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Three generations of zirconia: From veneered to monolithic. Part I

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This article presents the historical development of the different generations of zirconia and their range of indications, from veneered to monolithic zirconia restorations. Because of the large extent of this topic, it is divided into two parts. In Part I, the mechanical and optical properties of the three generations of zirconia materials are discussed critically and theoretically. A

short summary is given of the current scientific literature, investigating the third generation of zirconia comparatively regarding the properties discussed. (*Quintessence Int* 2017;48: 369–380; doi: 10.3290/j.qi.a38057. Originally published (in German) in *Quintessenz Zahntech* 2016;42(6):740–765)

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Increasing numbers of patients are choosing metal-free restorations, because they provide similar light-scattering properties to natural tooth structure and therefore achieve excellent esthetic results, while being biologically very well tolerated.¹ However, esthetics and biocompatibility are not the only essential criteria for selection of the framework material. Good mechanical properties of a dental ceramic,² enabling its use for fixed dental

prosthesis (FDP) restoration in the lateral tooth area, are also important.³ Zirconia is a dental ceramic with high flexural strength and fracture toughness (Fig 1). Zirconia has been widely used in the dental laboratory for over 15 years, whether as a framework material or a fully anatomical alternative. Interest is increasingly focused on the latter, given the efficient mode of production as a restorative option for the lateral tooth area.

GENERAL POINTS

As a raw material, zirconium (Zr) is a relatively soft, ductile, shiny, silvery metal. The oxide of the metal used in dentistry, zirconium dioxide (ZrO₂), known as zirconia, is generally obtained after an extensive and expensive process (Fig 2).

After an elaborate and, more importantly, cost-intensive production and purification process, it is available as a white, high-fusing, crystalline powder (Fig 3). Zirconia exists in monoclinic, tetragonal, and cubic phases

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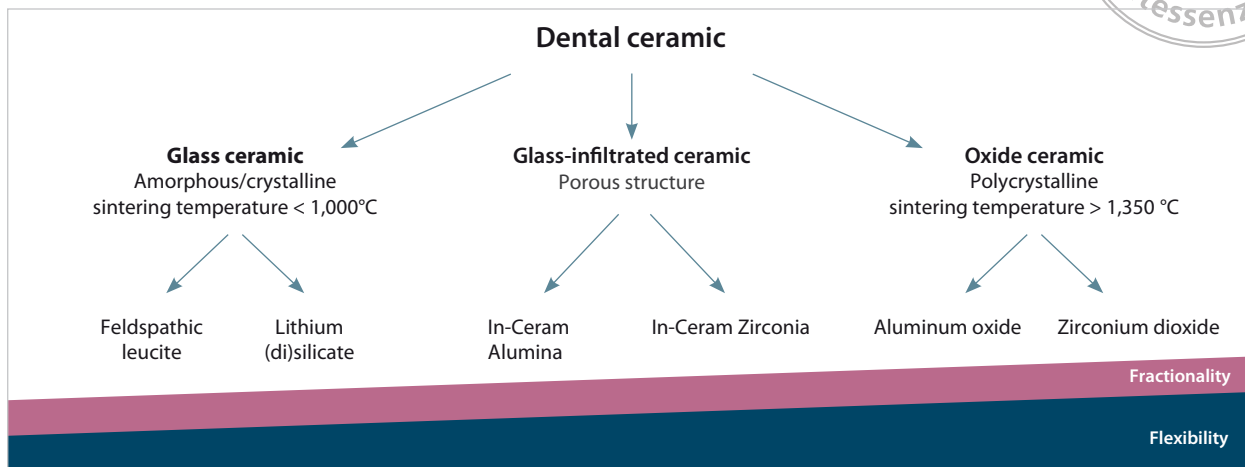
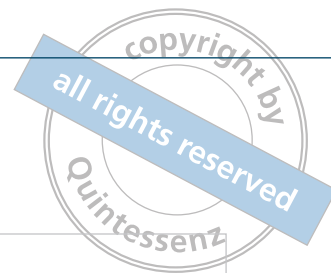


Fig 1 Types of dental ceramic.

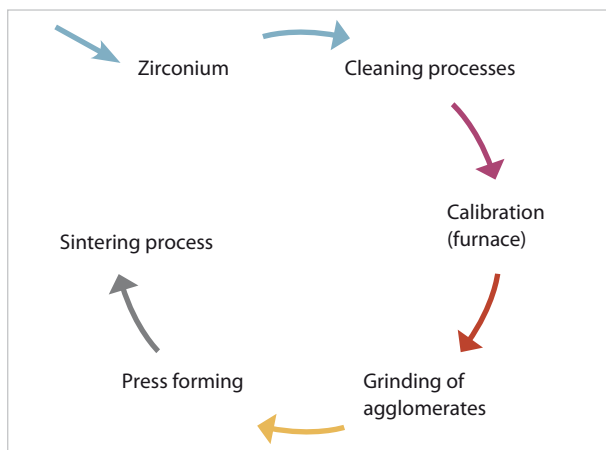


Fig 2 Preparation of zirconium dioxide powder.



Fig 3 Zirconia powder after the purification process.

(Fig 4). During the cooling process of a pure zirconia molten mass, the cubic phase first crystallizes out at a temperature of 2,680°C onwards and then undergoes transformation at 2,370°C into the tetragonal phase. At a temperature of 1,170°C, the transformation into the monoclinic phase, at which zirconia is available at room temperature, finally takes place. The last transformation, from the tetragonal to the monoclinic phase, is also described as a martensitic transformation and is characterized by an increase in volume of approximately 4%.

This abrupt increase in volume during the cooling phase makes it impossible to produce sintered ceramics from pure zirconia, because the increased volume always leads to excessively high tension and the devel-

opment of unwanted cracks in the ceramic structure. The martensitic transformation during the cooling phase can be prevented, however, by the addition of stabilizing oxides, which are incorporated into the crystal lattice of the zirconia (Fig 5). Through this, the structure is frozen, even at room temperatures, into the tetragonal or the new cubic-tetragonal condition. The zirconia most commonly found on the market is stabilized with yttrium oxide (Y-TZP). Panasonic supplies a dispersion or mixed ceramic, which uses lanthanide cerium to stabilize the zirconia (Ce-TZP/Al₂O₃).

The toughening induced by the transformation is derived from two different mechanisms. On the one hand, a spontaneous local transformation of the tetrag-

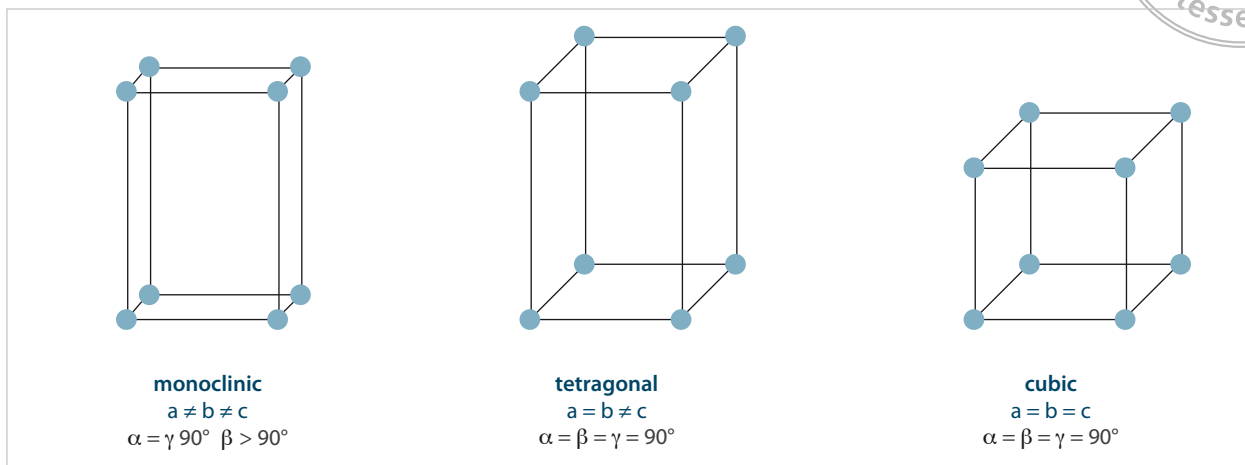


Fig 4 Zirconia in its three phases.

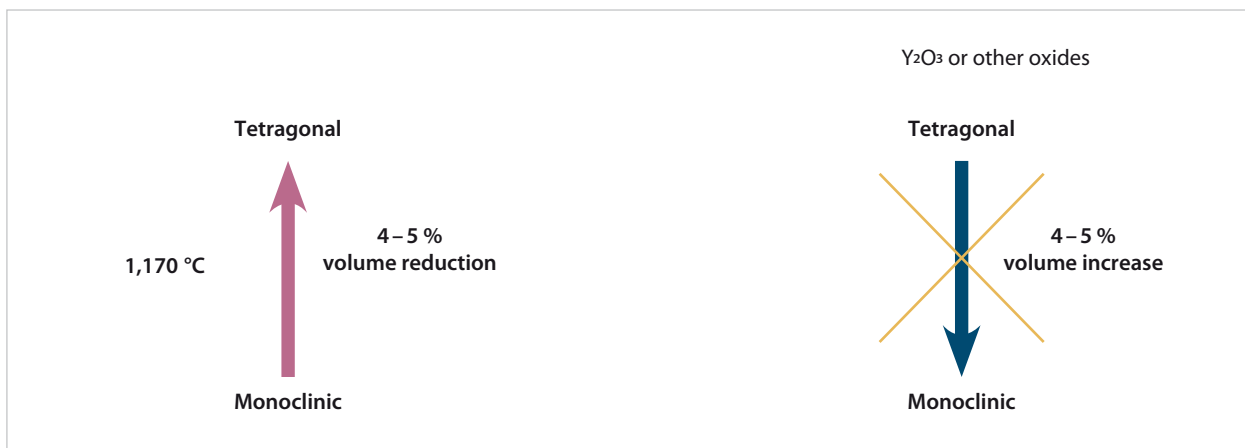


Fig 5 The zirconia phase conversion.

onal into the monoclinic phase can trigger the formation of fine microcracks, caused by the higher volume of the monoclinic crystal form. The spreading crack either peters out into these microcracks or is diverted to the zirconia particles. On the other hand, this transformation can also be induced by the high tensile stresses, which are always present at the tip of an expanding crack. The tensile stresses reduce the pressure of the matrix on the surrounding zirconia particles, which causes the tetragonal phase to transform into the monoclinic phase. The higher volume of the developing monoclinic crystal form leads in turn to a local compressive stress at the tips of the crack. Further growth of the crack is made more difficult by the com-

pression of the edges of the crack (Fig 6). This is known as transformation behavior.

The proportion of yttrium oxide has been increased in the new-generation zirconia. This leads to the formation not only of the metastable tetragonal phase but also of the cubic portions of the structure simultaneously. This mixed structure is known as fully stabilized zirconia and represents the third generation, in which, in contrast to the partially stabilized zirconia of the first and second generations, no transformation of the structuring phases takes place under induced stresses, according to the information provided by the powder manufacturer.⁴

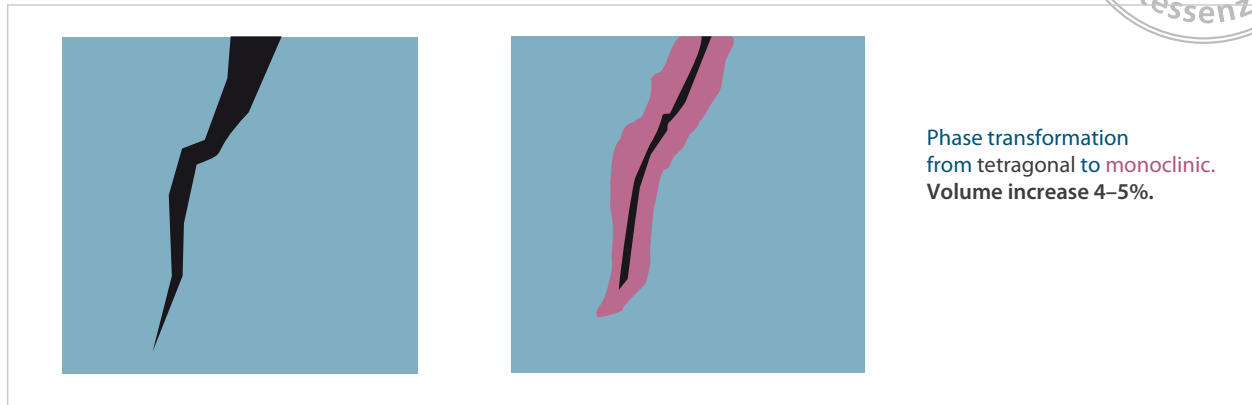


Fig 6 The behavior of zirconia at crack edges.

Cubic crystals have a higher volume. Firstly, owing to reduced residual porosity, they have higher light scattering at the grain boundaries, and secondly, they are less strongly bonded. Furthermore, the cubic crystal structures are more isotropic than the tetragonal structures, so incident light is emitted more evenly in all spatial directions.

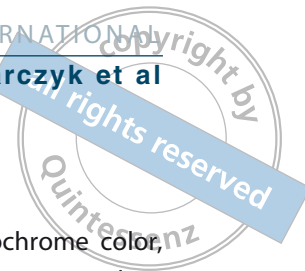
MECHANICAL PROCESSING OF ZIRCONIA

Zirconia is mechanically processed. For this, blanks with specific shapes are pressed from ZrO_2 powder. These can subsequently be processed using special computer-aided design/computer-assisted manufacture (CAD/CAM) machines or copy milling units.

Zirconia can be milled either in a soft chalk-like state (white state) with hard metal milling tools or in an already sintered state (HIP-ed) and therefore ground to a final Vickers hardness of about 1,200 HV with diamond grinding tools. The term “green body” was previously used, but this is inappropriate today because the “green body” still contains binders. A “white body” in contrast has already undergone pre-sintering at high temperatures; the binders were burnt out in this period and the material minimally hardened by this heat pretreatment. Zirconia milled in the “white state” must subsequently be sintered to achieve final hardness and final strength. The sintering parameters vary from manufacturer to manufacturer. During sintering, the

structure contracts by approximately 20 to 30%. Although HIP-ed zirconia achieves the highest initial strengths,⁵ the material was unable to establish itself on the market because of the long processing times and high tool wear. Most manufacturers of CAD/CAM systems have adapted to the processing of soft zirconia. The disadvantages of these versions are the cost-intensive special ovens for the subsequent sintering and the somewhat lower strengths.⁶ Nonetheless, strength is still far higher than the norm of 100 MPa, and, depending on the zirconia generation, can even reach values far above 1,000 MPa.

Many dental laboratories now possess a CAD/CAM system and can design their frameworks themselves on the screen, form-grind, or mill. Furthermore, numerous milling centers have been established in recent years which have specialized in CAD/CAM processing and supply a centralized form-grinding service for other laboratories/practices. This approach means that dental technicians are no longer obliged to invest in expensive CAD/CAM systems, which may be a financial burden to the laboratory when fewer orders lead to idle times. They purchase just the scan unit for data acquisition, scan in the model, carry out computer-aided designing of the restoration on the basis of the virtual model and send the three-dimensional (3D) construction data to the milling center. The restoration is produced and then undergoes further processing by the dental technician in later steps (eg, polishing, veneering, enameling).



With early CAD/CAM technology, the dental technician was restricted to a specific system when buying a scan unit. Now, however, scan units are supplied with what is known as open interfaces, which means that 3D construction data can be transferred or exported in a universally accessible data format. Thus the dental technician has the option of producing the restorations on different milling units. A further cost-effective option is provided by milling centers that also offer scanning in of the model and construct the framework themselves. In this case, a wax-up is often prepared by the laboratory and sent as well so that the laboratory can also determine the optimal geometry of the framework.

Finally, there is the option of producing zirconia restorations inexpensively using copy milling units. The framework is initially modeled from light-hardening plastic and subsequently pasted on one side into the holder of the copy miller. The zirconia blank is attached on the other side. By application of the pantograph principle, the milling in the zirconia blank is performed approximately 25% larger to compensate for the contraction on sintering. The copy milling procedure is performed manually by the technician in the “white body” state and presupposes as an unadaptable system that every zirconia blank exhibits exactly the same sintering shrinkage.

A summary of the technical and dental options for the production of zirconia restorations is presented in Fig 7.

CONVENTIONAL ZIRCONIA

Tetragonal, partially stabilized zirconia was developed over 15 years ago and is also known as conventional zirconia (first generation). Conventional zirconia has a high light refraction index and also possesses an extremely high number of interfaces because of the numerous very small crystal structures through which the light has to pass. This creates the opaque character for the material.

Two different kinds of the zirconia blanks are distributed by the manufacturer: industrially dyed or non-dyed (Fig 8). While the restorations made from dyed blanks already have a shade similar to that of teeth after form milling and sintering, restorations from non-

dyed blanks have a hard-white monochrome color, which can be an esthetic disadvantage in many indications (Fig 9). To get round this disadvantage, the restorations milled in the white body state can be dyed manually and individually with coloring oxides after the milling process and sintered afterwards. For dyeing, the form-milled open-pore framework is immersed for a short time in appropriate colored liquid (Fig 10). Alternatively, brushes can be used and color gradients equivalent to different color liquids of differing intensity can be painted on (Fig 11). The sintering process is performed after removing the excessive residual color while it is still wet and drying the framework. Another means of rendering white zirconia more esthetically pleasing is to use liner or stain. These are applied before veneering onto the densely sintered frameworks.

VENEERED ZIRCONIA

Because of the compromised esthetics of first-generation zirconia, the restoration framework is veneered with suitable glass-ceramics after being individually produced (Fig 12). The overall stability of a restoration is attributed to inner tensions. The inner tensions result, in turn, from the difference in the coefficients of thermal expansion (CTE) of the framework material and veneering ceramic and from the geometric structure of the crown and veneer. These inner tensions are also overlaid by the externally induced tensions (masticatory force). When the sum of the inner tensions and externally induced tensions exceeds the strength of the materials, a fracture develops. The combination of veneering ceramic and zirconia as framework material is one consisting exclusively of brittle materials. Both partners have no ductility and therefore are not able to compensate the overall tensions. Since the veneering ceramic has significantly lower strengths than the zirconia, it fractures more rapidly. This is known as chipping. In this context, chipping describes a fracture which is limited to the veneering ceramic.

Clinically, as well as in laboratory tests, a fracture is never observed in the interface between framework and veneer, but always within the veneering ceramic (Fig 13).

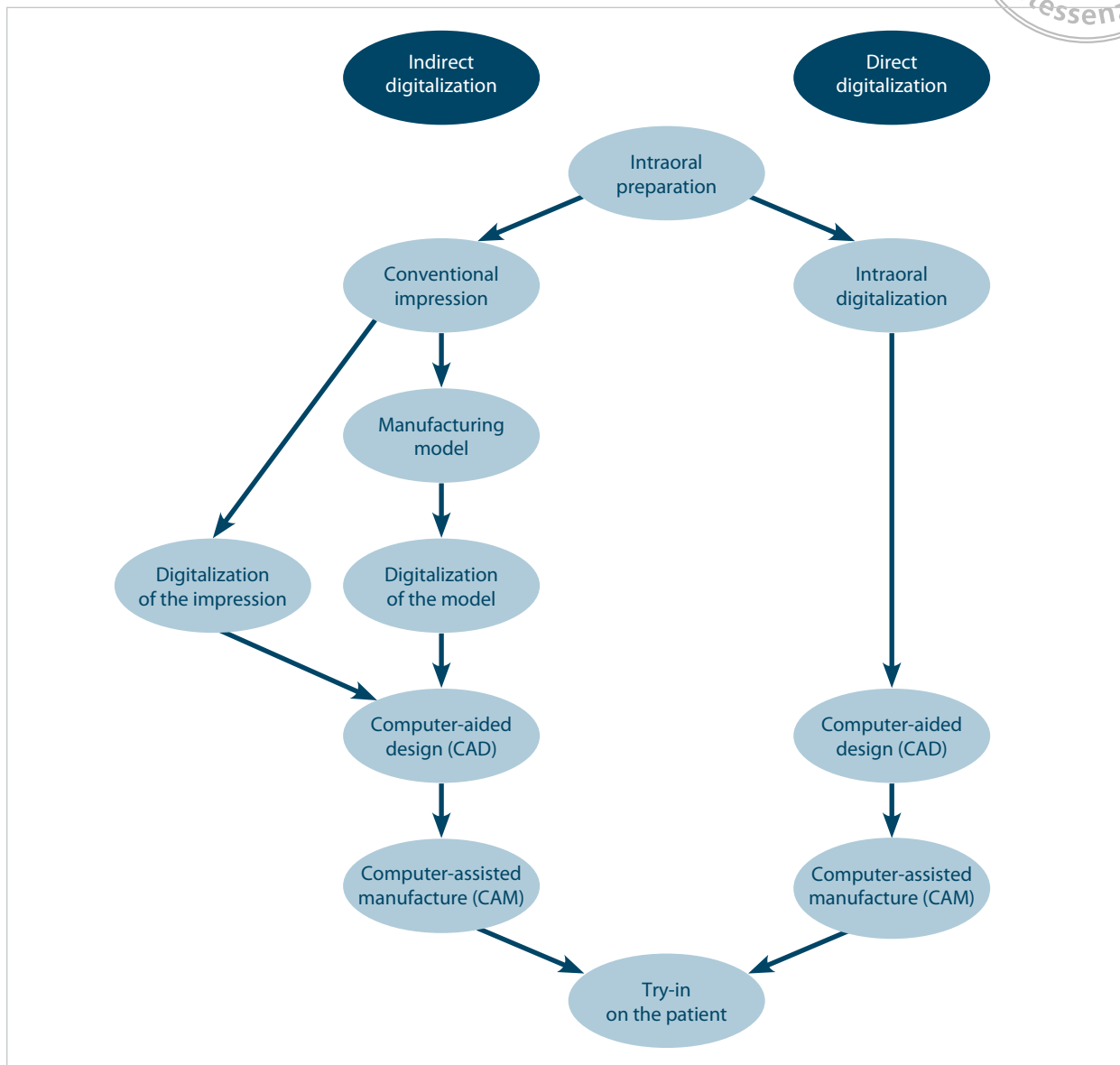


Fig 7 Options for the production of zirconia restorations.

An extremely thin layer of veneering ceramic remains on the framework material, and this is defined as a cohesive fracture (Fig 14). Because the cohesive fracture occurs in the veneering ceramic, it can reasonably be concluded that the bonding strengths between zirconia as framework material and the veneering ceramic are good. Only the weakest link in the chain, the veneering ceramic, fractures. A high number of clinical studies on veneered zirconia restorations report this problem.⁷

The design of the restoration framework has a critical influence on the overall stability of the restorations. Zirconia frameworks should be designed to be supportive anatomically and rounded, so that a higher fracture load is achieved and chipping minimized.⁸ Nevertheless, chipping occurs more frequently with zirconia restorations than with restorations made of metal-ceramic.^{9,10}



Fig 8 Example of a visibly colored blank. Most of the dyed blanks have a color similar to natural teeth.



Fig 9 A colored sintered zirconia fixed partial denture with the clearly recognizable white color.

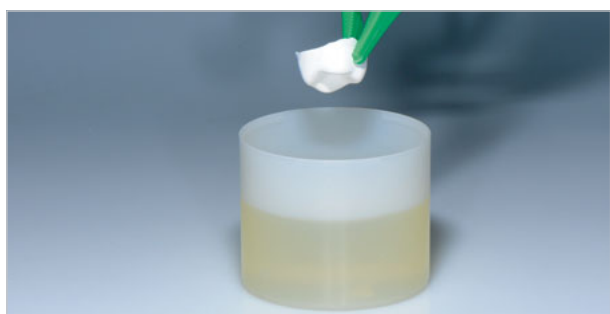


Fig 10 Dyeing of a white zirconia framework by the immersion method.

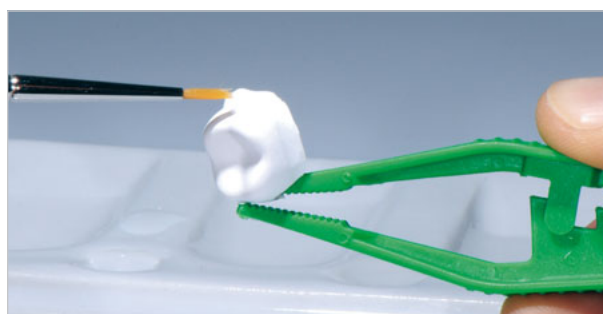


Fig 11 Individual coloring of zirconia frameworks using the brush technique.



Fig 12 Three-unit fixed partial denture (mandibular left second premolar to second molar) with scaffolding on Lava Frame (3M Espe) and veneer (Creation ZI-CT, Willi Geller, Mainingen, Austria) (MDT Otto Prandtner, Munich, Germany).

MONOLITHIC PROCESSING OF ZIRCONIA

To avoid the risk of chipping, veneering ceramic has recently ceased to be used and the zirconia now undergoes monolithic processing. Monolithic comes from “monolith” (from the Greek word “μόνολιθος/monólithos” meaning “single stone”) and, according to Wikipedia, essentially means “stone from one casting.” In materials

science, specimens are described as monolithic when they consist of one material and one unit. In dentistry, the non-veneered full cast crowns, pressed or milled glass-ceramic crowns without veneering, or non-veneered zirconia crowns are examples of typical monolithic restorations. In this way, the technician’s sophisticated manual veneering can thus be transferred to the computer and machine.

To be able to use the material monolithically, certain requirements must be met. Besides continuing long-



Fig 13 Chipping in veneering ceramic (Initial Zr, GC) on the second premolar of a three-unit zirconia fixed partial denture after 12 months of clinical use.

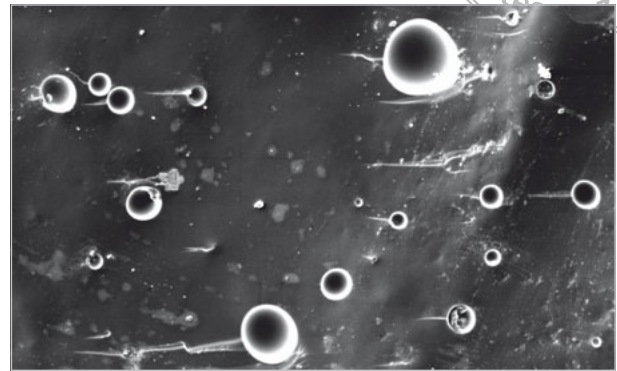


Fig 14 Test specimen after measuring the bond strength between zirconia and veneering ceramics. It can be seen that a thin layer of the veneer ceramic adheres to the zirconia (bubbles) and no fracture takes place directly in the interface between the two ceramics.

term stability, it is critical that the material becomes more translucent and thus more esthetically pleasing in visual terms. Translucency is treated as a separate topic and discussed in detail below. There are now three different ways to produce translucent zirconia, which have resulted in further generations of zirconia.

MONOCHROME VS MULTILAYER

Zirconia blanks are available as monochrome or multilayer blanks (Fig 15). The difference is that the monochrome blanks are consistently made in one color while the multilayer blanks are pre-layered and thus contain different shades. There is scientific evidence to the effect that the darker the color the higher the degree of opacity, ie the lower translucency becomes.¹¹ The color of the blanks is increasingly lighter and thus more translucent towards the incisal area. The dental technician can use CAD software to help to determine color sequences and intensities by positioning the constructed restoration in the blank. One advantage resulting from the combination of highly esthetic (color and translucency values are similar to those of natural teeth) and highly stable materials is better treatment with restorations with low space requirements. This works because wall thickness on the one hand and veneer layers on the other have more minimal designs if purely monolithic processing is not sufficient.

THE THREE TYPES OF ZIRCONIA

Modification of the sintering temperature with first-generation zirconia (3Y-TZP)

Conventional zirconia can be rendered more translucent by changing the sintering temperature.⁶ Studies show that not only the increase in sintering temperature but also the duration of the dwell time, the temperature increase, and cooling affect the translucency.¹² The larger the area (integral) of the sintering temperature, the higher the translucency. When a certain area is reached, the grain size of the material increases and the strength of the material reduces. In general, it can be stated that sintering temperatures of 1,600°C onwards lead to a decrease in flexural strength.⁶ Because of the negative behavior with regard to strength and more particularly to long-term stability, the first monolithic generation of zirconia failed to become established. Sintering temperatures are now less than 1,600°C for all work with zirconia.

Modification on the molecular level resulting in second-generation zirconia (3Y-TZP)

In 2012 to 2013, a second generation of zirconia was introduced. The number and grain size of the aluminum oxide (Al₂O₃) grains were reduced in this process and the latter were relocated in the zirconia framework (Fig 16). The repositioning of the Al₂O₃ grains, whose refraction index varies greatly from that of the zirconia

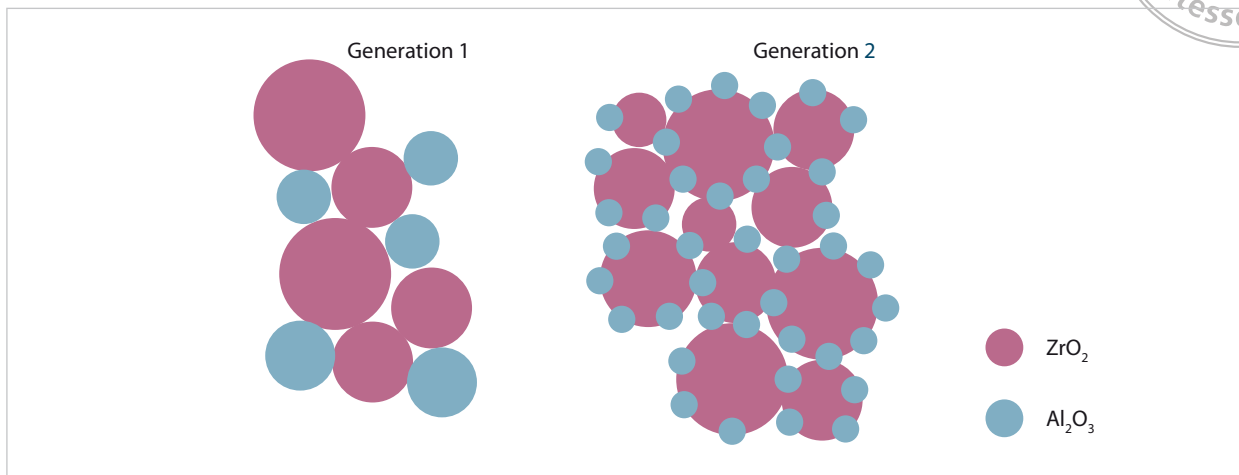


Fig 15 Illustration of first and second generation zirconia.

grains, takes place on the grain boundaries of zirconia. This meant that a higher transmittance of light with consistently good long-term stability and high strength were simultaneously achieved.¹³ In-vitro studies on this generation show not only higher translucencies but also higher strengths both initially and after diverse artificial aging processes.

Modification of the crystal structure resulting in third-generation zirconia (5Y-TZP)

Because second-generation zirconia was still inferior to the translucency of glass-ceramics, the desire for a more translucent zirconia was born. Third-generation zirconia was introduced at The International Dental Show 2015. This zirconia, controversially in comparison to the first and second generation, is not only metastable in the tetragonal phase but also contains a cubic-phase proportion of up to 53%. It is described, therefore, as fully stabilized zirconia with a mixed cubic/tetragonal structure. The cubic portions were achieved through higher endowment (approximately 9.3 wt%/5 mol%) of yttrium oxide. The cubic crystals have a higher volume compared to the tetragonal ones. This means that light scatters less strongly at the grain boundaries and residual porosities, making the material more translucent. Furthermore, the cubic crystal structures are more isotropic than the tetragonal structures,

which means that incident light is emitted more evenly in all spatial directions. This property also has a significant influence on translucency.

According to information from the suppliers of zirconia powder, no hydrothermal aging occurs with third-generation zirconia, which means that the material retains its microstructure and strength even with increasing wearing time.⁴ One disadvantage of this generation is the potentially lower fracture toughness of the material because of the cubic/tetragonal stabilization. However, at present there is hardly any independent scientific literature on this subject. The current data on third-generation zirconia are presented below.

CURRENT LITERATURE ON THE THIRD GENERATION

The translucency of third-generation zirconia was compared to the translucency of a LiSiO₂ ceramic by Harada et al.¹⁴ The following non-dyed zirconia materials were tested: Prettau Anterior (Zirkonzahn), BruxZir (Glidewell Laboratories), Katana HT, Katana ST, and Katana UT (Kuraray Noritake Dental), and the LiSiO₂ ceramic e.max CAD LT in color B1 (Ivoclar Vivadent). Rectangular (15 mm × 10 mm) test specimens (n = 5) with two layers, 0.5 and 1.0 mm thick respectively, were prepared for translucency measurement. Measurement was conducted in a spectrophotometer (Evolution 300 UV-Vis,



Figs 16a and 16b Monochrome vs. multilayer in crown form (a) and as platelets (b).

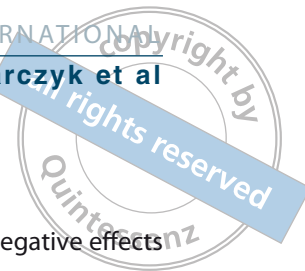
Thermo Scientific) with an integrating sphere. The total transmittance of light was measured as a percentage (Tt%) at a wavelength of 555 nm. The values were analyzed using Welch's robust test followed by the pairwise comparative post-hoc Dunnett's T3 test.

The following Tt% values were found in the test specimens with a 0.5-mm thickness: Prettau Anterior, 31.90 ± 0.49 ; BruxZir, 28.82 ± 0.22 ; Katana HT, 28.49 ± 0.14 ; Kanata ST, 31.67 ± 0.24 ; Katana UT, 33.73 ± 0.13 ; and for the control group IPS e.max CAD LT, 40.32 ± 0.25 . Essentially, significant differences were observed between the materials. The exceptions to this were BruxZir and Katana HT, as well as Prettau Anterior and Katana ST. These groups were in one range of values. In addition, it emerged that the Katana UT zirconia was significantly more translucent than other zirconia materials. The control group, IPS e.max CAD LT, however, showed significantly higher translucency values than all the zirconia materials.¹⁴

The following Tt% values were measured in the test specimens with layers 1.0 mm thick: Prettau Anterior, 22.58 ± 0.41 ; BruxZir, 20.13 ± 0.22 ; Katana HT, 20.18 ± 0.39 ; Kanata ST, 21.86 ± 0.39 ; Katana UT, 23.37 ± 0.27 ; and for IPS e.max CAD LT, 27.05 ± 0.56 . With this layer thickness as well, significant differences between the materials were observed. The following groups were exceptions to this: BruxZir and Katana HT, BruxZir and Prettau Anterior, Katana ST and Katana UT. These were also significantly more translucent than all other zirconia materials but less translucent than the control group IPS e.max CAD LT.¹⁴

In summary, it was observed that, at the layer thickness of 0.5 mm, Katana UT had significantly more translucent values than all other zirconia materials. However, the control group, IPS e.max CAD LT, had significantly more translucent values than all zirconia materials. With a layer thickness of 1.0 mm, Prettau Anterior, Katana ST, and Katana UT had significantly more translucent values than the remaining zirconia materials and fewer more translucent values than IPS e.max CAD LT.¹⁴

In relation to translucency values, it is important to emphasize at this point that test specimens with the same layer thickness were always compared to each other in the studies. Monolithic restorations made of LiSiO_2 glass-ceramic, however, need a higher minimum occlusal layer thickness of 1.5 mm, to be able to withstand the stresses in the mouth.¹⁵⁻¹⁷ It can be concluded that the material of the third-generation zirconia can be successfully used in clinical practice in the indications for monolithic restorations with lower occlusal strength and less occlusal tooth reduction. However, a study¹⁶ indicated that third-generation zirconia may be rather exposed to aging (low temperature degradation). The reason for this is the reduced content of Al_2O_3 particles in favor of yttrium oxide and a higher grain size.¹⁸⁻²⁰ The authors of this article also address the issue that Al_2O_3 particles increase the mechanical properties of zirconia.^{19,21-23} Since the proportion of Al_2O_3 particles is greatly reduced in relation to the second and third generation and this leads, in the third generation, in combination with the increased proportion of yttrium, to the development of a mixed framework with new



properties, reference is made, in the context of this study, to the importance of the mechanical properties and the urgent need for future studies on this.

The fracture load of crowns made from highly translucent zirconia (third generation, HTZ), less translucent zirconia (second generation, LTZ), and a LiSiO₂ glass-ceramic (LDS) was tested by Nordahl et al.²⁴ HTZ and LTZ crowns were produced with a layer thickness of 0.3, 0.5, 0.7, 1.0, and 1.5 mm. The LDS crowns were produced in layer thicknesses of 1.0 and 1.5 mm. Every group consisted of 10 crowns. All groups were artificially aged using thermocycling (5,000 cycles, 5°C/55°C) before fracturing load was measured. For the LTZ group breaking load values were between 450 N and 3,248 N; for the HTZ group between 438 N and 3,487 N; and for the LDS group between 1,030 N and 1,431 N. HTZ and LTZ crowns were within the same range of values and significantly higher than the LDS crowns ($P < .001$). Two types of fracture were observed, namely a complete fracture or an incipient crack in the crown. LTZ crowns with the layer thickness of 1.0 and 1.5 mm showed an incipient crack after testing fracturing load in most cases. The remaining crowns fractured completely.²⁴

In summary, it was observed that there are no differences in fracture load between second and third generation zirconia. The fracture load of the zirconia crowns was significantly higher than that of the LiSiO₂ crowns.²⁴

In comparison to the LiSiO₂ glass-ceramic, significantly higher strength values were observed in zirconia crowns with the same layer thickness. No difference was evident between the zirconia crowns of the third and second generation. This indicates that neither the change in grain size nor the higher endowment of yttrium oxide exerts an influence on the mechanical properties of third-generation zirconia. Furthermore, it was observed during this study that even a small increase in layer thickness from 0.5 to 0.7 mm leads to an increase in breaking load for zirconia crowns.²⁴ Fracture load increased by 31% for the HTZ crowns and by 55% for the LTZ crowns.²⁴ However, it was observed in a further study with regard to the change in layer thickness of monolithic Y-TZP ceramics (second generation)

that an increase in layer thickness has negative effects on translucency.²⁵

Udea et al²⁶ measured the permeability of visible light (400 to 700 nm) through four different layers (enamel layer [EL], transitional layer 1 [TL1], transitional layer 2 [TL2], body layer [BL]) of a multilayer-color zirconia block (Katana Zirconia Multi-Layered Disc [ML]) using a spectral photometer. Forty test specimens (thickness: 1 ± 0.05 mm) were tested in every color layer and analyzed statistically. Light permeability was expressed as a percentage of the passing light. The following means (standard deviation [SD]) were calculated: EL 32.8% (1.5), TL1 31.2% (1.3), TL2 25.4% (1.3), and BL 21.7% (1.1). Significant differences were found in all groups (analysis of variance, Student-Newman-Keuls test). The multilayered colored zirconia blank showed different capacities for light permeability in the four layers. For this reason, it appeared reasonable to use the material to increase the esthetic appearance of fully anatomical zirconia.²⁶

In summary, it was stated that four-layered pre-colored zirconia blanks offer advantages in terms of esthetics compared to monochrome materials.²⁶ The layers tested showed significant difference with regard to their light permeability with the enamel layer achieving the significantly highest value for permeability and thus looking the most transparent. The dentin layer, however, is most likely to look opaque because of the significantly lowest values for light permeability. These different shades of color are very helpful to design a natural looking appearance and improve the esthetic results of monolithic restorations. Because of the significantly different values for light permeability obtained for the layers of the blank, reference was made to potential differences in the physical properties within the individual layers. However, the authors assess this observation as harmless.²⁶

The results of this study²⁶ are particularly helpful in relation to the precise positioning of individual restorations in the blank. According to indication and esthetic requirements, the restoration can be placed higher or lower in the milling blank, helping to achieve an optimal result.



CONCLUSION

The historical development of zirconia for dental applications, with focus on the different generations, emphasizes the potential of this material for the manufacture of esthetic and high-quality restorations. It has been shown that the monolithic processing of zirconia is feasible and provides certain advantages. In particular, regarding the development of the third generation of zirconia, the optical properties are improved, even if current data on the mechanical properties are scarce.

Part II of this article focuses on the relevant guidelines for working with the generations of zirconia and includes a discussion of the optical properties based on the authors' own in-vitro and in-vivo measurements.

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