Zirconia and its novel compositions: What do clinicians need to know?

Jan-Frederik Güth, Prof Dr med dent/Bogna Stawarczyk, Priv-Doz Dr rer biol hum, Dipl Ing (FH), MSc/
Daniel Edelhoff, Prof Dr med dent/Anja Liebermann, Priv-Doz Dr med dent, MSc

For several years, there has been a clear trend in the dental market towards monolithic tooth-colored restorations. In this context, further developments, particularly in the field of zirconia ceramics, have led to considerable improvement in the materials’ optical properties. Modern zirconia materials can be divided into several cohorts, differing from each other with respect to their optical and mechanical properties. The knowledge about indications and limitations of each zirconia cohort is essential for a correct clinical application. Clinical long-term experience for the zirconia of the newest generations is still scarce and only in-vitro data are available. Despite all advancements, clinical long-term success remains closely linked to the specific indications, preparation, material selection, knowledge, and experience of the dental practitioner and dental technician, as well as an adequate luting mode and occlusal concept. Due to the high innovation rate within materials and CAD/CAM technology in general, clinicians and dental technicians need to be well informed in order to be able to work successfully with the various options.

Due to their high biocompatibility and esthetic potential, all-ceramic materials are a suitable alternative to metal-based restorations for many indications within restorative dentistry. Apart from a great number of glass ceramics, the class of dental ceramics also comprises different types of zirconia materials, which are continuously being enhanced and modified. Due to the great number of options available – also in the field of monolithic zirconia – the selection of a restorative material in everyday clinical practice has turned into a complex and challenging task.

At the same time, a clear trend towards monolithic restorations can be observed in the dental market. Crucial reasons for choosing monolithic restorations over frameworks veneered using a manual layering technique include reduced manufacturing expenses, higher reliability (improved Weibull modulus), and reduced thicknesses, leading to less invasive preparations. In addition, it is possible to create the morphology in a more accurate way, avoiding sinter shrinkage of the veneering ceramic. Besides the facilitation of the computer-aided design (CAD) process itself, this leads to a design-related reduction of the related chipping risk. Proper material selection remains decisive: there are considerable differences in the mechanical and optical properties of the available zirconia materials for monolithic clinical use. These differences are dependent on the material composition and manufacturing procedure. This article aims to provide assistance for clinicians who would like to correctly classify and adequately utilize zirconia materials for their adequate indications – because “zirconia” has become a general term for a wide range of novel zirconia-based materials.

Classification of modern zirconia materials

The basic objective of further developing zirconia materials was to increase their translucency in order to use them in specific indications for fabrication of monolithic restorations. To
achieve greater translucency, different strategies for the modification of the material composition could be pursued:

- reduction of the number of defects in the material structure, e.g., achieved by addition of a glass phase or a sintering additive
- refinement of the microstructure, so that grain boundaries will no longer interfere with the light that passes through
- increase of the grain size to reduce the number of boundaries
- creation in the material structure of a cubic phase, which has isotropic optical properties to avoid double refractions.

The great number of available options and parameters makes it difficult to keep track of current developments and to be sure what type of zirconia material is actually being held in the hands.

Zirconia can theoretically exist in three crystalline forms depending on the composition and temperature: monoclinic, tetragonal, and cubic. This results in a wide range of material options with different mechanical and optical properties. The production and processing of zirconia also has a decisive impact on the final properties. Furthermore, incorrect treatment of the material during the production of a restoration can cause phase transformations, affecting the mechanical properties in general and especially the coefficient of thermal expansion.

Zirconia materials can currently be divided into four types or generations according to their mechanical and optical properties. Figure 1 provides an overview of the available zirconia generations. This overview is used to facilitate orientation in everyday clinical practice.

**First generation: 3-mol%-yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP)**

3Y-TZP material is partially stabilized in the tetragonal phase, offers the highest mechanical properties, and was introduced to the dental market more than 25 years ago. Due to its outstanding biocompatibility and a flexural strength of more than 1,000 MPa, zirconia of the first generation is generally used as a framework material. Its mechanical properties enable its use in minimal wall thicknesses and for multi-unit restorations. However, due to its high opacity and the resulting compromised optical appearance, the material is predominantly used as a supporting framework structure. The first generation zirconia is therefore mainly indicated for the fabrication of frameworks that will be manually veneered as well as for the production of hybrid abutments in implant restorations. In-vitro and in-vivo investigations showed that these zirconia restorations offer a favorable mechanical stability and high clinical reliability.

According to the S3 guideline “All-ceramic crowns and bridges,” the use of veneered fixed dental prostheses (FDPs) with up to three units can be recommended for the anterior and posterior areas whenever sufficient anatomical support of the glass-ceramic layer is ensured by the framework design. Clinical data reveal a very good survival rate of 98.2% and a success rate of 92% after 10 years. The knowledge and skills of the practitioner regarding preparation design and adhesive cementation of zirconia, however, have a huge impact on the long-term success.
Due to its high opacity, first generation zirconia is contra-indicated for the fabrication of monolithic restorations. In order to make the material suitable for monolithic use, the material structure has been modified in various ways. The main focus was to improve the optical properties, especially increasing the translucency. The first approach of the material scientists was to alter the sintering parameters. The final sintering temperatures were increased to up to 1,600°C and the holding times were extended. These measures led to an increase of translucency, but at the same time, to a decrease of flexural strength with the appearance of structural defects. This strategy finally resulted in spontaneous fractures and reduced reliability and did therefore not prevail in the dental market. Instead, alternative methods were chosen to increase the translucency.

Fig 2a  Framework made of second generation zirconia with anatomical reduction in regions of the mandibular left second premolar and first molar (35 and 36). The fixed dental prosthesis anchor at the mandibular left second molar (tooth 37) has a monolithic design.

Fig 2b  Hand-veneered ceramic at mandibular left second premolar and first molar (teeth 35 and 36). Fixed dental prosthesis anchor at the mandibular left second molar (tooth 37) did not receive any glass ceramic layer but was polished and glazed.

Fig 2c  Fluorescence behavior of a framework structure made of second generation zirconia with anatomical reduction in regions of the mandibular left second premolar and first molar (teeth 35 and 36).

Fig 2d  Fluorescence behavior after manual veneering of the anatomically reduced parts in regions of the mandibular left second premolar and first molar (teeth 35 and 36) compared to the monolithically designed fixed dental prosthesis anchor at the mandibular left second molar (tooth 37).

Fig 2e  Lateral/occlusal view of the adhesively luted zirconia fixed dental prosthesis, manually veneered in regions mandibular left second premolar and first molar (teeth 35 and 36), monolithic in region mandibular left second molar (tooth 37). Laboratory work: MDT Marc Ramberger.
Second generation: 3-mol%-yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP) with reduced alumina content

Around 2013, an enhanced version of the 3Y-TZP materials was presented. The innovation was mainly based on a modification carried out on the molecular level: the number and size of the alumina grains (Al₂O₃) contained in the material structure were reduced. In addition, the alumina grains were placed at the boundaries of the zirconia grains, resulting in a higher level of light transmission and therefore translucency. At the same time, the in-vitro long-term stability was sufficient, and the flexural strength remained high.¹²,²⁰ Due to its durable strength and better optical properties, this type of zirconia is predominantly used as framework material for one- and multi-unit FDPs. Partially veneered restorations are also possible, allowing a defect-oriented preparation on the one hand and an attractive esthetic appearance on the other (Fig 2).

Third generation: 5-mol%-yttria-stabilized tetragonal zirconia polycrystals (5Y-TZP)

A further enhancement in the translucency of zirconia was achieved by an increase of the yttria (Y₂O₃) content to 5 mol%. This new type of material was introduced in 2015. It is described as a fully stabilized zirconia with cubic-tetragonal microstructure, colloquially named cubic zirconia. The cubic content amounts to approximately 50%. Because the cubic crystals are larger than the tetragonal crystals, light that is transmitted through the restorations passes fewer boundaries and porosities that might cause refractions. As a consequence, the material appears more translucent. The greater the amount of cubic crystals in the material structure, the higher the translucency. An increase of the amount of cubic crystals has, however, a negative impact on the mechanical properties such as flexural strength and fracture toughness. The translucency of the third zirconia generation is slightly lower than that of lithium (x)silicate, while their flexural strength and fracture toughness are higher. Consequently, third generation zirconia may be regarded as a possible alternative to high-strength glass ceramics.¹⁸,²¹

Most manufacturers recommend third generation zirconia – just like lithium (x)silicate – for the production of single tooth restorations, and FDPs with up to three units and one pontic between two crowns in the premolar region. It is, however, advisable to check the material’s instructions for use to obtain detailed information about the specific indications. In this context, it needs to be mentioned that there is (apart from investigation on their translucency behavior) a lack of clinical and also in-vitro data for the third generation zirconia. Figure 3 shows a three-unit FDP made of a third generation zirconia.
Fourth generation: 4-mol%-yttria-stabilized tetragonal zirconia polycrystals (4Y-TZP)

In order to increase the indication range for monolithic zirconia restorations, there is an ongoing effort to optimize the material properties through diverse modifications. In 2017, the fourth generation of zirconia was introduced. Compared to the third generation, the yttria content was reduced to 4 mol%, which led to an enhancement of the mechanical properties with a combined reduction in its light-optical properties. Depending on the manufacturer, fourth generation zirconia is indicated for short-span multi-unit FDPs.

Additional modifications

For different zirconia generations, multilayered or gradient-shaded zirconia blanks are available. These were developed to facilitate imitation of the color gradient of natural teeth (Figs 4 and 5). In addition, blanks that combine different zirconia generations (eg, multilayer) have recently been introduced to obtain the best possible mechanical and optical properties. These blanks consist, for example, of a body out of fourth generation zirconia (4Y-TZP) to ensure a slightly increased stability, and a third generation material (5Y-TZP) with higher translucency is selected for the incisal area for enhanced optical properties. Also, different combinations and mix forms are available from different manufacturers. Other zirconia blanks have integrated fluorescent particles (Fig 6).

Another trend is towards an acceleration of the sintering procedures (speed or super-speed sintering) for speeding up the manufacturing procedure. Depending on the geometry of the restoration, sintering may take only approximately 30 minutes. However, this is possible, only for materials that are specifically developed for a speed-sintering process. Also, there is still a lack of sufficient scientific data supporting speed sintering.

Cementation of zirconia restorations

Considering the luting process of zirconia restorations, there are differences between traditional cementation and adhesive luting with or without using additional adhesive systems. For translucent restorations made out of third or fourth generation zirconia, it is recommended to not use an opaque luting material in the visible area for esthetic reasons.

The major criterion for luting material selection is, however, the preparation design, which should be chosen based on the guidelines for all-ceramic preparations. For a traditional cementation using glass-ionomer cement, the prepared tooth stump should offer an adequate form of retention and resistance. The results of a clinical study with an observation period of up to 9 years revealed, for example, that all-ceramic crowns made of lithium disilicate (IPS e.max Press, Ivoclar Vivadent) cemented with glass-ionomer cement (Ketac Cem, 3M) showed no increased decementation rate when the prepared tooth presented a convergence angle of 10 degrees and a minimal stump height of 4 mm. A minimal stump height of 4 mm and a maximum convergence angle of 15 degrees may be regarded as clinical reference points in the decision of whether or not a traditional cementation procedure is possible.

Figs 5a to 5c  Zirconia with different compositions, each with shade and translucency gradient. (a) Katana Zirconia ML; (b) Katana Zirconia STML; (c) Katana Zirconia UTML. Laboratory work: MDT Josef Schweiger.
Cementation is described as a process that establishes a mechanical connection achieved via mechanical interlocking on the prepared tooth stump. An accurate fit of the restoration is essential. As long as the preparation guidelines regarding the form of retention and resistance are respected, it seems that even traditional placement methods with traditional cements do not cause a cumulative occurrence of cases with a loss of retention. Current studies running for up to 10 years, however, have revealed a significant increase of decementations, especially when FDPs were placed with zinc phosphate cement in the mandible. Accordingly, the authors recommended to critically reassess the use of this type of cement. Preparations for single crowns presented an average preparation angle of more than 26 degrees. Therefore, it seems to be debatable if it is possible to respect the given preparation guidelines in everyday practice. Against this background, adhesive luting seems to be beneficial. This method is more technique-sensitive and time-consuming than a cementation, but with better chemical bonding and low solubility compared to traditional cements. A better marginal integrity is also obtained. In this context, an adequate pretreatment of the tooth substance and the inner surface of the restoration is an important precondition for a reliable result.

Within the class of composite resin cements, a distinction can be made between luting materials with and without (self-etch) the use of an adhesive system based on their chemical composition. When self-etch composite resin cements are used, a conditioning of the tooth structure is not mandatory. Whenever enamel is present, an initial selective enamel etching step will, however, lead to a better bond quality and durable marginal seal. Due to the presence of acidic and phosphoric monomers in the formulation, separate conditioning of the dentin surfaces with primers is not recommended. Independent of the zirconia generation used, a chemical bond is established between the restorative material and the self-etch composite resin cement. Composite resin cements with additionally used adhesive systems based on dimethacrylate require separate conditioning with an adhesive system that contains phosphate. However, if the conventional composite resin cement contains phosphate monomers like MDP (10-meth-

Figs 6a to 6d  Optical comparison of different zirconia generations. (a) Fixed dental prosthesis (FDP) from maxillary right first premolar to first molar (tooth 14 to 16) and single crown maxillary right second molar (tooth 17) made of a second generation zirconia in visible light. (b) FDP from 14 to 16 and single crown 17 made of a second generation zirconia captured with an ultraviolet light source in order to reveal the fluorescence behavior of the material. (c) FDP from maxillary left canine to second premolar (tooth 23 to 25) with cantilever on the lateral incisor (tooth 22; experimental use outside indication range) and crown on the first molar (tooth 26) made of third generation zirconia, which has integrated fluorescent particles (Lava Esthetic, 3M); the same restorations captured under an ultraviolet light source (fluor_eyes, www.finest-dental.de). Laboratory work: MDT Josef Schweiger.
acryloyloxyethyl dihydrogen phosphate), it is not necessary to pretreat zirconia with a phosphate-containing adhesive system. After intraoral try-in, which is usually associated with saliva contamination, the restoration should be cleaned thoroughly. As zirconia is an oxide ceramic material that is free of glass particles, etching with hydrofluoric acid does not have the desired effect. Instead, moderate airborne-particle abrasion is recommended after the try-in (authors’ recommendation: pressure maximum 1 bar, distance approximately 10 mm, particle size ≤ 50 μm).

Cleaning with phosphoric acid needs to be reconsidered critically. Although phosphoric acid seems to be much more effective than cleaning with alcohol, a decrease of the bond strength is observed after artificial aging if phosphoric acid cleaning was used. This effect can be prevented only by a subsequent cleaning step with alcohol. The cleaning of zirconia surfaces with phosphoric acid cannot be recommended if adhesive luting is desired. Whenever the surface is not cleaned sufficiently with alcohol following phosphoric acid treatment, the phosphate groups in the phosphoric acid might occupy oxide binding sites. These binding sites are usually available for the phosphate monomers contained in the self-etch composite resin cement or the adhesive system to form a chemical bond. A high airborne particle-abrasion pressure with overly large particles should be avoided to prevent inducing superfluous surface damage, stresses, or micro cracks.

With their composition based on acidic monomers being responsible for bonding to the tooth surface, self-adhesive composite resin cements do not require a pretreatment of the zirconia surface. When conventional composite resin cements are used, a separate conditioning with an adhesive system that contains a phosphate monomer (eg, MDP monomer) is necessary to facilitate chemical bonding. MDP is a bifunctional monomer that is able to bond to zirconia with its phosphate group end and to the resin cement with its methacrylate end. In order to minimize potential sources of error, it is essential to strictly adhere to the specific luting protocols recommended for the adhesive system.

**Surface treatment following adjustment procedures (grinding)**

With regard to the protection of the antagonist enamel from abrasion, the surface of the restoration should be as smooth as possible. When it comes to monolithic zirconia restorations, this is particularly important as inadequately polished surfaces might have extremely sharp edges, which could potentially harm the antagonist.

For veneered zirconia restorations, surface treatment after the adjustment of premature contacts is decisive, as problems with chipping are reported. Chipping is defined as a fracture of the veneering ceramic, which is often observed for rough, insufficiently polished surfaces. In order to minimize the chipping risk, it may be necessary to send the restoration back to the laboratory after intraoral adjustments. Depending on the size of the adjusted surface, it is recommended to put the restoration through a second glaze firing (more than 1 mm²) or to repolish the area. For polishing, which may also be carried out in the dental office, different (usually multi-step) polishing systems are available, consisting of silicone polishers with different grain sizes. If the polishers are used in the recommended order (from coarse to fine), good results can be obtained. The ceramic polishing systems are suitable for veneering ceramic and zirconia.

Monolithic zirconia restorations may also be polished in white state prior to sintering. As the material is very soft and the substance can be easily removed, the polishing should be performed carefully.

**Assessment of monolithic zirconia restorations based on the available literature**

Basic support in selecting the best suitable dental ceramic material is provided by the S3 guideline “All-ceramic crowns and bridges” published in 2014. Due to the insufficient amount of clinical data available and the lack of results from long-term observation periods, however, modern monolithic restorations based on zirconia are not included in this guideline. So far, very little is known about the new zirconia generations and scientific data are scarce. Yet, the specific properties of these new material classes and the numerous unsolved issues for clinical use catch the interest of users and scientists alike. At the moment, it is only possible to assess and classify these new monolithic zirconia materials based on the available scientific data (mostly in-vitro data) and the expertise of the authors.

Especially regarding single tooth restorations, tooth-colored monolithic zirconia is in strong competition with other all-ceramic materials with clinical long-term data. In laboratory investigations, however, monolithic zirconia restorations show higher fracture loads than crowns made of alternative ceramics like lithium disilicate. This makes less invasive preparation designs for monolithic zirconia crowns possible. In laboratory tests, for example, single crowns with a layer thickness of 0.5 mm showed a sufficient fracture load and in-vitro performance independent of the placement method (adhesive luting 1,628 ± 174 N, cementation 1,357 ± 340 N).
What plays a decisive role in this context is an adequate form of retention and resistance required to avoid a loss of retention. One investigation shows, however, that there is a tendency towards a too conical preparation (mean convergence angle of 26 degrees in single crown preparations).\textsuperscript{32} It is essential that practitioners put a strong focus on an exact preparation, which might prevent an early loss of retention.\textsuperscript{26} In addition, the results point to the fact that in the busy everyday clinical routine, an adhesive luting protocol might be a useful preventive measure against possible retention loss.\textsuperscript{28} In the material selection process, when assessing the criterion “minimum possible layer thickness,” the clinician should always take into account the level of destruction of the tooth. In this context, it is essential to check critically if an alternative, even less invasive form of restoration and preparation (eg, onlay, overlay, veneer, partial crown) using alternative types of material is feasible.\textsuperscript{40}

Another aspect that should be respected in the context of material selection is the abrasive wear behavior of the materials themselves and especially their effect on the antagonist.\textsuperscript{41} The clinical data available on this topic are also insufficient to provide advice for or against using specific materials or material classes. It is ultimately up to the restorative team to implement a well-balanced occlusal concept. To ensure the desired results, it is advisable in this context to strictly adhere to the recommended protocols.

Practitioners should be careful in drawing conclusions from investigations focusing on specific materials and to transfer findings to other zirconia generations. This is due to different amounts of yttria in the formulations and differences in the aging behavior. Even if initial in-vitro data show promising results, clinical studies that focus on monolithic zirconia in various indications need to be initiated. Their results will be able to provide sufficient clinical evidence for the use of this new material class.

Conclusion

A decisive improvement of the optical properties of ceramic materials has been achieved through further developments. Still, clinical long-term success is strongly linked to the selection of the correct indication, preparation, and material, the knowledge and experience of the dental practitioner and technician, and adequate luting procedure and occlusal concepts. The high innovation rate in material and CAD/CAM technology development demands good knowledge of the practitioner for the optimal and successful use of all available options.

References


