Original Paper

Zirconia Use in Dentistry-Manufacturing and Properties

LUIZA NISTOR[1], MĂDĂLINA GRĂDINARU[1], RADU RÎCĂ[1], PETRE MĂRĂȘESCU[1], MIHAELA STAN[1], HORIA MANOLEA[1], IONESCU AUGUSTIN[1], IREN MORARU[1]

[1]Faculty of Dentistry, University of Medicine and Pharmacy of Craiova

ABSTRACT: Several types of metal-free ceramics have been developed to meet the patients demand for natural looking appearance restorations. Owing to their biocompatibility and good mechanical properties zirconia has been successfully used in recent years as a dental biomaterial. Due to its high opacity zirconia cores are generally covered with ceramic veneers that provide a more natural appearance but have frequent incidence of chipping. As an alternative to veneered zirconia full-contour zirconia restorations become more widely used nowadays. The paper reviews the current knowledge and scientific data of the zirconia use in dentistry in order to compare the zirconia based dental restorations with the metal-ceramic ones and also the two types of dental restoration based on zirconia, veneered or monolithic zirconia.

KEYWORDS: *Veneered zirconia, monolithic, manufacture, properties*

Introduction

Aesthetics, functionality and biocompatibility make dental medicine a constant challenge in the manufacture of dental restorations. The development of materials science, robotics and biomechanics has radically changed the approach to replacing human anatomical components [1]. In order to be able to offer the optimal solution without compromise, perfectly integrated in the physiognomy of each patient, but also the resistance in time against the masticatory forces, precision, perfection, quality, the specialists have increasingly emphasized the use of biocompatible materials for the dental prosthetic restorations using modern technologies as CAD/CAM.

Computer-aided design (CAD) and computer-aided manufacturing (CAM) systems represent modern technologies that use computers to gather the data, in our case from the oral cavity, to design the future dental prosthesis, and to manufacture a large range of products. These technologies are used in many areas, but dental CAD/CAM applications were not available until the and of the 1970s. Among the pioneers of CAD/CAM technology use in dentistry we can include Bruce Altschuler, Francois Duret, Werner Moermann, Marco Brandestini, who have managed to develop CEREC®, the first commercially available dental CAD/CAM. [2,3,4].

The dental CAD/CAM systems consist of three basic devices. The data acquisition device consists of an intraoral imaging camera with which the prosthetic field is optically imprinted. An optical impression may be obtained directly from the oral cavity, but can also be obtained outside the oral cavity by scanning a stone model obtained after a classical impression. The data processing and the design of the future restoration can be done on the basis of algorithms integrated into the operating system, by user setting of the limits of preparation and future restoration on the monitor image and by consulting a database with default restoration designs.

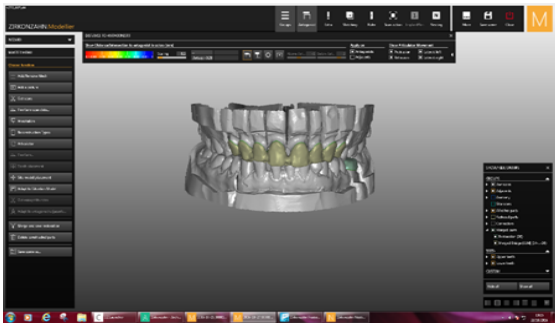

Fig.1. Virtual restoration design

The milling device consists of one or more micromotors coordinated by the central data processing unit. [4,5,6].

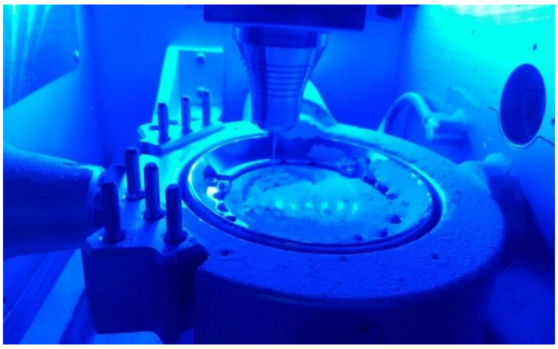

Fig.2. Zirconia blank milling

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An 8 unit framework structure was designed digitally in order to be milled from zirconia and veneered afterwards with specific porcelains in the dental lab-Fig.1. Milling faze of zirconia blank is captured in Fig.2.

Dental restorations made with CAD/CAM technology have become very popular lately due to the fact that high-quality restorations can be obtained in a reduced predicted time, thus increasing efficiency by automating the manufacturing steps. Computer-aided design and manufacturing allows the use a wider range of materials for different types of dental prosthetic structures.

However, the introduction of new technological systems together with new materials like zirconia in the educational curriculum led to new problems. Thus, the emergence of a large number of materials in a short time leads to a crisis of the professional staff with an adequate training, which leads to an increase in the working time while the costs are still high [7].

The zirconia use in medicine started as a hip replacement material from 1970s [8]. Its use in dentistry started in the 1990s for root canal posts, then for prosthetic abutment, but the development of its use in the dental prosthetics started with the opportunity for manufacturing ceramic posterior fixed partial prosthesis. More recently, zirconia has also begun to be used as a material for making dental implants [9].

Zirconia has been introduced into dental practice as an alternative to metal-ceramic dental restorations.

Compared to the traditional porcelain fused to metal restorations, zirconia restorations have better esthetics, due to their excellent optical properties and especially due to the absence of the black line, caused by metal in the cervical line of the traditional restorations. Even the opacity may differ between the different systems available on the market, the overall properties of zirconia make it a first choice today in the cases with high aesthetic requirements [10].

The purpose of our study was to review the current knowledge and scientific data of the zirconia use in dentistry in order to compare the zirconia based dental restorations with the metal-ceramic ones and also the two types of dental restoration based on zirconia, veneered or monolithic zirconia. We tried to answer these questions by evaluating the manufacturing process, the biocompatibility, the optical and mechanical properties of the zirconia used in dentistry.

Yttria-stabilized zirconia (Y-TZP)

Today, in dentistry, it is usually used a modified yttria (Y2O3) tetragonal zirconia polycrystalline (Y-TZP), because it has great mechanical properties and very good tear resistance than other regular ceramic masses [11,12]. The addition of yttria is meant to stabilize the transformation of the crystalline structure under the conditions of increased temperature, but also to improve the physical properties of zirconium [11]. Thus, the Y-TZP may reach 1000 Mpa while the fracture toughness of 4-5 MPa is also superior to the regular dental ceramics. One characteristic of Y-TZP zirconia is especially this high resistance to fractures because the tetragonal beads are transformed from the monoclinic phase, which leads to the compression of the forces around the defects, preventing their propagation [13]. The wider range of clinical situations were Y-TZP zirconia may be used is related to its superior mechanical properties compared to other dental ceramics. While the first integral ceramic dental restorations were limited to single-tooth restorations or small bridges, these zirconia structures may be used in larger prosthesis both in the anterior or posterior region of the oral cavity [14] being one of the few aesthetic solutions that can be used in the lateral area [15]. All of which added to classical uses like posts and cores [16] or more recently as a material for dental implants [17].

Manufacturing

CAD/CAM materials used in dental restorations are usually blocks and discs fully or partially sintered. The state of these blocks and discs differentiate the fabrication of dental restorations.

Dental prosthetic restorations made from zirconia may be obtained using the CAD-CAM technology with two possible methods [11,14].

In the first technique the prosthetic restorations are milled from zirconia blocks already sintered which means there is no shrinkage to the final structure [11,14], but there are some disadvantages such as the reduced life-time of the burs, due to their great wear and the numerous flaws that occur during the machining that may diminish the mechanical properties of the final prosthesis [11]. In this method the Y-TZP blocks are subjected to a first sinterisation at temperatures below 1500^0C increase their density. Then the blocks are subjected to a high pressure at the same temperatures in an inert gas atmosphere, which allow the obtaining of a very high density of more than 99% of the theoretical one [18].

In the second method the zirconia prosthesis is milled from a block [11], replicating the form of the final prosthesis but with bigger dimensions so it compensates for the shrinkage that occurs after sintering.

Fig.3. Zirconia milled framework

An oversized zirconia (Zirkonzahn Ice Zirkon Translucent) structure after milling is shown in Fig.3.

Then, the ceramic is fired and the framework contracts to the final dimension [14]. The non-sintered zirconia blanks result following a cold pressing process that compacts the zirconia powders. In this way we obtain a very small pore size and an good distribution of the components within the blank [19]. The next step is machining by immersion in solutions of various metal (cerium, bismuth, iron or a combination thereof) and the coloring of the restorations. As it goes through the last sintering phase the color is developed. The solution concentration has a direct impact on the final shade. A satisfactory coloration can be obtained using concentrations as low as 0.01mol%. For a good result we must follow the manufacturer's instructions as the final sintering temperature influences the color obtained [18]. The zirconia framework acquires its final mechanical properties at the end of the sintering process when it suffers a contraction at about 25%, which means it returns to its correct dimensions [19]. In order to optimize the fitting of the restoration it's imperative to know the exact volume shrinkage information for every zirconia blank block. The vast majority of blocks have barcodes that give information regarding the density of the milling block to the computer and so we can adequately mill the framework oversize [20]

Fig.4. Oversized zirconia framework before sintering

Milled oversized zirconia framework, detached from the blank, can be seen in Fig.4. Sintering is mandatory in the final stages to eliminate any stress induced by the surface milling action and to achieve the proper density.

Fig.5. Adjusting sintered zirconia framework

Previously sintered zirconia structure is adjusted in order to have a proper shape for ceramic veneering as in Fig.5.

In order to achieve an aesthetic appearance of the zirconia ceramic restoration a multilayer covering technique is used for veneering zirconia framework with compatible ceramics. Fig.6 shows the applied layers of Zirkonzahn Ice Zirkon Ceramics (Ceramic Dentine A1, Ceramic Enamel S1, Ceramic Transpa Neutral)

Fig.6. Layering ceramics on zirconia framework

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After applying glaze and stain materials (Glaze Plus, stain color tissue and stain color Prettau A1) on fired ceramic layers (Ice Zirkon Ceramics) a final prosthetic restoration is obtained as seen in Fig.7.

Fig.7. Zirconia ceramics final restoration

Figures presented above are part of a zirconia ceramic restoration manufactured in the dental laboratory. The manufacturing process took a few days due to specificity of materials used and fabrication. Trough CAD/CAM implementation this final dental restoration was done in an effective way due to prompt framework digital design, precise milling and adjustment of zirconia framework. After veneering, the obtained zirconia ceramic restoration met all aesthetic requirements mainly thanks to zirconia framework properties.

Compared to the alternative methods, milling full blocks of sintered zirconia takes a lot of time. This is costlier because requires a more frequent change of the diamond burs. That is why non-sintered zirconia can be considered a more convenient solution [21].

Monolithic vs. veneered zirconia

Chipping & fracturing

In the beginning, the application of high-crystalline zirconia in dental restoration was limited to substructures because of its high opacity. Veneering is usually applied over zirconia cores to instate a more natural appearance [22]. Regarding veneered-zirconia restorations porcelain compatibility is a concern. The latest studies regarding ceramic restorations report a large amount of porcelain chipping, cracking, delamination and fractures [23].

The most important downsides reported on zirconia by most studies refer to the wear and even clinical failure of the coating material and not so much to the resistance of the supporting structure. The fractures of the coating material also known as chipping are reported as the most frequent clinical problem, regardless of the applied zirconia veneer system. The fracture rates of the coating (veneer) are at 2-9% for crowns after 2 to 3 years and at 3-36% for dental bridges after 1 to 5 years [24]. It is very important that the whole system zirconia core with ceramic coating to have a good stability in time [25].

The chipping of veneering porcelain on zirconia-based ceramic frameworks can be attributed to the influence of many factors: the difference between the thermal expansion coefficient between the zirconia and ceramics, the absence of humidity within the material after the ceramic coating, the ceramic firing process, the phase transformation of zirconia at core-veneer interface due to thermal or mechanical stress influences, the occurrence of defects during the different procedures a correct base conception to support the applied ceramics, a suitable handling in the dental laboratory, the deficiency of uniform support of the veneering ceramic due to the shape of the zirconia core, the connector shape and some less frequent biological complications [26]. The bonding mechanism between zirconia and veneering ceramics remains unascertained. There are no clear arguments regarding the existence of chemical bonding between the two materials. The strength of the bonding connection between porcelain and zirconia is lower than that between porcelain and metal [12]. Prosthesis fracture at the connector area is another drawback that studies refer to. For fixed dental prostheses in the posterior region a connector of at least 4mm diameter was recommended. [27].

By modifying the firing procedures, the occurrence of chipping can be effectively decreased [28] and we can make full zirconia fixed dental prosthetics, with no ceramic coating. Such one-material zirconia FDPs necessitate higher translucency with better mechanical properties all the more so when they are to be used in the anterior region [25].

CAD/CAM manufactured monolithic zirconia restorations have a superior translucency hence their increased reputation. As its popularity continues to rise there are some worries regarding the monolithic or full-contour zirconia in dental applications, such as, the matching color to the other teeth, long-term chemical stability, clinical wear behavior, the surface porosity [29].

The one-piece zirconia restorations may be reliable clinical solution especially in the molar areas with big occlusal forces. They exclude the complication of veneering material chipping and offer good biological and mechanical properties [30] and on the other hand in the presence of a reduced prosthetic space seems that the one material restorations have the first clinical option.

Properties of Zirconia

An abundance of raw materials can be found in nature for zirconia fabrication (about 0.02% of the earth crust) such as zircon minerals ($ZrSiO_4$) and baddeleyite (β-ZrO_2). Large deposits of zirconia are present in Brazil as baddeleyte while in Australia and India we may found them as $ZrSiO_4$ [31].

Zirconium is a transition metal element, and it has a pure crystalline form as a white and ductile metal and it has an amorphous form as a blue-black powder. Even it is the 18-th element in earth crust as spreading, zirconium may be found in nature only combined with silicate oxides or as a free oxide. [32]. Zirconia occurs in three phases: monoclinic (m), cubic (c), and tetragonal (t). In pure ZrO_2 the monoclinic phase is stable up to 1170°C; but the transformation on cooling appear 100°C below 1170°C. when it cools down it has a volumetric expansion of 3-4%. The cracks may appear as this volume change is sufficient to exceed the elastic limit of the ZrO_2 [33]. Passerini and Ruff et al., cited by Lughi V., found that zirconia may remain stable at room temperatures by alloying it with other cubic oxides, called stabilizers [31]. Until now the most used stabilizers to apply biomaterials are CaO, MgO, Y_2O_3 and CeO_2, but only ZrO_2-Y_2O_3 has a self ISO standard for surgical use [31].

Biocompatibility

After extensive evaluations of zirconia's biocompatibility no local or systemic cytotoxic effects or adverse reactions have been found. The bone response of zirconia in vivo and the inflammation adjacent to zirconia have been shown to be acceptable. Additionally, bacteria and pathogen seem to adhere to zirconia just as much as other materials do [8].

Optical properties

The most important components of esthetic tooth appearance are: color, fluorescence, opalescence and translucency. One major drawback of full contour zirconia restorations is their opacity [34].

Translucency

Lately, colored zirconia with improved translucency [35-36] has been developed to closely match colors of human teeth. The flexural strength of this new material is 900-1400MPa and has a fracture resistance of up to 6MPam1/2. These conveniences have made it the zirconia used more and more for crowns and bridges in lateral applications [36]. For excellent esthetics, it is important to reproduce the translucency of the natural tooth, as it provides an enchanted natural appearance of the prosthetics. Translucency is the substance property that allows the passage of light and its dispersion, and then the objects will not be seen clearly through the material. This property could be defined as a state between transparency and complete opacity [37]. Translucency can be regulated by controlling the absorption, reflection, and transmission of light through the material. The translucency is higher when the reluctance is low and the transmission is high [38]. In a few studies it has been reported that translucency is affected by the layer's thickness [39] and by the grain size [40].

X-ray opacity

The dental restorative materials have different degrees of opacity which provides helpful information for diagnose. The zirconia can be added in dental filling composite materials because it represents an X-ray opaque agent. In a study conducted in order to assess the X-ray opacity of zirconia, four different materials (pure titanium, NANOZR, Y-TZP, alumina plates) with the same thickness (0,2-2mm) and human tooth were tested against an X-ray agent. It has been found that Y-TZP and NANOZR showed increased opacity [41].

Wear behavior

It is important to assess the wear behavior of monolithic zirconia restorations, but of a bigger clinical importance is the wear of the enamel of natural antagonists teeth opposed to the zirconia material [42].

Progressive wear of teeth is a normal manifestation in the human dentition. Many factors contribute to the dental wear such as food, bruxism, the oral muscles forces, enamel thickness and hardness, pH and nature of the saliva and the dental materials. All these factors have different wear behavior which modify the wear process as well [43]. The physiological wear is altered when we use restorative materials with different wear rates [44].

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A small amount of studies has tried to explain the influence of zirconia ceramic directly on enamel wear. From the in vitro studies we have reached the conclusion that there seems to be an agreement that polished full zirconia crowns have the lowest mean weight loss values of the antagonistic human enamel [45,46,47,48] and this strongly related to its very smooth surface that increases its biologic compatibility and lowers its abrasiveness [10] and results in a decreased level of antagonistic wear than other ceramics [29]. After glazing and polishing and one final glazing zirconia presented important opposing enamel wear, and while the veneering ceramic exhibit even more important wear on the antagonist [47]. However further clinical studies are required to support the results of the in vitro testing.

Low temperature degradation (LTD)

Although zirconia has a lot of advantages as a dental material a process called low temperature degradation (LTD) occurs in vivo.

Studies conducted present LTD as an ageing process of zirconia, referring to the surface degradation with the grain pullout and a subsequently microcracking of the structure mainly due to the presence of water.

Usually, LTD begins at the surface of polycrystalline zirconia and then it will develop within the depth of the material. The transformation of one grain is followed by an expansion in volume and will lead to micro-cracking and modifications to the other grains. This process of surface degradation is emphasized by the penetration of water and this transformation progresses from one grain to the next one. This progression of the conversion zone determines severe micro-cracking, grain pullout and, in the end, surface roughening, which finally determine a lower strength of the entire piece. Any factor like the grain size, the stabilizer quantity or the residual stresses may be disadvantageous to the stability of tetragonal zirconia and a certain degradation degree may occur at low temperatures. [49].

Kobayashi et al. reported that a slow *t→m* transformation from the metastable tetragonal phase to a more stable monoclinic phase can happen when the humidity raises even with low temperatures and leads to potential microcracking and decreasing strength of zirconia [50].

The experimental observations on ageing have been briefed by Yoshimura cited by Lawson [51]. Thus, it seems that the degradation depends on the time and occurs most rapidly at temperatures of 200-300°C. Even it is caused by the tetragonal-monoclinic transformation, the phenomenon it is always accompanied by micro- and macro-cracking. The process develops from the exterior and continues inside the sample. In the presence of water the transformation develops faster. The transformation may be slowed of it is used a lower grain size and a bigger amount of stabilizer.

Another study conducted by Sebastian Wille et al. showed that the same ageing process (LTD) occurs also in shaded zirconia. The coloring method has no significant influence on the phase transformation proportions and the flexural strength during LTD. It was concluded that the ratio of the phase transformation of zirconia due to low temperature depends on the time elapsed [52].

Conclusions

After its discovery as a dental material, zirconia, under various forms, is used worldwide in order to replace metal-ceramic restorations. It is obvious that the usage of ceramic-zirconia versus metal-ceramic restorations it is more suitable due to biocompatibility, the appearance as close as possible to the natural teeth. Monolithic zirconia restorations proved better mechanical properties, but they offer a limited tooth color reproduction, while the final surface state and wear behavior still raise some questions.

It must be considered in future that the perfectibility of technology and materials will follow. This is why further studies and researches are needed to improve wear behavior and optical characteristics of the zirconia prosthetic structures and to minimize the risk of low temperature degradation in vivo.

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Corresponding Authors: Mădălina Grădinaru, Radu Rîcă,
University of Medicine and Pharmacy of Craiova, Faculty of Dentistry,
Petru Rares str., no 2-4, e-mail: olivia.gradinaru7@gmail.com, radu.rica@gmail.com