology make it possible to produce all-ceramic restorations using prefabricated blanks. The advantage of this is that industrially pre-fabricated ceramics blanks have defined physical properties and are used without thermal transformation, meaning that processing errors can be reduced (Kunzelmann *et al.*, 2006).

### 2.5.2 CAD/CAM Components

The contemporary CAD/CAM systems consist of three components (Luthardt *et al.*, 2001a; Luthardt *et al.*, 2001b; Tinschert *et al.*, 2004)

1. The scanner, which scans the dental preparation provided by the dentist either intraorally or extraorally by reference to tooth models. For inlays and single crown frameworks, just the surface data of the prepared teeth need to be digitized. For FPD frameworks or additional occlusal characterization, further

data from the neighboring teeth and antagonists, as well as from the spatial relation of the prepared teeth to one another, are required.

2. The software CAD consists of a computer unit used for the three-dimensional planning and design of restorations on the computer screen. The software programs available today offer a high level of intervention and permit the design and production of an individually adapted restoration.

Systems which have no CAD component are not considered as CAD/CAM systems and they are described as only CAM systems (Witkowski, 2005).

The hardware CAM covers different production technologies for converting the virtual restoration into a dental restoration. At present, computer-controlled milling or grinding machines are mainly used. They machine the restoration from the full material block consisting of prefabricated metal or ceramic. As a rule, after the CAM production, some manual corrections and final polishing or individualization of the restoration with staining colors or veneering materials are required to be carried out by the dental technician (Luthardt *et al.*, 2001a; Luthardt *et al.*, 2001b).

### 2.5.3 CAM techniques

The CAM technologies can be divided in three groups according to the technique used (Witkowski, 2005).

#### 2.5.3.1 Subtractive Technique from a Solid Block

The CAM technique most commonly applied in manufacturing frameworks for single crowns and FPDs is to cut the contour out of an industrially prefabricated, solid block of different material. When industrial prefabricated zirconium dioxide blocks are used, the restoration can be shaped, as mentioned before, both before and after the block is sintered. Some examples of such systems are shown on figure 2.4.

#### 2.5.3.1.1 The Lava system (3M/ESPE Dental AG, Seefeld, Germany)

The LAVA™ system by 3M ESPE processes partially sintered zirconia ceramic as yttrium-stabilized blanks and is designed for manufacturing frameworks for crowns and fixed partial dentures. The central unit uses an optical scanner to scan multiple units at once. The software automatically finds the margin, suggests pontics and designs the desired framework (Giordano, 2002). Afterwards, with the milling machine, an oversized coping from partially sintered zirconia is milled out to compensate for sintering shrinkage. The dental technician can also send a model to a milling center, which then performs the scanning, design, milling and sintering. Alternatively, the dental technician can scan the model with the Lava™ Scan ST scanner, design the framework with the CAD Lava™ Design software and then send the data via internet to a Lava™ milling center (Giordano, 2002; Kunzelmann *et al.*, 2006). After milling, but before sintering the restoration can be immersed in a staining solution to be coloured (Kunzelmann *et al.*, 2006).

### 2.5.3.2 Additive Technique by Applying Material on a Die

There are three different systems that apply the framework material on a die of a prepared tooth (Witkowski, 2005):

With the Procera system (Nobel-Biocare AB, Göteborg, Sweden) alumina or zirconia is dry pressed directly against an enlarged die and the temperature is raised to a temperature similar to the presintering stage. At this point in the process, the enlarged and porous coping is stable. Its outer surfaces are milled to the desired shape and the coping is removed from the enlarged die and sintered into the furnace for firing to full sintering. During this cycle, the coping shrinks to fit the dimensions of the original working die.

The WOL-CERAM-EPC-CAM-System (Wol-Dent, Ludwigshafen, Germany) generates the ceramic framework of crowns and FPDs directly on the die of the master model with means of electrophoretic dispersion method within a few minutes. The outside contour is shaped by a CAM process. Then, the coping is removed from the die and sintered at high temperature (1140°C) (Wolz, 2002; Witkowski, 2005).

The third system involves the solid direct form fabrication technique, which generates copings and frameworks for FPDs of pure $Al_2O_3$ and $ZrO_2$ ceramics in a production center (CE.NOVATION, Inocermic, Hermsdorf Germany). The dispersed super-fine nanoceramic powders consist of particles well below 100 nm in diameter. With this technology, the frameworks attain high strength and calculable sintering shrinkage (Brick *et al.*, 2003). These new technologies are relatively new and need further development (Witkowski, 2005; Strub *et al.*, 2006).

#### 2.5.3.3 Solid free form fabrication

This category includes new technologies originating from the area of rapid prototyping, which have been adapted to the needs of dental technology (Strub *et al.*, 2006). The first system applying this technology for dental use was the wax plotter technique, which works according to the ink jet principle. The machine builds (solid free form) frameworks and full crowns in wax for the casting technique in alloys and titanium (Wax Pro 50, Cynovad, Montreal, Canada) (Witkowski, 2005). A second technology originating from rapid prototyping is the stereolithography (Perfactory, Delta Med, Frieberg, Germany). In this technique, the restoration is produced from light sensitive plastic, which can be converted into any desired alloy with the casting technique (Witkowski, 2003). Occlusal splints and diagnostic templates for oral implantology can also be produced with this technique. Another technique is the selective laser sintering (SLS), which allows to build up frameworks of sinterable powder materials. The materials are applied sequentially, or layer by layer, on the spots that are indicated from the CAM-model, and are then fused by means of a laser (Strub *et al.*, 2006).

### 2.5.4 Materials

The material groups available for the various CAD-CAM systems are as follows:

Silicate ceramics; glass-infiltrated aluminium oxide ceramics; densely sintered aluminium oxide ceramics; densely sintered zirconium dioxide ceramics (yttria-tetragonal-zirconia-polycrystal), manufactured as green stage, presintered stage and completely sintered stage; titanium; precious alloys; nonprecious alloys; acrylics of improved strength and castable acrylics (Witkowski, 2005).

### 2.5.5 Industrial preparation of zirconium dioxide ceramic (for the CAD/CAM)

*Processing*

The industrial production of the oxide ceramics begins with the cold isostatic pressing of the raw material and shaping methods, which result in stable chalk-similar “green bodies” with a high primary density (Tinschert *et al.*, 2001b).

Additionally there is  the possibility to “hip” densely sintered oxide-ceramic blanks i.e. to consolidate at 1000 bar and 50°C under the sintering temperature again by hot-isostatic pressing (HIP: Hot Isostatic Postcompaction) in order to improve their stability against the growth of microcracks and thus the mechanical long-term behavior of the oxide ceramics (Christel *et al.*, 1989). This procedure was introduced in 1986 by the company Metoxit (Rieger, 2001).

The HIP technology runs in three stages: (1) Presintering of the Y-TZP without pressure in a non-oxide atmosphere up to approx. 95% of the theoretical density (2) warm isostatic pressing process during which the residual porosity is removed (Christel *et al.*, 1989); (3) white-firing in an oxygen-containing atmosphere, whereby the white color of the material is restored.

The final strengthening of the formed “green” and “hipped” white bodies takes place afterwards in an oxidizing atmosphere at 1350-1550°C.

### 2.5.6 Methods for the processing of zirconium dioxide ceramics by means of CAD/CAM procedure).

Three methods can be differentiated as manufacturing methods (Tinschert *et al.*, 2004; Witkowski, 2005):

a) The processing of green, presintered ceramic blanks

b) the processing of partially sintered, so called “white” blanks,

c) the processing of densely sintered blanks

#### ➢ Processing of Green blanks

With this procedure a framework is milled out of a prefabricated porous block, which is manufactured by primary compression of the oxide-ceramic output powder and thus it is easy to process. The framework is subsequently densely sintered.

A model is before digitized and the form of the framework is linear increased (about 20%), in order to compensate the shrinkage during the sintering process (Raigrodski, 2004b). The advantage of this procedure is the faster processing and the smaller wear of the milling instruments.

Investigations showed a reduction of the mechanical characteristics after the processing of densely sintered zirconium dioxide, which could be avoided with this procedure, because the subsequent sintering consolidates the milled raw blanks. (Luthardt and Musil, 1997; Luthardt *et al.*, 1998; Kosmac *et al.*, 1999). Small corrections by the dental technician are nevertheless necessary because of the non-linear contraction.

- **Processing of “white” partially sintered blanks**

The white blanks become pre-sintered under pressure at 1000°C. They have about 55-70% degree of compression, which makes them still relatively porous. This procedure integrates the advantages of the “green” and fully sintered blanks, but on the other hand there is more wear of the milling instruments and also a certain shrinking of the blanks during sintering, which must have been accurately estimated.

- **Processing of fully sintered blanks**

This process takes place after the final sintering of the ceramic blanks and the resulting ceramics show very good accuracy and physical properties (Graber and Besimo CE, 1994; Luthardt and Musil, 1997).

This procedure is however time-consuming and costly because of the wear of the milling instruments (Tinschert *et al.*, 2004).

Examples of different zirconium dioxide products according to the degree of sintering are (Kunzelmann *et al.*, 2006; Strub *et al.*, 2006; Denry and Kelly, 2008):

Milling at green stage: ZirkonZahn® (Steger, Brunneck, Italy), CE.NOVATION® -System (CE.NOVATION, Hermsdorf, Germany)

Milling at white stage : Lava™ Frame für LAVA™ (3M ESPE, Seefeld, Germany),Vita YZ Cubes® (Vita Zahnfabrik, Bad Säckingen, Germany) for CEREC InLab® (Sirona, Bensheim, Germany), IPS e.max ZirCAD (Ivoclar Vivadent AG, Schaan, Liechtenstein) für CEREC InLab®, Sirona, Bensheim, Germany), ZS-Blanks® for EVEREST® (KaVo, Biberach, Germany), Ceramill Zi (Amann Girrbach, Pforzheim, Germany), DC Shrink® for PRECIDENT® (DCS Dental, Allschwil, Switzerland).

Milling at completely sintered or “HIPed” stage:  DC-Zirkon® für Precident® (DCS Dental, Allschwil, Switzerland), ZH-Blanks® for EVEREST® (KaVo, Biberach, Germany), Denzir® for DECIM® (Decim AB, Skellefteå, Sweden), HIP-Zirkon für Etkon® (Etkon AG, Gräfelfingen, Germany).

## 2.6. Studies on surface and heat treatment of zirconia

The usual steps for the fabrication and placement of an all-ceramic restoration with a zirconia frame involve grinding of the material in different stages, polishing, sometimes sandblasting and heat treatment. These surface treatments affect critically the properties of the material and thus its long-term stability and success.

### 2.6.1 Grinding

The influence of grinding on the flexural strength of zirconia ceramics is contradictory and related to the volume percentage of transformed zirconia, which in turn depends on the metastability of the t/m phase transformation, the grinding severity and the locally developed temperatures(Gupta, 1980; Green, 1983; Swain, 1985; Swain and Hannink, 1989; Kosmac *et al.*, 1999; Kosmac *et al.*, 2000).

Many authors studied the effect of milling and grinding of Y-TZP and showed that these procedures reduce the flexural strength and reliability of the material (Xu *et al.*, 1997; Kosmac *et al.*, 1999; Luthardt *et al.*, 2004; Curtis *et al.*, 2006b), while on the other hand grinding under other conditions seems to be beneficial for the strength of the material (Xu *et al.*, 1997; Guazzato *et al.*, 2005b; Denry and Holloway, 2006; Sato *et al.*, 2007) or even have no significant effect (Curtis *et al.*, 2006b).

Garvie et al. (1975) were the first to demonstrate that grinding increases the strength of ceramics containing metastable tetragonal zirconia. This is due to the T→M transformation on the surface of the material and the development of compressive strains from the transformation-related volume increase at a depth of several microns under the surface (Garvie *et al.*, 1975; Gupta, 1980; Green, 1983). The surface compressive stresses prevent microcrack formation or propagation, but also surface and subsurface damage is promoted by grain pullout due to the volume increase and the formation of microcraters (Denry and Holloway, 2006).

Apart from the strained tetragonal grains, a rhombohedral zirconia phase has been found to form after grinding, with similar consequences on the behavior of zirconia as the tetragonal phase (Denry and Holloway, 2006).

Several studies have shown that grinding with coarse grit tools produce deep surface flaws, high surface roughness and extensive heat that reduce the flexural strength of zirconia and may determine the strength of the restoration (Kosmac *et al.*, 2000; Ardlin, 2002; Tinschert *et al.*, 2004).

More recently, Xu et al. reported an improvement in strength of Y-TZP upon fine grinding with 25 mm grit size diamond wheels, whereas coarser grinding resulted in strength reduction (Xu *et al.*, 1997). Curtis found no significant effect of the fine grinding to the flexural strength. However, Xu et al. did not correlate strength to the relative amount of transformed monoclinic phase obtained upon surface treatment.

Swain and Hannink showed that manual grinding with low rotation speed is more effective than lapper-machine grinding in inducing the t/m transformation (Swain and Hannink, 1989) and increasing the surface compressive layer (Ardlin, 2002). They demonstrated that in the case of machine grinding the local development of temperatures exceeded the m→t transformation temperature, causing reverse transformation (Kosmac *et al.*, 2000; Ardlin, 2002).In this instance, the deep defects introduced by grinding are no longer counteracted by the transformation-induced compressive stresses and act as stress concentrators, lowering the mean flexural strength of the ceramic. The authors did not examine the strength response, however, since the strengthening mechanism of zirconia is mainly related to the t→m transformation, a greater mean flexural strength is anticipated when a larger amount of monoclinic phase is detected on the surface of the ceramic. On the basis of the study conducted by Swain and Hannink, Kosmac et al. inferred that the locally developed temperature must have exceeded the m→t transformation temperature. According to the same author the use of water spray during grinding reduces stresses, resulting in a decrease of the critical flaw size by about 30% (Kosmac *et al.*, 2000).

Luthardt examined the effect of CAD/CAM machining on zirconia crowns. They found that grinding of the inner surface induces surface flaws and microcracks at the internal surface of the occlusal region (Luthardt *et al.*, 2004). As shown in failed restorations, these areas concentrate the greatest tensile stresses during clinical loading. Thus, it is important that the concentration of microcracks in these areas is minimized.

Fine-grained Y-TZP materials exhibit high strength after sintering, but are less tolerant to the damage caused by grinding than the tougher coarse-grained Y-TZP, as the grinding-induced cracks extend deeper in its mass (Kosmac *et al.*, 2000).

Guazzato found that the orientation of grinding has no significant effect on the strength of the material and that flaws distributed perpendicular to the grinding orientation initiate fracture when the specimen is loaded (Guazzato *et al.*, 2005b).

The final effect of grinding on material strength depends on the amount of the transformed monoclinic phase (thickness of the transformed layer), the metastability of the t→m transformation, the grinding severity and on the locally developed temperatures (Guazzato *et al.*, 2005b).

### 2.6.2 Sandblasting

Sandblasting of the inner surface of a restoration is usually used to enhance the adhesion strength of the luting agent to the framework (Kern and Wegner 1998). Several studies have also pointed out, that sandblasting of zirconia increases the flexural strength of the material (Kosmac *et al.*, 1999; Guazzato *et al.*, 2005b; Curtis *et al.*, 2006b; Wang *et al.*, 2007; Sato *et al.*, 2007). According to Kosmac, sandblasting provides a powerful technique for strengthening Y-TZP at the expense of somewhat lower reliability (Kosmac *et al.*, 2000). Guazzato also showed an increase of the flexural strength after sandblasting, which was attributed to the higher amount of monoclinic phase detected (Guazzato *et al.*, 2005b), which corresponds to the results of Sato and Ishgi (Ishgi, 2006; Sato *et al.*, 2008).

During air abrasion the sand particles cause significant damage to the material’s surface, which is characterized by erosive wear and lateral cracks. However, a thin layer of compressive stresses because of the transformed M-phase is formed, which counteracts the strength degradation caused by the sandblasting-induced flaws and effectively increases the strength (Kosmac *et al.*, 1999; Guazzato *et al.*, 2005b). The layer of the surface flaws caused by air abrasion does not exceed the layer of compressive stresses created by the phase transformation (Papanagiotou *et al.*, 2006), which according to De Kler is up to 27 µm {De Kler , 2007 309 /id}. Lower temperatures and stresses are developed than in grinding which induces more effectively the t→m transformation (Guazzato *et al.*, 2005b).

In another study Curtis et al. found an increase of the strength as well as of the reliability of dry stored sandblasted zirconia contrary to Kosmac, which was explained by the combination of compressive stresses and low surface roughness (Curtis *et al.*, 2006b)

Sandblasting after grinding reduces the critical flaw size of the grinded surface, because it greatly levels the material surface and removes the larger grinding-induced crack (Kosmac *et al.*, 1999).

On the other hand, other studies have shown that sandblasting before the cementation of Y-TZP restorations mechanically assists the growth of pre-existing flaws, reducing the strength and lifetime of the restoration (Zhang *et al.*, 2004).

### 2.6.3 Heat Treatment

Several studies indicate that heat treatment influences the core materials in several ways even when the temperatures are below the core materials' own sintering temperature (Cattell *et al.*, 2002; Guazzato *et al.*, 2004b; Balkaya *et al.*, 2005; Isgro *et al.*, 2005; Sundh *et al.*, 2005).

Heat treatment of Y-TZP has been studied by several authors and in most studies it was found to have a counteracting effect to surface treatment on the flexure strength of zirconia. It has often been considered as an aging accelerator for orthopedic implants of yttria-stabilized zirconia (Deville *et al.*, 2006; Chevalier, 2006)

Heat treatment induces a reverse phase transformation and thus a reduction of the monoclinic phase {De Kler , 2007 309 /id;Guazzato, 2005 2 /id;Sato, 2007 69 /id}, which leads to the release of the compressive stresses on the surface of the material and a reduction of its strength (Kosmac *et al.*, 2000; Guazzato *et al.*, 2005b). According to Oilo microcracks generated during the milling procedure or surface treatment may propagate during firing because of the alterations of the grain size and the relieved stresses (Oilo *et al.*, 2008). This effect of the heat treatment with the m→t transformation may occur instantly as a given temperature is reached and regardless of the holding time (Guazzato *et al.*, 2005b).

Denry et al. showed in a study, that annealing of ground or ground and polished specimens leads to the disappearance of residual strains (Denry and Holloway, 2006), while Ishgi et al. found that all groups in their study had a negligible amount of monoclinic phase after firing and that firing reduced the flexure strength of the ground specimens (Ishgi, 2006).

Contrary to these studies, Wang et al. and Ruiz et al. in their studies found the flexural strength of zirconia to be insensitive to heat treatment (Ruiz and Readey, 1996; Wang *et al.*, 2007).

Under clinical conditions, a greater amount of monoclinic phase on the surface and therefore a greater flexural strength may be desirable. On the other hand, an excessive amount of M-phase could lead to microcracking (Guazzato *et al.*, 2005b) and predispose the material to a more rapid moisture-assisted transformation over time and loading in the acidic and aqueous oral environment (De Aza *et al.*, 2002).

Even though many authors have showed that annealing of surface treated zirconia leads to a reduction of its flexural strength, several manufacturers recommend a “Regeneration firing” in case of a surface modification of the material after sintering (for example Vita at 1000°C for 15 min; Ivoclar Vivadent

1050°C for 15 min). This firing is supposed to prevent the tension, which is created between the frame and the veneering ceramic due to the alteration of the CTE of the monoclinic Y-TZP (Vita Zahnfabrik, 2004; Ivoclar-Vivadent, 2008).

Nevertheless this recommendation should be seen critically, as the heat treatment of Y-TZP also in temperatures below 1000°C and independent of the holding time leads to a reverse transformation and the release of the compressive stresses (Guazzato *et al.*, 2005b), which no longer counteract the flaws caused by the surface modification, thus lowering the strength of the material (Kosmac *et al.*, 1999; Kosmac *et al.*, 2000; Sundh *et al.*, 2005; Guazzato *et al.*, 2005b).

## 3. Aim of the study

Aim of this study was to evaluate the effect of sandblasting and/or wet grinding with fine burs as well as the effect of subsequent thermal treatment on the flexural strength and reliability of a Y-TZP ceramic (LAVA™, 3M ESPE, Seefeld, Germany).

## 4. Outline of the study

180 disc-shaped specimens of a Y-TZP ceramic were delivered from the manufacturer. The specimens were randomly divided in one control group and 5 test groups of 30 specimens each. In the control group C the discs were left as delivered without further modification. The discs of group S were sandblasted with $Al_2O_3$ on the top surface, while the ones of group G were mildly ground with a fine-grained diamond bur on one side. The specimens of group SG were first sandblasted with alumina and were then ground with a fine-grained diamond bur. The top surface of the discs in group SF were first abraded with alumina

and subsequently annealed at 1000°C and the ones of group GF were first ground and then annealed at 1000°C. During the surface treatment of the specimens, some of them were damaged and were excluded from the study, thus resulting in the following distribution:

Group C: 30 discs

Group S: 30 discs

Group SG: 27 discs

Group G: 30 discs

Group SF: 29 discs

Group GF: 28 discs

The roughness of the modified surface of five randomly chosen samples of each group was measured. Specimens of all groups were then examined with X-Ray diffraction analysis, in order to assess the status of the remaining monoclinic phase on the surface of the material.

Subsequently all specimens were loaded in a universal testing machine until fracture occurred.

Figure 4.1 shows the outline of the study:

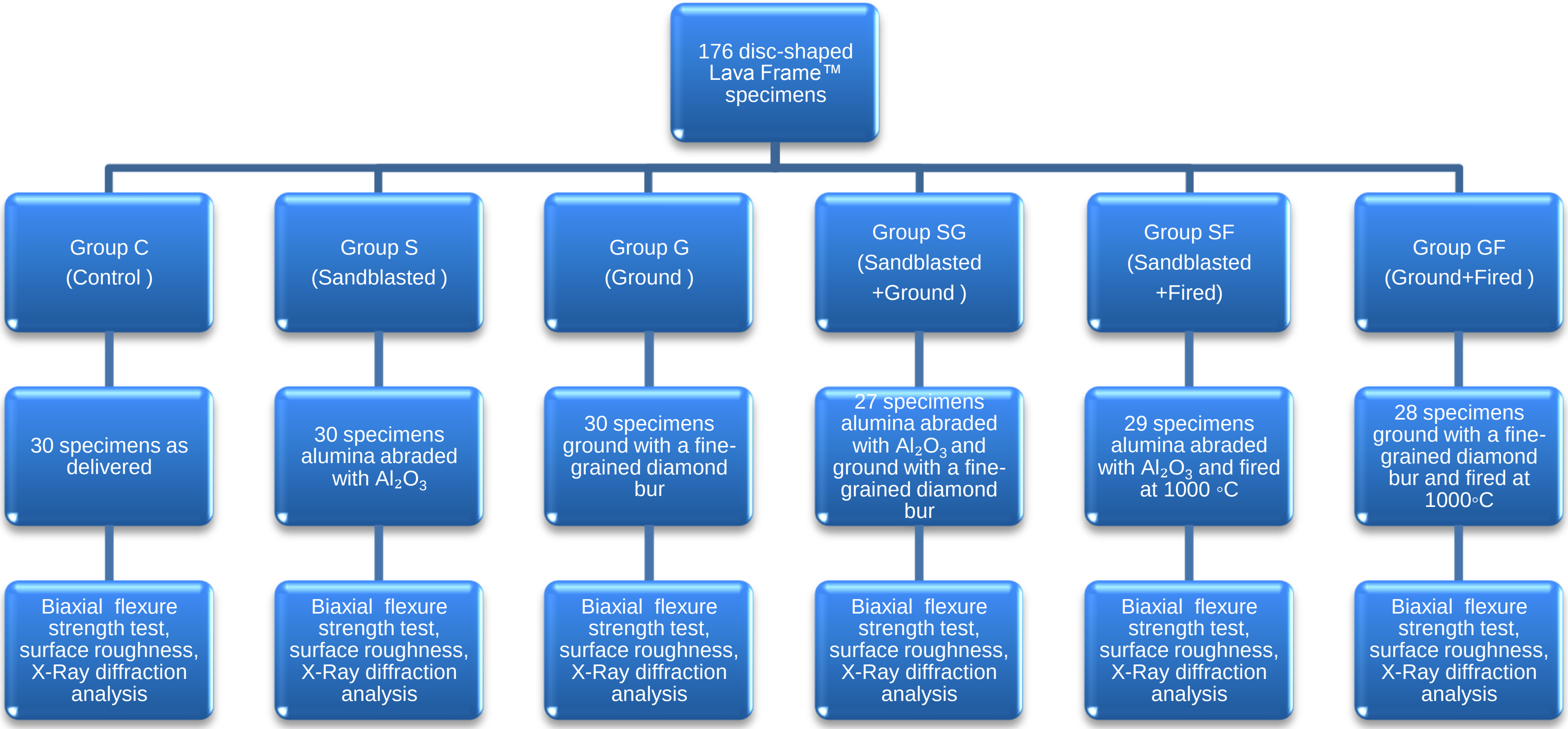

Fig. 4.1. Outline of the study.

# 5. Materials and methods

## 5.1 Material used for the fabrication of the Y-TZP discs

180 Lava™ Frame discs (3M ESPE, Seefeld, Germany) were delivered from the manufacturer.

Lava™ Frame is the partially sintered zirconia ceramic processed by the Lava™ system as yttrium-stabilized green blanks . The Lava™ system (see also chapter 3.1.1.) comprises of a CAD/CAM procedure for the fabrication of Lava™ crowns and bridges made of zirconia for anterior and posterior applications. The frameworks are fabricated using CAD/CAM manufacturing techniques for pre-sintered zirconia blanks. The milled framework, whose size has been increased to compensate for the shrinkage during sintering, is sintered in a special high temperature furnace (Lava™ Therm), thus leading to a high strength restoration.

The Lava™ Frame zirconium oxide frameworks are fabricated by milling centers.

The physical properties of the material are shown on table 5.1.

**Table 5.1. Physical properties of Lava™ Frame (source: Lava™ Brochure, 3M/ESPE Dental AG, Seefeld, Germany).**

| | |
|---|---|
| Density (ρ): | 6.08 g $cm^{-3}$ |
| Flexural Strength (s) (Punch test) | > 1100 MPa |
| Fracture Toughness ($K_{IC}$): | 5-10 MPa √m |
| Young's modulus of elasticity (E): | > 205 GPa |
| CTE: | $10 \times 10^{-6}$ $K^{-1}$ |
| Melting point: | 2700 °C |
| Grain size: | 0.5 µm |
| Vickers hardness | 1250 HV |

## 5.2 Fabrication of the specimens

180 disc-shaped specimens of Lava™ Frame (3M/ESPE Dental AG, Seefeld, Germany) zirconia ceramic were supplied by the manufacturer.

The Lava™ Frame poles were initially trimmed to a diameter of 20.2 mm and then sliced in discs of 1.7 mm thickness with a carbide blade. After removing the surface to a thickness of 1.51 mm with a SiC sand paper (grit 320 µm, P400), the discs were sintered in a Lava™ Therm furnace according to the recommendations of the manufacturer.

The delivered disc specimens had a diameter of 16mm and an average thickness of 1.2 mm according to the ISO Norm 6872 for testing ceramics.

On delivery the specimens were randomly divided in 6 groups of 30 specimens as follows:

Group C (control)

Group S (sandblasted)

Groups SG (sandblasted and ground)

Group G (ground)

Group SF (sandblasted and fired)

Groups GF (ground and fired)

## 5.3 Microscopy after preparation

Five random specimens were inspected under a light microscope (Wild Heerbrugg AG, Heerbrugg, Switzerland) at x12.5 magnification prior to testing to ensure that they were free from cracks and other processing defects.

## 5.4 Measuring of the specimens

The dimensions of the specimens were measured with a digital caliper (Digimatic CD-4 BS, Mitutoyo Corporation, Japan) before and after the preparation of the specimens. The thickness of each specimen was calculated as the mean of three measurements taken at random sites.

## 5.5 Preparation of the specimens

- **Control group**

In group C (control group) the specimens were left without any modification of the surface.

- **Sandblasting**

The specimens of group S (sandblasted group) were mounted on a metal table with double-faced adhesive tape (Tesa mounting tape, Tesa AG, Hamburg, Germany) and the metal table was set in the middle of the sandblasting apparatus ( PG400, Harnisch & Rieth, Winterbach, Germany). The blasting tip was fixed at a distance of 20mm from the specimen and perpendicular to them with double-faced adhesive tape (Tesa mounting tape, Tesa AG, Hamburg, Germany). The sandblaster unit was equipped with a nozzle of 2 mm diameter.

The alumina abrasion regime was carried out for 20 sec for each specimen at a distance of 2cm at 2 bar with 50µm $Al_2O_3$ (Harnisch & Rieth, Winterbach, Germany). Abrasion was carried out uniformly across the specimen surface by moving the metal table to different directions to avoid formation of areas of localized stress.

For the group SF (sandblasted and fired) the same regime was followed prior to the heat treatment.

For the group SG (sandblasted and ground) the same regime was carried out prior to grinding.

After surface treatment the specimens were cleaned with ethanol in an ultrasonic bath (Sonorex RH, Bandelin, Berlin, Germany) for 15 min and then air-dried.

- **Grinding**

The specimens of group G were ground on the top surface with a fine-grit diamond bur (ISO-No. 806 314 111514 014, Komet Brasseler, Lemgo, Germany). The burs had a mean grain size of 30 µm, while the part of the burs with the diamond grains had a length of 8mm, thus covering exactly half of the surface of the zirconia discs.

The diamond burs were mounted on a red-ring dental handpiece ( INTRA Compact 25 LHC, Kavo Dental, Biberach, Germany). The handpiece was mounted on an apparatus designed for standardized grinding.

The specimens were fixed with double-faced adhesive tape (Tesa mounting tape, Tesa AG, Hamburg, Germany) on an acrylic block, which was fixed on a metal holder. The metal holder could be moved in two directions (on the “X” and “Z” axis) by rotating two metal wheels; one for each direction.

The handpiece was mounted on a holder that could be rotated 360 degrees and fixed in one position. The position of the holder with the handpiece could also be adjusted in two directions (on the “Y” and “Z” axis) by rotating a wheel for each direction. By adjusting these three elements, the surface of the diamond bur lay on and parallel to the surface of the disc specimen. The holder with the handpiece could then be moved manually on the “X” axis on a metal rail during grinding.

After adjusting the position of the handpiece and thus the diamond bur on the top surface of the specimen, the specimen was ground at a rotation speed of 20000 rpm (the optimal speed according to the manufacturer) for 6 seconds by moving the holder with the handpiece manually back and forth on the “X” axis.

Subsequently the specimen was dismounted and mounted again on the acrylic block rotated at 180° on the horizontal level and the regime was repeated to prepare the other half of the top surface of the specimen.

The diamond burs were exchanged with new ones after grinding of five specimens.

For the group GF the same regime was followed prior to heat treatment.

For the group SG the same regime was carried out after sandblasting of the specimens of the group.

After surface treatment the specimens were cleaned with ethanol in an ultrasonic bath (Sonorex RH, Bandelin, Berlin, Germany) for 15 min and then air-dried.

Figure 5.1 shows the apparatus used for the grinding of the probes.

- **Heat treatment**

After the surface modification, the specimens of groups SF and GF were heat treated. The firing procedure was carried out in a ceramic furnace (Vita Vacumat 50 Vita Zahnfabrik, Bad Säckingen, Germany) for 10 minutes at 1000 °C. The specimens were allowed to slowly cool down and the furnace was opened when the temperature reached 600 °C. The specimens were fired at this temperature after testing two samples fired at different temperatures; one at 1000°C and one at 1150°C with X-Ray diffraction analysis. The analysis showed no difference in the amount of monoclinic phase between the samples and it was decided to carry out the firing procedures at the lower temperature in compliance with the recommendations of the manufacturer (3M ESPE, Seefeld, Germany) for the “Regeneration firing”.

During the surface treatment of the specimens, some of them were damaged and were excluded from the study, thus resulting in the following distribution:

Group C: 30 discs

Group S: 30 discs

Group SG: 27 discs

Group G: 30 discs

Group SF: 29 discs

Group GF: 28 discs

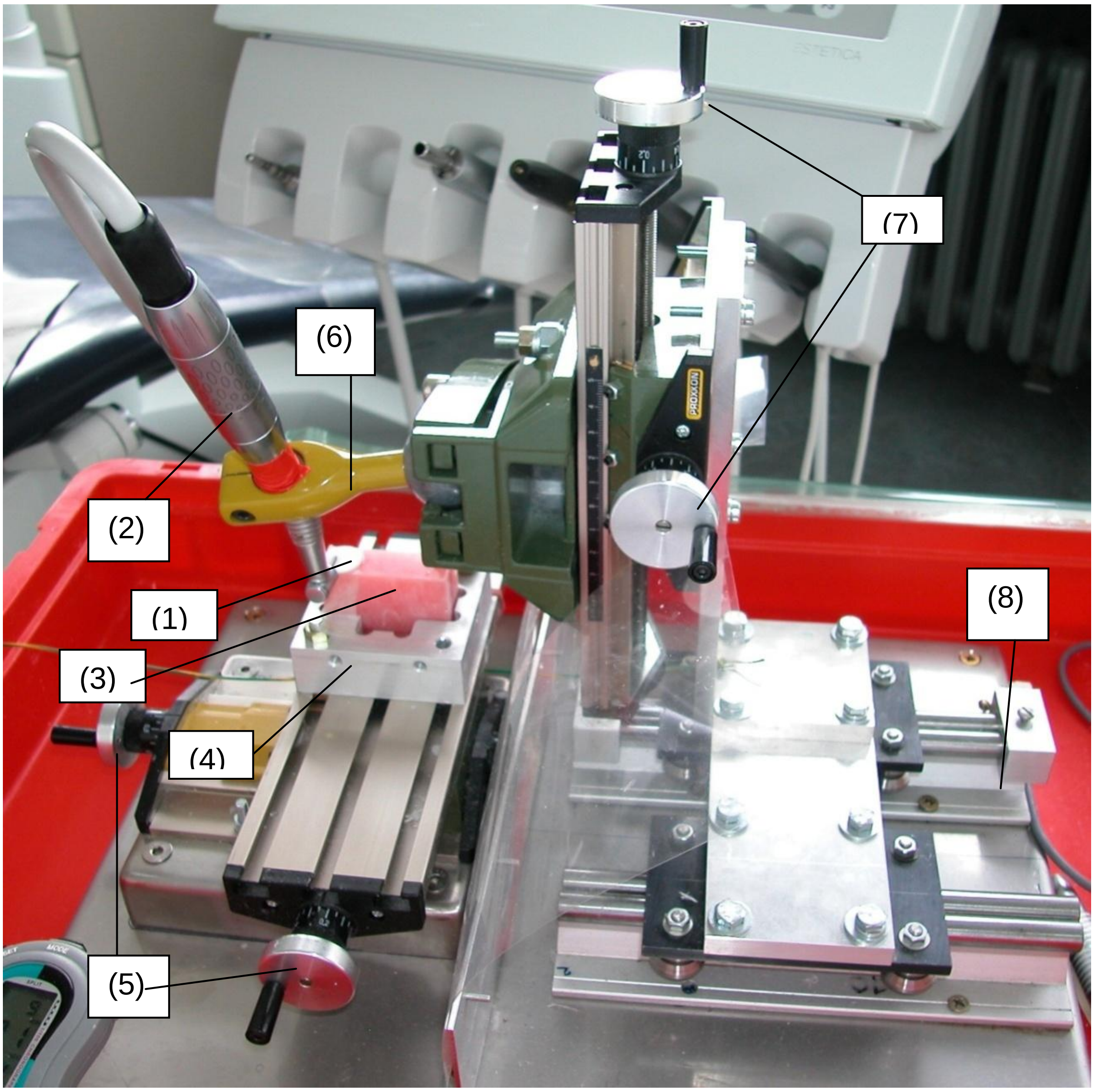

Fig. 5.1. Apparatus used for the grinding of the probes: 1) Zirconia disc sample,

2) Dental handpiece, 3) Acrylic block, 4) Metal holder, 5) Metal wheels, 6) Holder, 7) Metal wheels, 8) Metal rail.

## 5.6 Measurements after the treatment

Following the surface treatment of the specimens, the zirconia discs were once again measured as described above. The thickness of each specimen was calculated as the mean of three measurements taken at random sites.

## 5.7 Microscopy after preparation

Five random specimens of every group were inspected under a light microscope (Wild Heerbrugg AG, Heerbrugg, Switzerland) at x12.5 magnification prior to testing to ensure that they were free from cracks and other processing defects.

## 5.8 Tests

### 5.8.1 Surface morphology

The morphology of two random specimens of every of the six groups was examined with a scanning electron microscope (Leo 1430, Zeiss, Oberkochen, Germany) at 50, 100, 1000 and 2000 magnification and was fotodocumented. Aim was to display the micromorphology of the surface of the specimens and identify the impact of the surface treatments.

### 5.8.2 Surface roughness

A profilometer (Perthometer R6P, MAHR GmbH, Göttingen, Germany) was used to determine the roughness of the tensile stress surface of 5 random specimens of every group. Five measurements (profiles) with a scan length of 5.6mm were performed on five random probes of each group with the exception of group GF, where only pieces of three specimens could be used after the flexure strength test for this purpose. For the groups G, SG and GF the measurements were carried out perpendicular to the grinding direction.

The variable for surface roughness Ra was recorded, where Ra is the arithmetic mean profile deviation. The mean values of the recordings were used in the analyses.

### 5.8.3 X-Ray diffraction analysis

X-ray diffraction (XRD) analysis was employed to examine the disc-shaped ceramic specimens following alumina abrasion and grinding, in order to assess the influence of the surface modification and the firing procedures on the phase composition and the occurrence of phase transformations in the Y-TZP ceramic. XRD was performed at 3M ESPE (3M ESPE, Seefeld, Germany) using a D8 Discover Diffractometer (Bruker AXS, Karlsruhe, Germany). Specimens' surfaces were scanned with Cu Ka X-Ray and diffraction data were collected from the 2θ range between 10° and 90° with a step size of 0.0196°. A quantitative value of phase compositions of the Y-TZP ceramic was not calculated.

### 5.8.4 Biaxial flexure strength test (piston-on-three-ball test)

The biaxial flexure test was performed according to the ISO 6872 for ceramics.

- **Biaxial flexural strength test fixture:**

For the support of the test specimen, three hardened steel balls with a diameter of 3.2±0.5 mm positioned 120° apart on a support circle with a diameter of 10mm were used. A 0.5 mm thick plastic foil was placed at the center of the sample's surface to achieve homogenous load distribution. The sample was placed concentrically on these three supports and the load was applied with a flat punch with a diameter of 1.2 mm at the center of the specimen.

- **Testing machine and loading:**

Using a universal-testing machine (Zwick, Z010, Ulm, Germany), all samples were loaded at a cross speed of 1mm/min until fracture occurred (Fig. 5.2 and 5.3).

The loads required for fracturing the samples were recorded with the Zwick testXpert® 12.0 software.

### 5.8.5 Statistical analysis

Multiple comparisons of the results for the flexural strength and the surface roughness were made utilizing multiple Welch tests, because the requirement of variance equality for a one-way analysis of variance (ANOVA) was not met. The p values, which were calculated with the Welch tests, were adjusted with the Bonferroni-Holm method.

The variability of the flexural strength values was analyzed using the Weibull distribution and calculating the Weibull module (m) and the characteristic strength $\sigma_0$, which is the flexural strength at a 63.2 % failure probability.

The bi-axial flexure strength data was ranked in ascending order and Weibull analysis was performed on the resultant data to establish the reliability of the material by determining the probability of failure as a function of the applied stress (International Organization for Standardization, 1999). The intercept of the y-axis was $\ln(\sigma_0)$ and the gradient of the graph was m signifying the reliability of the specimen group to have undergone testing. The Weibull analysis was performed on the flexural strength data by plotting ln ln[1/(1-Pf] against ln σ, where Pf is the probability of failure and σ is the tensile stress. The gradient of the strength distribution data (m) was determined by superimposing a regression line along the data points to calculate the Weibull modulus for each specimen group. A high value of m indicates a high homogeneity in the defect population and a more predictable rate of failure observed as a steep slope with a reduced scatter of data and increased reliability.

The statistical analysis was performed with the help of Prof. Dr. K. Dietz at the Institute for Biometry and Statistics of the Eberhard-Karls University, Tübingen, Germany. For this purpose the software “JMP”, Version 7 was used.

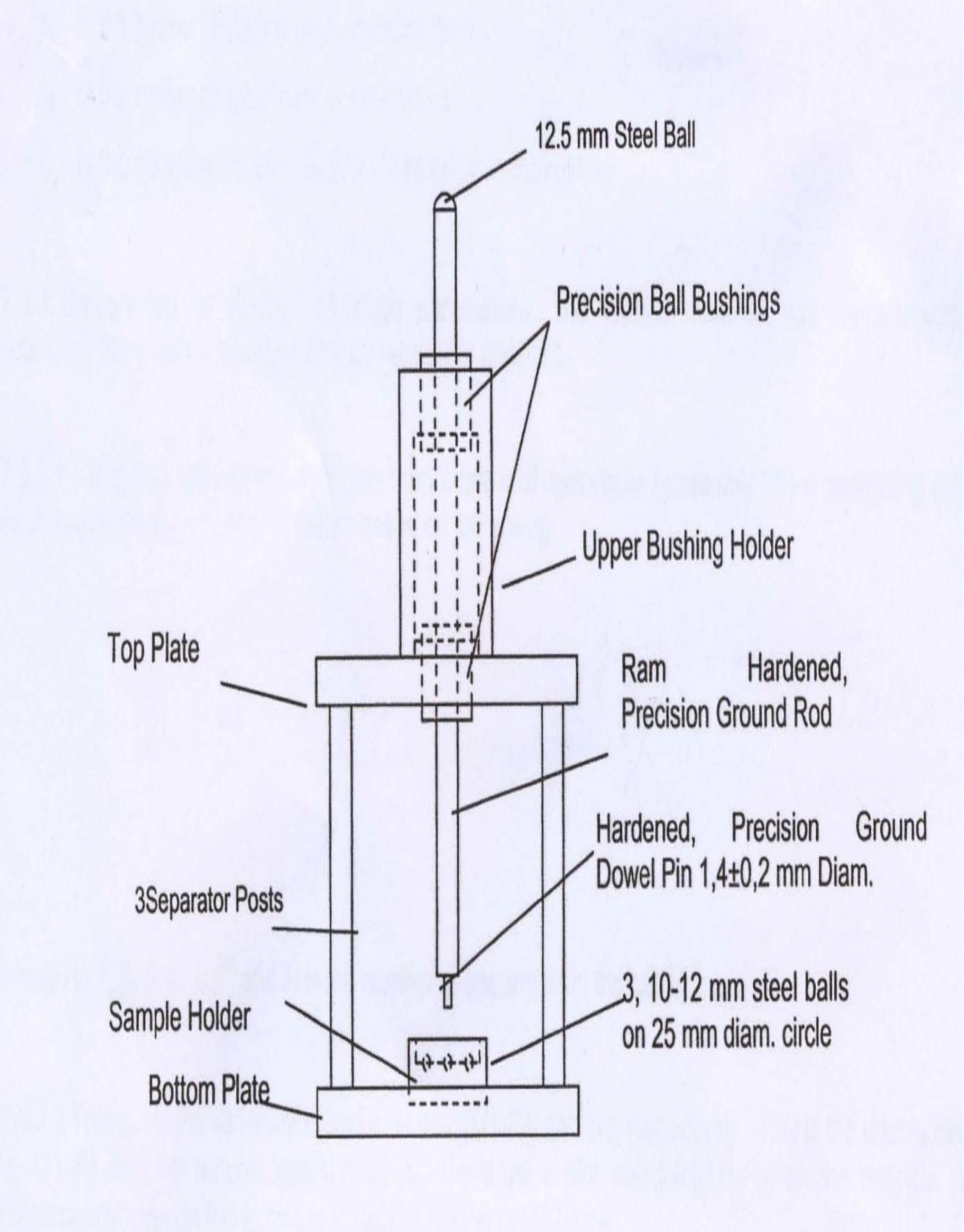

Fig. 5.2. Schematic drawing of the biaxial flexure test.

Fig. 5.3. Picture of the apparatus for the biaxial flexure strength test.

## 6. Results

### 6.1 Flexure Strength

Data of the biaxial flexure strength testing of all groups are presented graphically in figure 6.1.

In general, all surface treatments tend to increase the mean flexural strength of the material and the following heat treatment tends to decrease it.

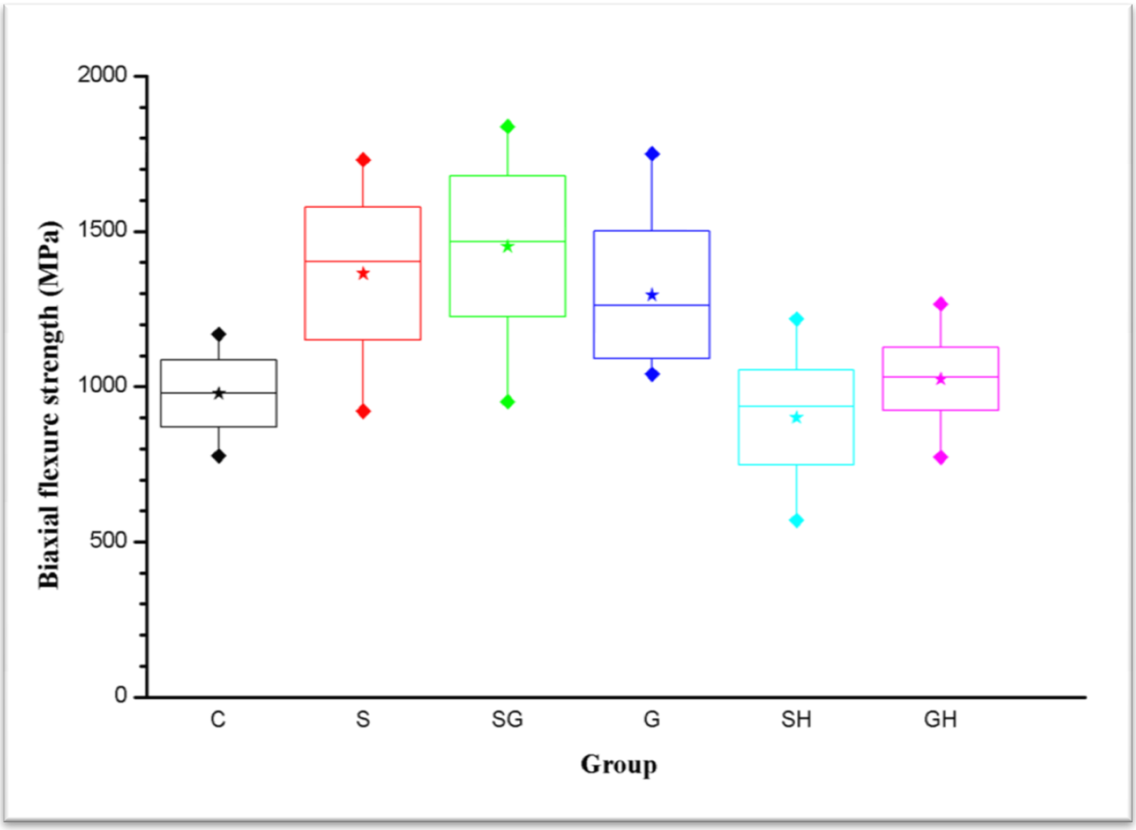

Fig. 6.1. Box-plot diagramm comprising the biaxial flexure strength of the six tested groups. The central box shows the data between the standard deviation. The mean flexure strength is presented as a star in the box. The median value is presented with a horizontal line within the box. The maximum and minimum values are illustrated via the upper and lower strokes.

The average flexural strength and standard deviation of the tested groups, as well as the maximum and minimum values are shown on table 6.1.

The statistical analysis revealed that the surface treatment of the zirconia probes had a significant effect on the flexural strength. Groups S, SG and G had significantly higher strength than the control group. There was no significant difference of strength between the groups S and SG and S and G, but the group SG had significantly higher strength than group G.

The thermal firing following surface treatment (Groups SF and GF) reduced significantly the strength of the surface treated specimens, but it had no significant effect compared to the control group, while there was also a significant difference found between the two groups, that underwent heat treatment subsequent to heat treatment ( 6.1).

**Table 6.1. Flexural strength (s), surface roughness (Ra), Weibull module (m) and characteristic strength ($\sigma_0$) of the tested groups.**

| Surface condition | Roughness Ra (µm) | Mean flexural strength (MPa) | S.D. of strength (MPa) | Max. strength (MPa) | Min. strength (MPa) | m | $\sigma_0$ (MPa) |
|---|---|---|---|---|---|---|---|
| **Control** | 0.77 | $978^{A,B}$ | 108 | 1169 | 777 | 10.94 | 1024 |
| **Sandbl.** | 0.7 | $1364^{D,C}$ | 213 | 1731 | 921 | 7.6 | 1452 |
| **Sandbl. +Ground** | 0.8 | $1452^{D}$ | 228 | 1837 | 952 | 7.4 | 1547 |
| **Ground** | 0.56 | $1296^{C}$ | 205 | 1749 | 1041 | 7.4 | 1382 |
| **Sandbl. +Fired** | 0.6 | $901^{A}$ | 154 | 1218 | 570 | 6.9 | 963 |
| **Ground +Fired** | 0.94 | $1024^{B}$ | 101 | 1266 | 773 | 12.14 | 1068 |

*Average flexure strength of the groups with same superscript letter was statistically not significantly different.

## 6.2 Scanning electron microscopy (SEM)

SEM showed that the control group is characterized by a rather rough surface with several weakly attached grains on the surface (Fig. 6.2-A).

Air-borne particle abrasion resulted in uniformly damaged surfaces with pitting, small surface defects and randomly orientated scratches and cracks, but less grains on the surface than the control group (Fig. 6.2-B).

The ground surface is characterized by numerous parallel scratches with deformed and displaced material at the edge of the scratches, but all in all smoother than the previous groups (Fig. 6.2-C).

The sandblasted and ground surface is similar to the ground surface, but rougher with parallel scratches and minor cracks visible between the traces left by the diamond bur (Fig. 6.2-D).

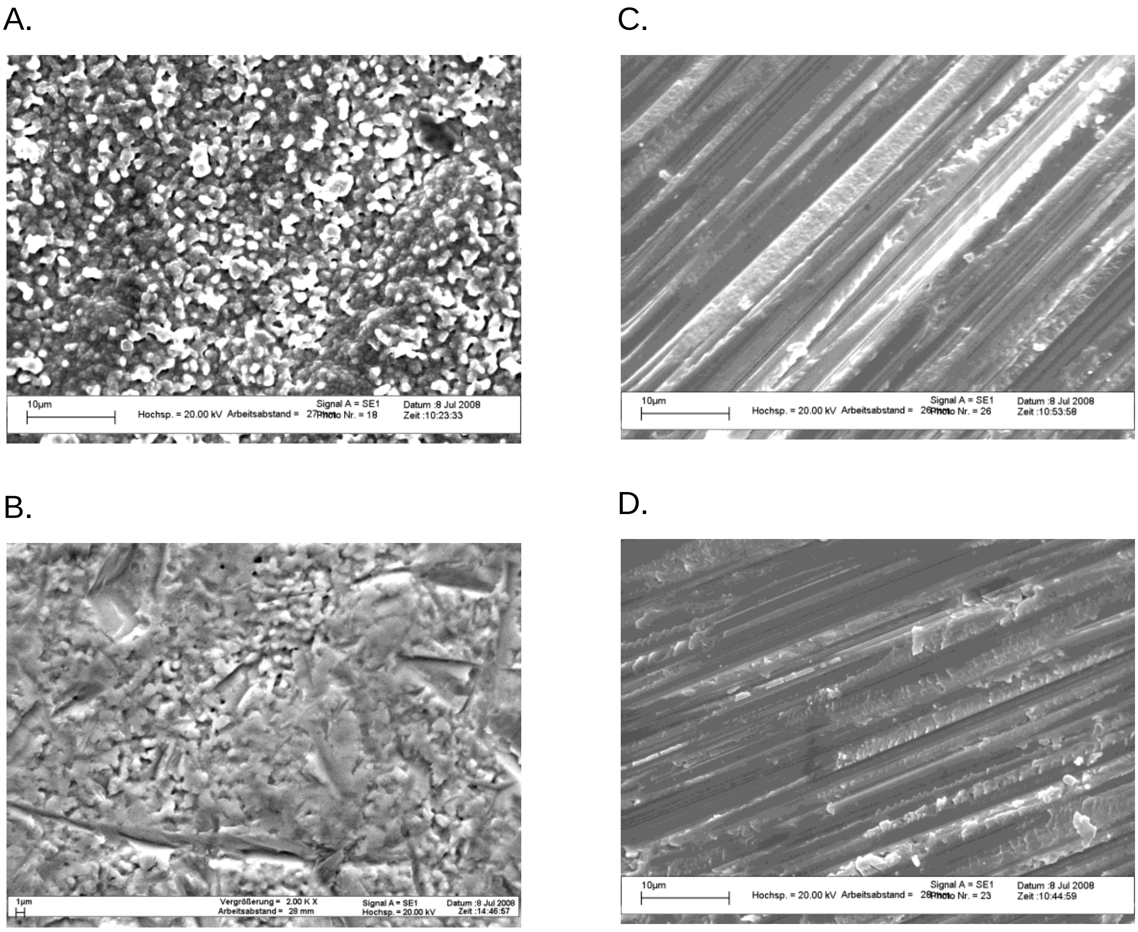

Fig. 6.2. SEM. A) Control: Weakly attached surface grains. B) Sandblasted: Pitting and small surface defects, but less surface grains. C) Ground: Parallel scratches, smoother surface D) Sandblasted and ground: Rough surface, scratches and minor cracks.

### 6.3 Reliability

Weibull statistical analysis of the biaxial flexural strength data yielded a plot of failure probability shown on Fig. 6.3 and two characteristic parameters for each test group, the characteristic strength $\sigma_0$ (which is the scale parameter) and the Weibull modulus m (which is the slope parameter).

For all test groups, the highest reliability of strength was obtained for the group GF, as indicated by the m-value, followed by the control group. The Weibull module of the three groups with surface modification (S, SG, G) dropped to approximately two thirds of the initial value (control group) after the surface treatment. Firing after sandblasting lead to a further drop of the m value, whereas firing of the ground specimens lead to the highest Weibull modulus of the tested groups. The results are summarized in Table 6.1.

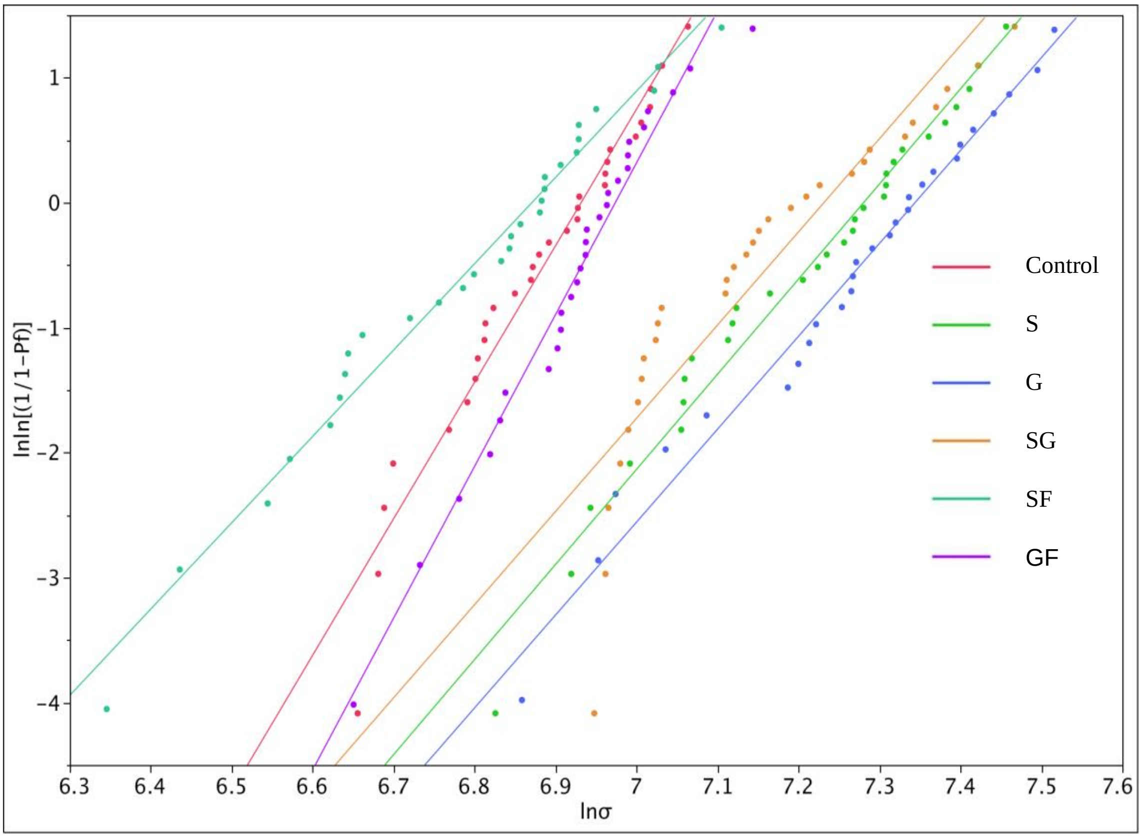

Fig. 6.3. Failure probability plots of the tested groups.

## 6.4 Surface roughness

The statistical analysis of the results of the surface profilometry indicated, that there was no significant correlation between the surface roughness and the flexure strength of the probes.

The results of the measurements are presented in table 6.1. As indicated by the measured variable Ra, the ground and fired zirconia discs had the highest surface roughness, followed by the sandblasted and ground (SG) and the control group, while the lowest surface roughness was found for the ground specimens.

As presented in table 6.2. the roughness of group G was significantly lower than in groups C, S and SG, while between the groups C, S and SG no significant difference was found. The group GF had also a significantly higher roughness than the groups S, G and SF and also group SF compared to the control group.

**Table 6.2. Comparison of the surface roughness. 0 indicates no significant difference; 1 indicates that the difference is statistically significant.**

| Group1 | Group2 | Significant |
|---|---|---|
| C | SG | 0 |
| G | SF | 0 |
| S | SG | 0 |
| C | S | 0 |
| SG | GF | 0 |
| S | SF | 0 |
| C | GF | 0 |
| SG | SF | 0 |
| S | GF | 1 |
| C | SF | 1 |
| S | G | 1 |
| SG | G | 1 |
| SF | GF | 1 |
| G | GF | 1 |
| C | G | 1 |

## 6.5 X-Ray diffraction

The results of the X-Ray diffraction for the groups C, S, SG and G before the heat treatment are presented in figure 6.4. The monoclinic peak is almost exclusively at 28.2° (in the range of values 20-40° of the 2θ scale). As seen on the peak of the monoclinic phase in figure 6.5. the greatest amount of monoclinic phase was found in the sandblasted specimens, followed by the sandblasted and ground. Lower amounts of monoclinic phase were obtained for the group G and for the control group the monoclinic phase was negligible. The main peak of the tetragonal phase is detected at 30.2°.

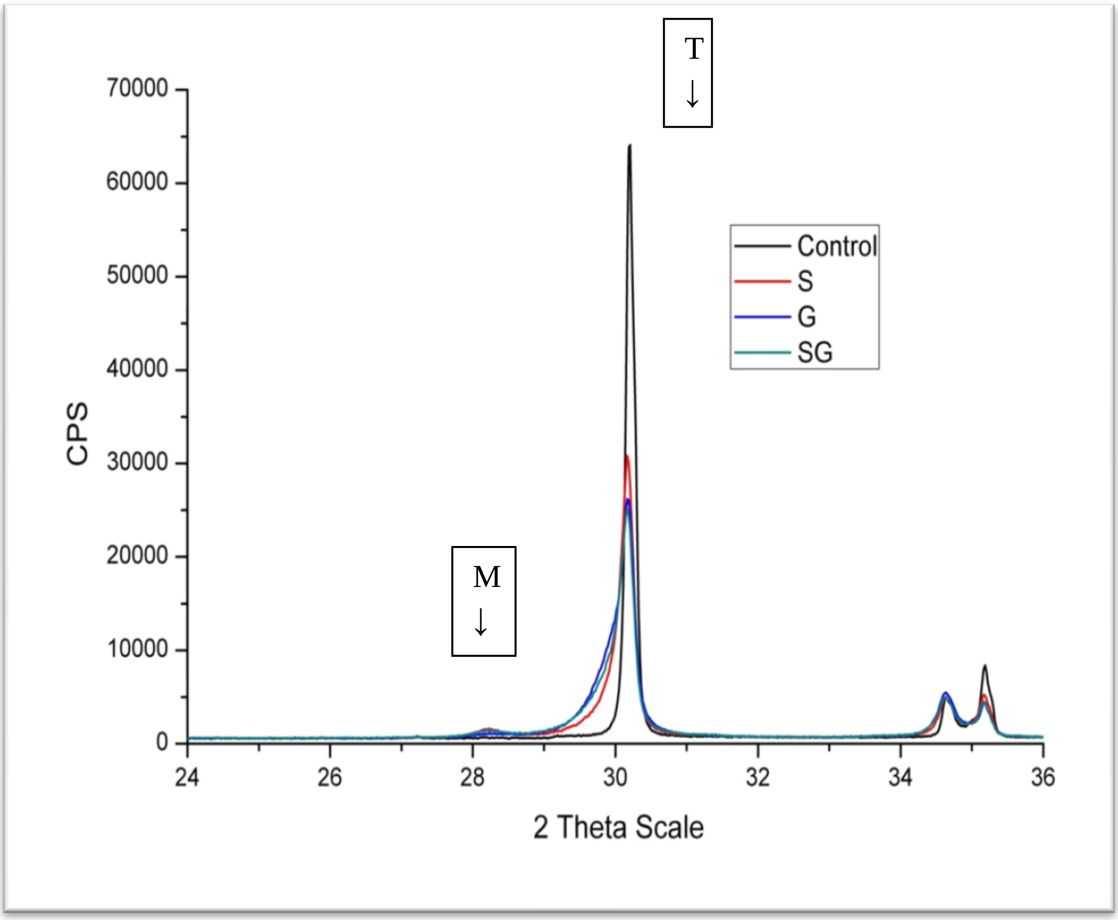

Fig. 6.4. XRD pattern obtained by the surface of the control, sandblasted, sandblasted and ground and ground Y-TZP discs. “T” the tetragonal and “M” the monoclinic zirconia phase.

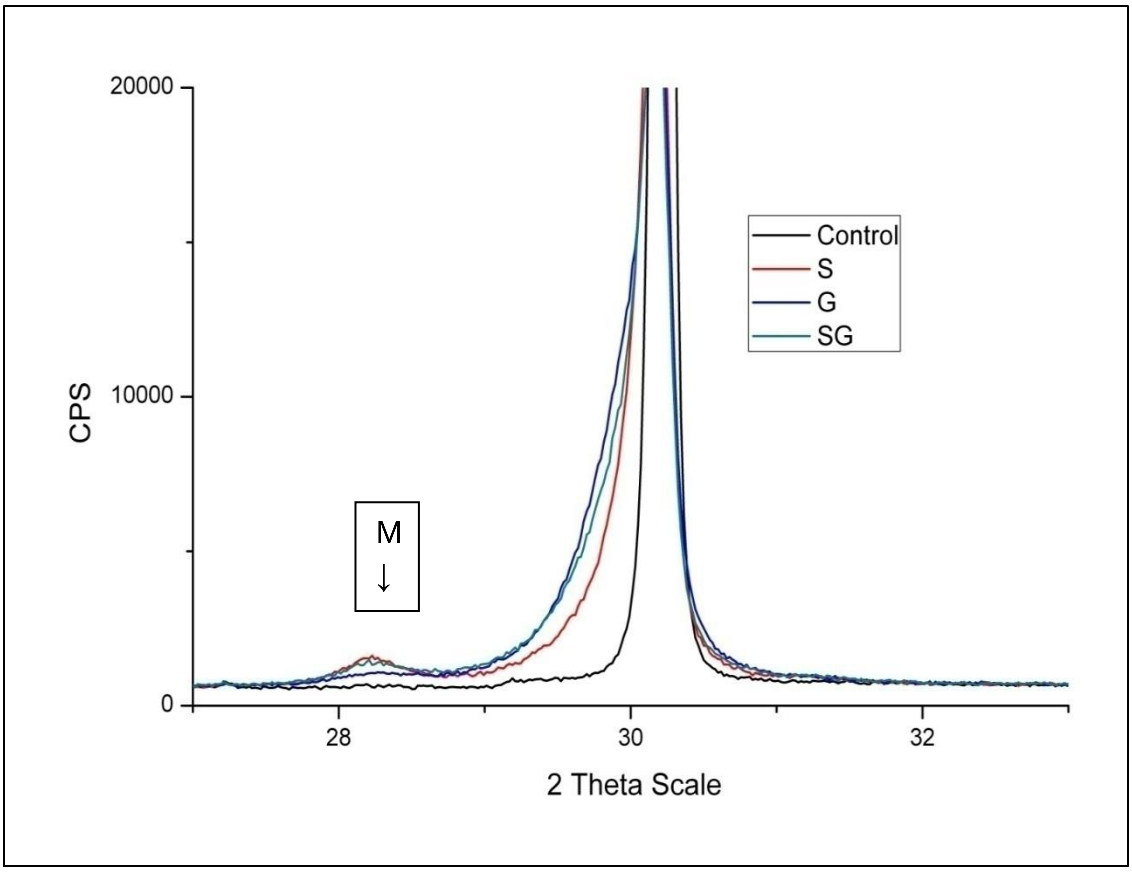

Fig. 6.5. Magnification of Fig. 6.4. between 28° and 32° of the 2θ scale. “M” the monoclinic zirconia phase.

Apart from the phase transformation, also a lattice distortion is observed in the surface treated groups, as indicated by the widening of the tetragonal peaks. The highest lattice distortion is found for the ground and sandblasted and ground discs, followed by group S.

According to the XRD patterns obtained from the zirconia surfaces after firing, heat treatment resulted to the disappearance of the monoclinic peak of the surface treated specimens for all three groups S, SG and G, as well as to the reduction of the lattice distortion, as shown on figure 6.6. Nevertheless, as presented in figure 6.7. the regeneration of the lattice was not complete, as the tetragonal peaks of all groups remain wider than the one of the control group. The firing procedure had no effect on the XRD pattern of the control group. (The

XRD patterns prior and after heat treatment are presented pairwise in chapter 11).

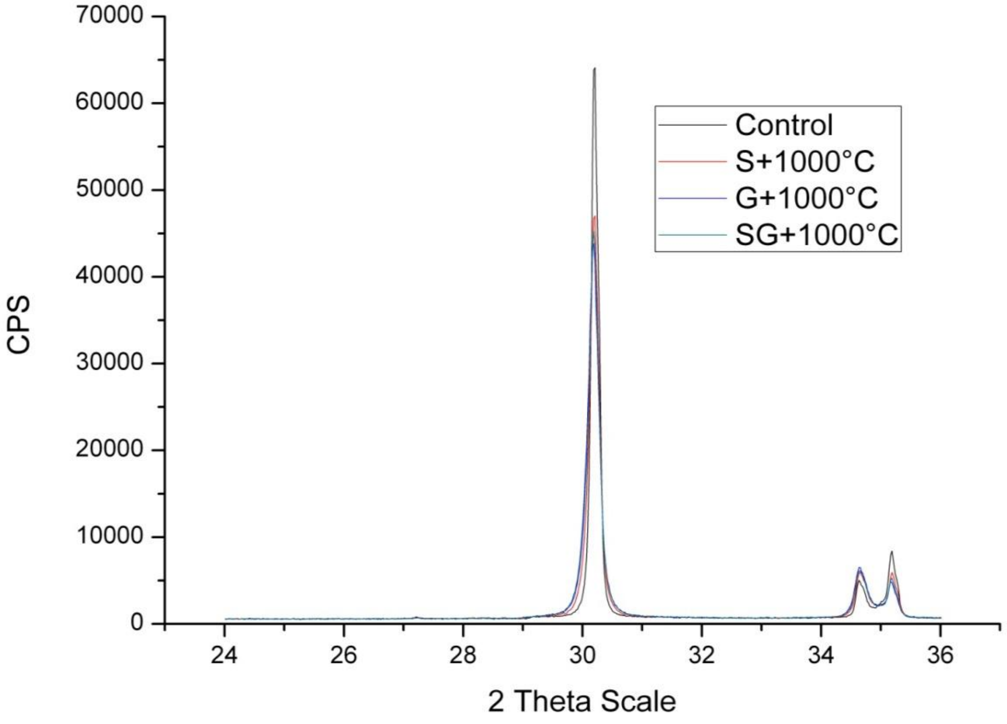

Fig. 6.6. XRD pattern obtained by the surface of the control, sandblasted, sandblasted and ground and ground Y-TZP discs after firing.

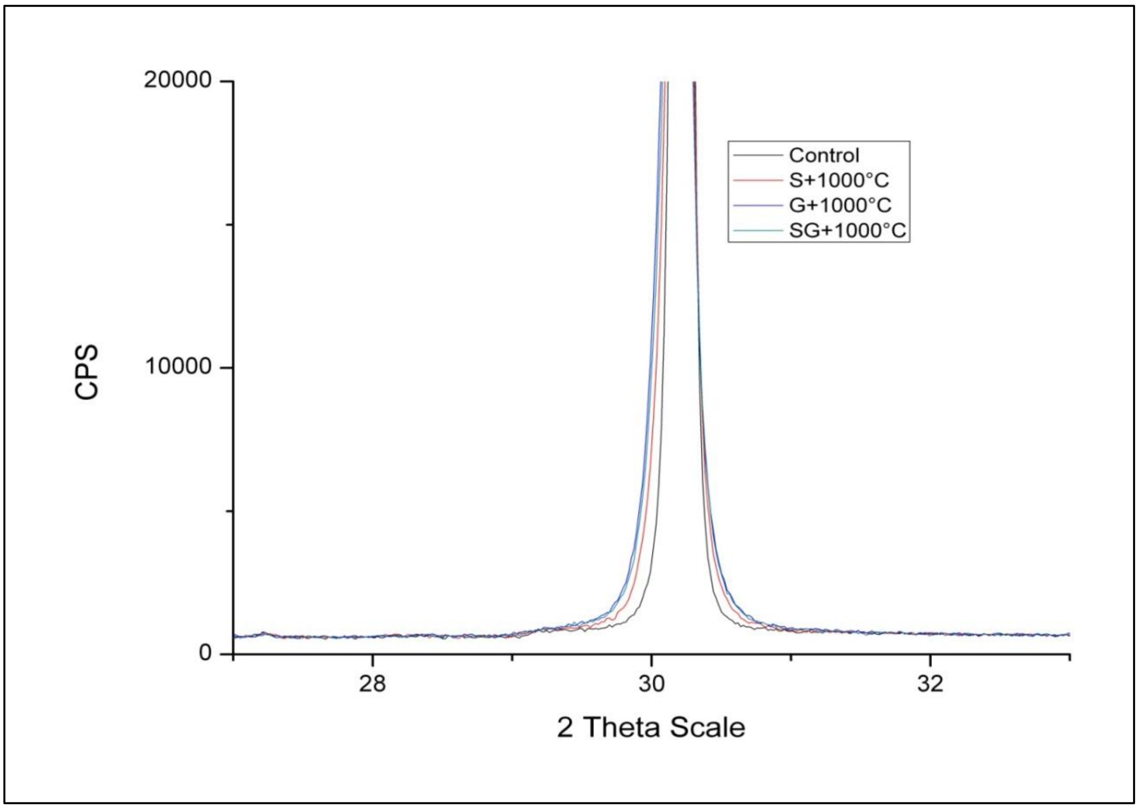

Fig. 6.7. Magnification of Fig. 6.6. between 28° and 32° of the 2θ scale.

# 7. Discussion

## 7.1 Effect of alumina abrasion

The results of the present study revealed that the alumina abrasion regime with 50μm particles increased the flexural strength of the zirconia material. This is in partial agreement with the results of several authors (Kosmac *et al.*, 1999; Kosmac *et al.*, 2000; Zhang *et al.*, 2004; Guazzato *et al.*, 2005b; Papanagiotou *et al.*, 2006; Wang *et al.*, 2007; Oilo *et al.*, 2008). This increase is related to the phase transformation that occurs on the surface and leads to a layer of compressive stresses, which opposes the externally applied, crack-propagating tensile stress (Kosmac *et al.*, 2000; Curtis *et al.*, 2006a; Curtis *et al.*, 2006b).

Sandblasting of zirconia causes erosive wear of the material leading to lateral cracks (Mencik, 1992; Kosmac *et al.*, 2000; Xu L *et al.*, 2000). Nevertheless, the flaws caused by the alumina abrasion in this study don’t seem to exceed the thickness of the compressive stress layer, otherwise the flexure strength would have dropped (Peterson *et al.*, 1998).

Furthermore, as seen on figure 6.2. sandblasting increased the flexural strength possibly also by removing weakly attached surface grains and by the elimination of milling and grinding trace lines, also mentioned by Wang and Kosmac (Kosmac *et al.*, 1999; Wang *et al.*, 2007). This is also proved by the results of the profilometry, that show a reduced surface roughness compared to the control group.

The fact that Curtis et al. did not find a significant increase of the flexure strength after sandblasting could be attributed to the fact, that the pressure used for the abrasion regime (4.8 bar) was higher than the one used in the current study (2 bar), as well as in the other studies (Guazzato 0.5 bar, Wang 0.5 bar, Kosmac 4 bar).

The results of the X-Ray diffraction analysis revealed that the sandblasted specimens had the highest peak of the monoclinic phase, which is in agreement with the results of Guazzato et al. and Kosmac et al. and explains the enhancement of the strength (Kosmac *et al.*, 1999; Guazzato *et al.*, 2005b). In the present study the exact amount of the phase composition was not measured. The knowledge of the exact amount of every phase present in the material could support better the results of the author for the specific material. Nevertheless, the results of Curtis et al., who also studied the LAVA™ Frame, highlighted that LAVA™ is a dual phase material, predominantly consisting of tetragonal and cubic phase (Curtis *et al.*, 2006b) making up the reminder of the structure (Morena, 1986). Curtis showed that alumina abrasion also generates a transformed cubic phase on the surface of the material, which was associated with a toughening mechanism generating surface compressive stresses (Curtis *et al.*, 2006b). It can be suggested that also in the present study the lattice distortion observed in the X-Ray diffraction results after sandblasting was due to the transformed cubic phase of the material, which together with the increased monoclinic phase counteracted the external stresses and led to a high flexural strength.

## 7.2 Effect of grinding

The grinding regime of this study resulted in a significant increase of the strength of the material compared to the control group and close to the strength of the alumina abraded specimens. Several authors have come to similar results (Xu *et al.*, 1997; Guazzato *et al.*, 2005b; Sato *et al.*, 2007), whereas others have found a negative (Xu *et al.*, 1997; Kosmac *et al.*, 2000; Luthardt *et al.*, 2002; Curtis *et al.*, 2006b; Wang *et al.*, 2007) or no significant effect of grinding procedures on the flexural strength of Y-TZP materials.

The positive effect of grinding is probably related to the conditions, under which the grinding procedures were carried out. In the studies of Kosmac et al. and Curtis et al. both authors performed a severe grinding regime with coarse grit burs, high rotation speed and no water spray cooling, which led to a decrease of the strength and generated radial cracks extending from the grinding grooves into the bulk (Kosmac *et al.*, 2000; Curtis *et al.*, 2006b). Swain and Hannink have previously showed that manual grinding with low rotation speed is more effective than lapper-machine grinding in inducing the t/m transformation (Swain and Hannink, 1989) and increasing the surface compressive layer (Ardlin, 2002). Furthermore, Xu et al. found that grinding with a fine grit diamond wheel results to an increase of the strength, while using coarse grit wheels reduces the strength of the zirconia and according to Kosmac using water spray during grinding reduces the critical defect size up to 30% (Kosmac *et al.*, 1999). The grinding conditions of this study were in agreement with these findings, which favored the retention of the transformed phase (Swain and Hannink, 1989; Guazzato *et al.*, 2005b), explaining why the flexural strength did not drop as in other studies (Kosmac *et al.*, 2000; Curtis *et al.*, 2006b; Wang *et al.*, 2007).

Curtis et al. also investigated a fine grinding regime using water spray, which resulted in not significantly higher strength than the control group, contrary to the current study and previous studies (Albakry *et al.*, 2004; Guazzato *et al.*, 2005b). This could be related to the high rotation speed (300.000 rpm) used during grinding, which may have resulted to a reduced phase transformation on the surface, as severe grinding has been proven to be less effective in initiating t→m transformation (Gross and Swain, 1986; Virkar and Matsumoto, 1986; Urabe K *et al.*, 1998).

Surface profilometry revealed a lower surface roughness than the control group, contrary to the findings of Curtis et al. and Wang et al., which again maybe explained by the grinding conditions used in this study.

The XRD pattern of the ground specimens shows a somehow lower monoclinic peak than the sandblasted group, which is in agreement with the study of Guazzato, but on the other hand the distortion of the lattice as indicated at the tetragonal peak is bigger than in the sandblasted group. This combination creates a toughening mechanism and results to a significantly higher flexural strength of the LAVA™ discs.

### 7.3 Effect of sandblasting and grinding

The biaxial flexure strength test revealed that the combination of sandblasting and grinding was most effective in increasing the strength of the material, contrary to the findings of Kosmac (Kosmac *et al.*, 1999). In the present study the group SG had the highest strength of all groups with a statistically significant difference with all groups except for the sandblasted group. Kosmac et al. in their study used sandblasting with coarse alumina particles (110µm) and higher pressure, as well as dry grinding with coarse grit burs, which resulted in lower strength and very low amount of monoclinic phase.

The conditions of the alumina abrasion and grinding regime in the present study did not cause extensive flaws of the material or high stresses and favored the phase transformation on the material surface. As confirmed by the XRD pattern, this regime led to a higher monoclinic peak than in the ground group and also a bigger lattice distortion than in the sandblasted group. The combination of these two effects seems to have resulted in the highest strengthening effect of all tested surface modifications.

The somehow higher surface roughness of the group did not affect the strength and could be related to a rather higher pressure during grinding of the specimens. According to Wang, the macroscopic surface roughness doesn’t act as stress concentration site, but it is the sharp cracks and scratches that act as crack initiation sites. In this case, probably the surface was macroscopically rough with no deep, sharp flaws. Also the SEM images reveal a surface very similar to that of the ground group.

It is important to stress here that the specimens used in this study as a control group were not extensively polished, contrary to other studies (Guazzato *et al.*, 2005b; Wang *et al.*, 2007). That means that several of the machining and grinding induced flaws and weakly attached surface grains were still present, as shown by the results of the microscopy and profilometry. Further polishing may minimize the fabrication induced flaws and result in a greater flexural strength (Guazzato *et al.*, 2005b) and thus a smaller difference for the strength between the modified groups and the control group.

## 7.4 Effect of heat treatment

Heat treatment resulted to a reduction of the mean strength for the sandblasted as well as the ground group. This counteracting effect of annealing to surface treatment on the flexure strength has been observed by several authors {De Kler , 2007 309 /id;Guazzato, 2005 2 /id;Ishgi, 2006 73 /id;Kosmac, 2000 6 /id}.

Heat treatment induces a reverse phase transformation {De Kler , 2007 309 /id;Guazzato, 2005 2 /id;Sato, 2007 69 /id}, which leads to the release of the compressive stresses on the surface of the material and a reduction of its strength (Kosmac *et al.*, 2000; Guazzato *et al.*, 2005b). According to Alcala and Oilo microcracks generated during the milling procedure or surface treatment may propagate during firing because of the alterations of the grain size and the relieved stresses (Alcala and Anglada, 1997; Oilo *et al.*, 2008). Denry et. al. showed in a study, that annealing of ground or ground and polished specimens leads to the disappearance of residual strains (Denry and Holloway, 2006).

The cracks may propagate further into the material during the firing process due to the alteration in grain sizes and grain boundaries accompanied with relieved stress (Alcala and Anglada, 1997).

The heating may also lead to changes in the shape of porosities and impurities embedded in the specimens, facilitating crack propagation (Chevalier, 2006). Additionally, some authors suggest that the material’s original ability to undergo a phase transformation to arrest crack growth may be reduced by heating (Alcala, 2000).

After annealing at 1000°C the mean strength of the sandblasted samples dropped from 1364 MPa to 901 MPa and for the ground from 1296 MPa to 1024 MPa, which is the “Griffith strength” of the material, i.e. the strength of damaged but unconstrained material, which reflects the contribution of the compressive stresses generated by the surface treatments to the overall strength (Kosmac *et al.*, 2000). The mean strength of group SF was about 10% lower and the mean strength of group GF was higher than that of the control group, but the difference was not significant. This means that the surface flaws induced by the surface treatments were not detrimental for the material. Nevertheless, the strength of annealed ground discs was significantly higher than that of group SF. These findings are also in agreement with the study of Guazzato et al. and partially with the study of Kosmac et al.

Contrary to these studies, Wang et al. found the flexural strength of zirconia to be insensitive to the firing procedures (Wang *et al.*, 2007). This is a predictable result, taking into account that the authors in this study didn't find a significant difference in the strength between the control and the sandblasted (with 50 µm particles) group, which means that there were no high compressive stresses on the surface and thus the heat treatment couldn't have any compressive stress releasing effect.

Even though the firing was carried out at a temperature lower than the sintering temperature of the material, a reverse phase transformation took place. Several studies indicate that heat treatment influences the core materials in several ways even when the temperatures are below the core materials' own sintering temperature (Cattell *et al.*, 2002; Guazzato *et al.*, 2004b; Isgro *et al.*, 2005; Sundh *et al.*, 2005), whereas Swain and Hannink indicate the 700°C as the temperature, above which a reverse transformation occurs (Swain, 1989). This effect of the heat treatment with the m→t transformation may occur instantly as a given temperature is reached and regardless of the holding time (Guazzato *et al.*, 2005b). This could be explained by the fact, that the compressive stress layer is thin and only superficial, so the deeper parts of the bulk don't need to reach that temperature, but only the surface.

The XRD pattern on figure 6.5.4 shows that annealing led to the disappearance of the monoclinic peak of the surface treated specimens. On the other hand, the distortion of the lattice at the tetragonal peak was reduced but not completely reversed and this reduction of the distortion was greater for the sandblasted specimens. It could be suggested that this remaining lattice distortion is the reason, that the ground and heated discs had a significantly higher flexure strength than the sandblasted and heated specimens and higher strength than the control group.

## 7.5 Reliability

It is well known, that by investigating solely the mean flexure strength, the properties of the ceramics cannot be accurately characterized (Papanagiotou *et al.*, 2006). The statistical analysis is important, when analyzing strength data, because ceramics have a wide variability in failure strengths, which is related to incorporated flaws.

Reliability is discussed in terms of Weibull parameters m and $\sigma_0$. Higher values indicate a more homogenous flaw distribution or that the flaws were located in areas of less stress and thus greater reliability, whereas the opposite is expected for low values. In the present study both sandblasting and grinding, as well as their combination increased the flexure strength of the material but at the expense of a somewhat lower reliability compared to the control group. These results are in partial agreement with the results of other authors (Kosmac *et al.*, 2000; Wang *et al.*, 2007), while Guazzato, Papanagiotou and Curtis made in their studies contradicting observations, finding higher m values compared to their control groups after sandblasting or fine grinding. Taking into account, that the initial m values of the control groups in these studies were rather low (between 7.5 and 8.5), it could be suggested that the control groups had a rather inhomogeneous initial flaw distribution after fabrication, which may have been improved after the surface treatment maybe by removing some bigger surface flaws.

Contrary to the studies of Wang et al. and Curtis et al., where the authors related the m values and the flexure strength directly to the surface roughness of the treated specimens, no correlation was found between them in the current study.

Subsequent firing of the discs resulted in the lowest Weibull module for the sandblasted and fired group and in the highest for the ground and fired group. Although as seen from the flexure strength results, neither sandblasting nor grinding induced flaws had any detrimental effect to the performance of the material, it could be suggested, that the grinding procedures under the conditions of the present study removed some pre- existing surface flaws of the material, which in combination with some remaining lattice distortion after firing resulted in such a high reliability of the material. This could have been more effective in the group GF, which was the last group that was treated, taking into account that the method used could be applied more standardized after already having processed the other groups and having realized how to avoid mistakes during the procedure.

Wang observed in his study an increase of the Weibull module after sandblasting and annealing, while Guazzato, in partial agreement to the current results, that firing increased the m for the ground group, but decreased it for the sandblasted specimens. Nevertheless, the m value was higher than that of the control group. Also Oilo observed a decrease of the scatter after firing, indicating that the initial variation in the ground surface evened out during the firing process (Oilo *et al.*, 2008).

As zirconia is a glassfree material, whether this is related to reverse transformation or due to relieving of any present pre-stresses, it remains a point for further investigation (Guazzato *et al.*, 2002; Guazzato *et al.*, 2005a; Wang *et al.*, 2007). Although all tested groups had m values within the range of 5 to 15 quoted for dental ceramics, the lower m values of most of the groups indicate that various treatments can affect the reliability of clinical performance of the material (Papanagiotou *et al.*, 2006).

Nevertheless, it must be noted, that despite the decrease of the m value in some groups, all groups had a Weibull characteristic strength higher than 900 MPa, which results in acceptable low failure probability of the material up to bending stress level of 500 MPa (Kosmac *et al.*, 2000).

### 7.6 Clinical relevance of the results

The present study shows that surface modification and heat treatment have a counteracting effect on the biaxial flexure strength of zirconia. Furthermore, the specific influence of each treatment may be different than what was observed by other authors, due to variations of the methods used as well as the properties of the investigated materials.

Surface modification of Y-TZP ceramics results to a phase transformation which creates a layer of surface compressive stresses because of the volume increase (Piconi and Maccauro, 1999). On the other hand, during the veneering firing procedures a tensile stress is necessary on the surface of the frame material, while the veneering material should have compressive stresses (Kappert, 2008). Due to the pre-existing compressive stresses on the zirconia surface this mechanism may not work effectively, because the CTE difference observed during the firing procedure between frame- and veneering material cannot be properly used, which would mean that the risk for chipping during clinical use increases (Kappert, 2008). On the other hand, according to Guazzato the reverse phase transformation occurs instantly as a given temperature is reached (Guazzato *et al.*, 2005b). Since the veneering firing lasts a few minutes, this would suggest that a “regeneration firing” before the veneering firing may be excessive.

Nevertheless, Oilo et al. have showed that additional firings after the first firing have little or no effect on the strength and reliability of the material and multiple firings as performed at the dental laboratory do not further deteriorate the material (Oilo *et al.*, 2008).

According to the results of the current study sandblasting increases the flexure strength of the material but with a lower reliability, while subsequent annealing results to strength lower than that of the control group, as well as lower reliability. These observations show, that firing has no benefits for sandblasted zirconia and the material should not be sandblasted prior to firing procedures and that the commonly used method of some laboratories to use air abrasion on zirconia frames prior to veneering is risky and excessive and should be avoided. On the other hand, sandblasting with low pressure (0.5-2 bar) could be used effectively on the inner surface of restorations after the firing procedure and before cementation, especially with resin cements, thus creating a layer of compressive stresses as well as strengthening the bond.

In the present study it was also observed, that grinding under the specific conditions increased the biaxial flexure strength of zirconia, but again with somewhat lower reliability. Subsequent annealing of the ground material resulted in flexural strength still higher than that of the control group and the highest reliability. These results lead to the conclusion, that corrections of sintered zirconia frames can be made at the laboratory or during the clinical “try-in” phase, as long as the grinding procedure is carried out with fine grit burs, low rotation speed and water cooling. This procedure might reduce some inherent or machining-induced flaws on the surface of the material. Subsequent annealing will release the surface compressive stresses, which is necessary for the veneering material and will also increase the reliability of the zirconia and keep the strength at higher levels than the control material.

Since multiple firings have no negative effect on the strength and reliability of the material (Oilo *et al.*, 2008), it is recommended to carry out a “regeneration firing” before the veneering firing procedure, in order to be sure, that there is no compressive stress on the surface of the frame material already from the beginning of the veneering firing procedure.

Furthermore, in the case of zirconia implant abutments, sometimes minor corrections have to be done at the dental laboratory, while there are also some companies that offer implant abutments that can be ground “chairside”. In those cases, subsequent firing could be beneficial and increase the reliability, while also retaining a high flexural strength.

As the main function of the underlying framework is to support the ceramic veneer and to carry the loading forces, different laboratory tests are used to evaluate the internal strength of zirconia frameworks. On the other hand, these tests don’t take into account clinical factors like the nature of human occlusion and the loading environment. Nevertheless, they offer a controlled environment for evaluation of the variables of interest (Wang *et al.*, 2007).

Under clinical conditions, a greater amount of monoclinic phase on the surface and therefore a greater flexural strength may be desirable. On the other hand, an excessive amount of transformed phase could lead to microcracking (Sato and Shimada, 1985a; Guazzato *et al.*, 2005b) and predispose the material to a more rapid moisture-assisted transformation over time and loading in the acidic and aqueous oral environment (De Aza *et al.*, 2002). Since zirconia is the strongest of all dental ceramics, an initially weaker, but more reliable material may be preferable. Further studies need to be done, to assess the long-term clinical results of the different surface modifications.

## 8. Conclusions

Aim of this study was to assess the effect of surface treatments and subsequent annealing on Y-TZP ceramics. Within the limitations of this in-vitro study, following conclusions were drawn:

- Sandblasting, grinding and their combination as performed in the current study increased the biaxial flexure strength of the investigated material.
- The Weibull module was between 6.9 and 12.4 for all tested groups.
- Firing after air abrasion decreased the strength and the reliability of the Y-TZP ceramic. Sandblasting before the veneering procedure should be avoided and used only before cementation, in order to increase the adhesion of the cement to the core material.
- Grinding procedures after sintering should be done with low rotation speed, fine grit burs and water spray cooling.
- Firing after grinding increased the reliability of the material, whereas the strength remained higher than the control specimens.

- If any grinding procedures are carried out after sintering of Y-TZP ceramics, a “regeneration firing” is recommended prior to veneering of a restoration or the placement of an implant abutment.
- Further studies need to assess the aging behavior and long-term clinical performance of surface treated Y-TZP ceramics.

## 9. Summary

Objective: The purpose of this study was to evaluate the influence of different surface treatments and subsequent annealing on the flexural strength and reliability of a Y-TZP dental ceramic.

Materials and methods: Six groups of 27 to 30 zirconia discs (LAVA™ Frame; 3M ESPE, Seefeld, Germany) underwent one of the following treatments: no treatment, sandblasting with alumina particles (50 µm, 2 bar), grinding with fine grit diamond burs (ISO-No. 806 314 111514 014, Komet Brasseler, Lemgo, Germany), sandblasting and subsequent grinding, sandblasting and subsequent annealing or grinding and subsequent annealing. Surfaces of random specimens were observed with scanning electron microscopy and their roughness was measured with a profilometer. After treatment, the biaxial flexure test was used to calculate the flexural strength of the discs and X-Ray diffraction analysis was employed to assess the influence of the surface modifications and the firing procedures on the phase composition and the occurrence of phase transformations in the Y-TZP ceramic. The data was analyzed utilizing multiple Welch tests with adjustment of the p values with the Bonferroni-Holm method, whereas the survivability was estimated using Weibull analysis.

Results: All surface treatments significantly increased the flexural strength of the material and subsequent heat treatment decreased it, but to a level not significantly different from the control group. All groups had lower m values than the test specimens, except for the ground and fired group, which had the highest reliability.

No correlation was found between the surface roughness of the discs and the flexural strength.

Conclusions: The present study suggests, that sandblasting and grinding can be used to increase the strength of the material in expense of somewhat lower reliability. Sandblasting should be employed only after the firing procedures to improve the adhesion of the cement to the material. Grinding procedures should be followed by a “regeneration firing”, in order to increase the reliability of the Y-TZP material, while also keeping a high flexural strength.

## 10. Zusammenfassung

Ziel: Ziel dieser Studie war, den Einfluss verschiedener Oberflächenbehandlungen und der anschließenden Wärmebehandlung auf die Biegefestigkeit und die Zuverlässigkeit einer Y-TZP Keramik zu überprüfen.
Materialien und Methoden: Sechs Gruppen mit 27 bis 30 Zirkoniumdioxid-Scheiben (LAVA ™ Frame, 3M ESPE, Seefeld, Deutschland) bekamen eine der folgenden Behandlungen : keine Behandlung, Sandstrahlen mit Aluminiumoxid-Partikeln (50 µm, 2 bar), Beschleifen mit feinkörnigen Diamanten (ISO-No. 806 314 111514 014, Komet Brasseler, Lemgo, Deutschland), Sandstrahlen und anschließendes Beschleifen, Sandstrahlen und anschließenden Brand oder Beschleifen und anschließenden Brand. Oberflächen von zufällig ausgewählten Proben wurden mit Raster-Elektronen-Mikroskopie untersucht und deren Rauheit wurde mit einem Profilometer gemessen. Nach der Behandlung wurde der biaxiale Biegeversuch zur Bestimmung der Biegefestigkeit der Scheiben verwendet und Röntgenbeugungsanalyse wurde angewendet, um den Einfluss der Oberflächen- und Wärmebehandlung auf die Phasenzusammensetzung zu beurteilen und das Auftreten von Phasenumwandlungen in der Y-TZP Keramik festzustellen. Die Daten wurden unter Verwendung von multiplen Welch-Tests und Anpassung der p-Werte mit der Bonferroni-Holm Methode analysiert,

während die Überlebensfähigkeit mittels Weibull Analyse geschätzt wurde. Ergebnisse: Alle Oberflächenbehandlungen haben die Biegefestigkeit des Materials signifikant erhöht und die anschließende Wärmebehandlung hat sie verringert, jedoch zu einem von der Kontrollgruppe nicht signifikanten Niveau. Alle Gruppen hatten niedrigere m Werte als die Testproben mit der Ausnahme der beschliffenen und gebrannten Gruppe, die die höchste Zuverlässigkeit aufwies. Zwischen der Oberflächenrauhigkeit der Scheiben und der Biegefestigkeit wurde keine Korrelation gefunden. Schlussfolgerung: Die vorliegende Studie legt nahe, dass Sandstrahlen und Beschleifen verwendet werden können, um die Biegefestigkeit des Materials zu erhöhen, jedoch auf Kosten einer etwas niedrigeren Zuverlässigkeit. Sandstrahlen sollte nur nach dem Keramikbrand zur Verbesserung des Haftverbundes des Zementes an dem Material angewandt werden. Ein Regenerationsbrand sollte dem Beschleifen folgen, um die Zuverlässigkeit des Y-TZP Materials zu erhöhen, wobei auch eine hohe Biegefestigkeit bewahrt werden kann.

# 11. Appendix

**Table 11.1. Results of the multiple comparisons of the mean flexural strength of the groups. 0 indicates no significant difference; 1 indicates that the difference was statistically significant.**

| Gruppe 1 | Gruppe 2 | F Ratio | DFDen | Prob > F | BH | sig |
|---|---|---|---|---|---|---|
| S | G | 1.6 | 57.9 | 0.2100 | 0.0500 | 0 |
| S | SG | 2.2 | 53.4 | 0.1409 | 0.0250 | 0 |
| C | GF | 2.9 | 56.0 | 0.0963 | 0.0167 | 0 |
| C | SF | 4.9 | 49.9 | 0.0310 | 0.0125 | 0 |
| SG | G | 7.3 | 52.6 | 0.0091 | 0.0100 | 1 |
| SF | GF | 12.9 | 48.6 | 0.0008 | 0.0083 | 1 |
| G | GF | 41.7 | 43.1 | <.0001 | 0.0071 | 1 |
| C | G | 56.6 | 43.9 | <.0001 | 0.0063 | 1 |
| S | GF | 61.2 | 42.1 | <.0001 | 0.0056 | 1 |
| SG | GF | 79.8 | 35.7 | <.0001 | 0.0050 | 1 |
| C | S | 78.3 | 42.9 | <.0001 | 0.0045 | 1 |
| G | SF | 70.4 | 53.8 | <.0001 | 0.0042 | 1 |
| C | SG | 97.3 | 36.2 | <.0001 | 0.0038 | 1 |
| S | SF | 91.9 | 52.8 | <.0001 | 0.0036 | 1 |
| SG | SF | 110.8 | 45.2 | <.0001 | 0.0033 | 1 |

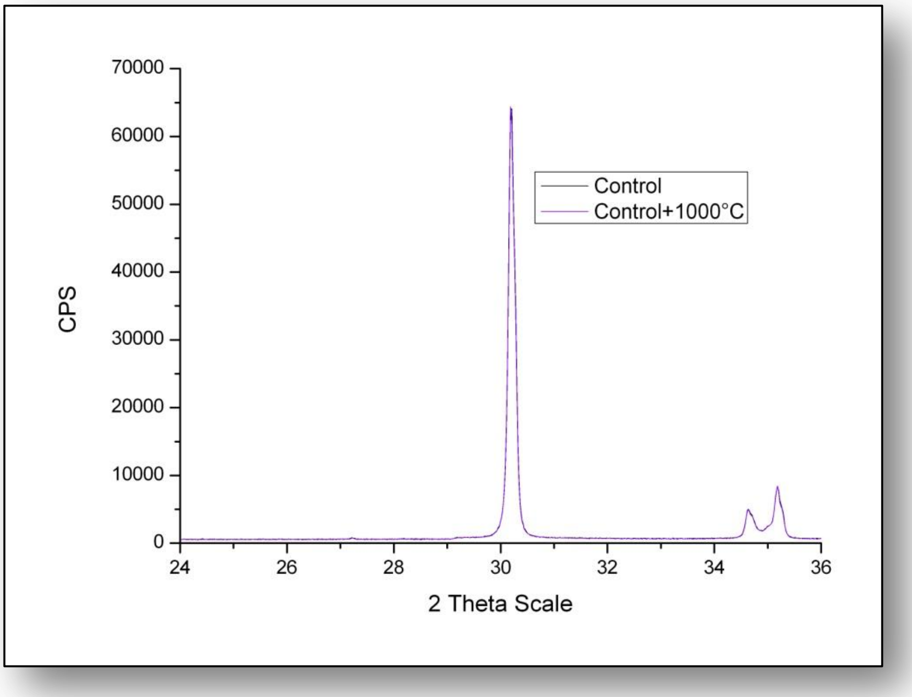

Fig. 11.1. XRD patterns of the control group before and after heat treatment.

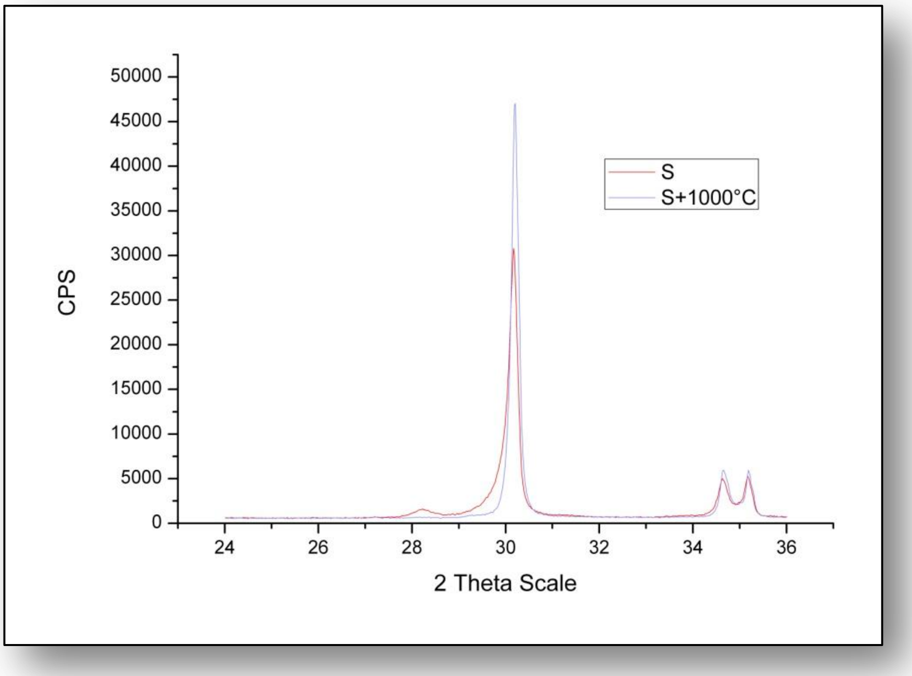

Fig. 11.2. XRD patterns of the sandblasted group before and after heat treatment.

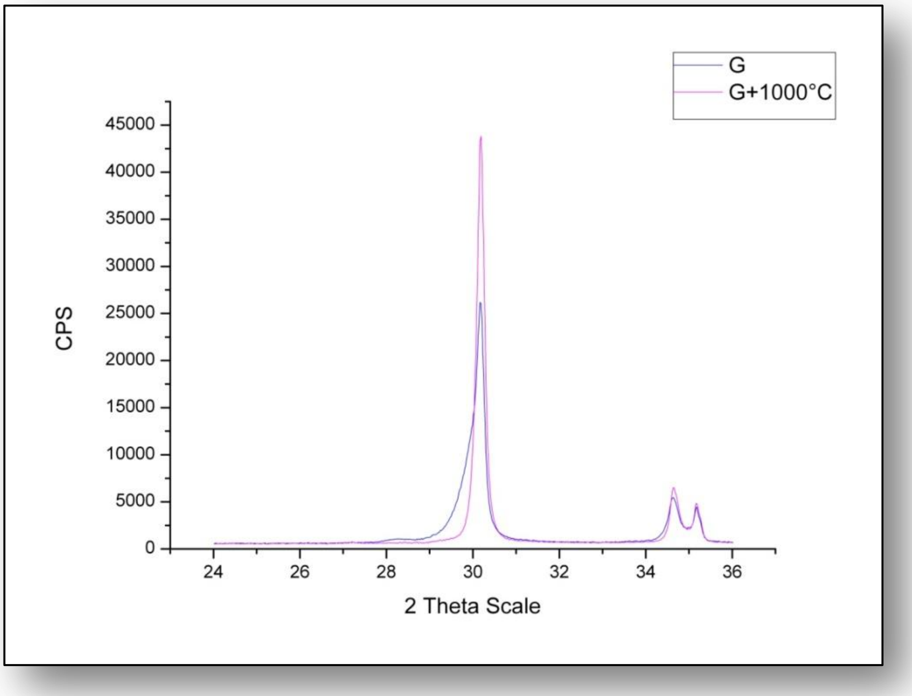

Fig. 11.3. XRD patterns of the ground group before and after heat treatment.

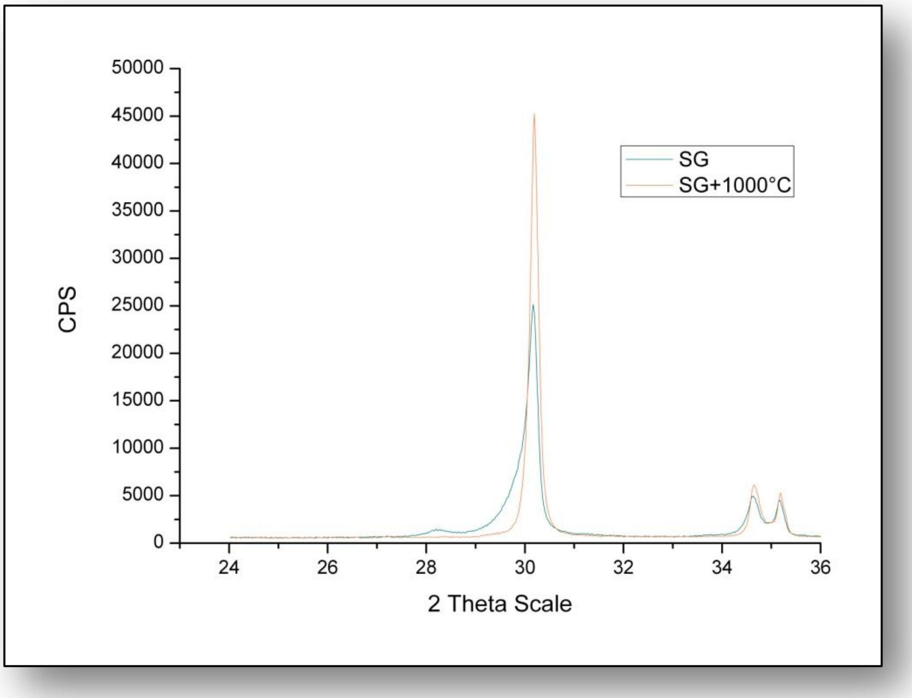

Fig. 11.4. XRD patterns of the sandblasted and ground group before and after heat treatment.

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