

Davor Špehar¹, Marko Jakovac²

Nove spoznaje o cirkonij-oksidnoj keramici kao gradivnom materijalu u fiksnoj protetici

New Knowledge about Zirconium-Ceramic as a Structural Material in Fixed Prosthodontics

¹ Privatna ordinacija dentalne medicine, Bjelovar

Private dental practice, Bjelovar

² Zavod za fiksnu protetiku Stomatološkog fakulteta Sveučilišta u Zagrebu

Department of Prosthodontics, School of Dental Medicine University of Zagreb

Sažetak

Dentalna keramika danas je jedan od osnovnih gradivnih materijala u fiksnoj protetici. Naime, povećani estetski zahtjevi potaknuli su nastanak novih keramičkih materijala kako bi se izbjegla upotreba metalnog skeleta te dobio potpuno keramički rad s mehaničkim svojstvima koja dovoljno dobro podnose jače okluzalne sile. Od svih dosadašnjih keramičkih materijala cirkonij-oksidna keramika ima najbolja mehanička svojstva i jedino se njome možemo koristiti za, u rasponu, dulje fiksnoprotetske radove. No unatoč tomu, estetska svojstva nisu zadovoljavala jer nije bilo translucenčnosti. Zbog toga se na cirkonijev dioksid počelo u slojevima nanositi (slojevati) ostale keramike. Nakon što se počeo upotrebljavati u dentalnoj medicini, cirkonijev dioksid smatrao se idealnim materijalom za fiksnu protetiku koji će vrlo brzo zamijeniti metal-keramičke radove. No tijekom kliničke uporabe te u studijama *in vivo* i *in vitro* pokazalo se da i dalje postoji mnogo problema, unatoč poboljšanjima. U ovom preglednom radu željeli smo otkriti nove spoznaje o cirkonij-oksidnoj keramici i tehničkim postupcima koji bi mogli povećati kliničku uspješnost i dugovječnost radova od toga materijala.

Zaprimitljeno: 25 veljače 2015.

Prihvaćen: 22. svibnja 2015.

Adresa za dopisivanje

Doc.dr.sc. Marko Jakovac
Sveučilište u Zagrebu
Stomatološki fakultet
Zavod za fiksnu protetiku
10 000 Zagreb, Gundulićeva 5
Tel: 4802 123
jakovac@sfzg.hr

Ključne riječi

fiksni protetski rad, dentalna keramika, cirkonijev dioksid, dentalna ljuska, translucencija

Uvod

Dentalna keramika jedan je od glavnih gradivnih materijala u modernoj fiksnoj protetici. Kao materijalom u dentalnoj medicini, cirkonijevim dioksidom koristimo se od 1970. godine kada su se istraživale različite površine dentalnih implantata (1). Prvi put upotrijebljen je u fiksnoj protetici kada su male količine aluminijeva oksida (Al_2O_3) u staklom infiltriranoj keramici zamijenjene kristalima cirkonijeva dioksid-a (ZrO_2). Razvoj cirkonijeva dioksida pratio je poslije razvoj i poboljšanje CAD/CAM tehnologije, jer je to bio jedini način za komercijalnu izradu radova u fiksnoj protetici od toga materijala. Da bismo razumjeli vrijednosti cirkonij-oksidne keramike i njezinih mehaničkih svojstava, moramo poznavati razvoj dentalnih keramika općenito.

Većina dentalnih keramika sastoji se od amorfne faze i kristala čija količina i veličina određuju njihova mehanička svojstva. Amorfni dio sastoji se uglavnom od SiO_2 (staklo) i daje keramici prirodan izgled (translucenciju) te osigurava kemijsku vezu s kompozitnim cementom. Glinična keramika, kojom se još i danas vrlo često koristimo, većim se dijelom sastoji od stakla i sadržava malu količinu kristala pa ne

Introduction

Dental ceramics represent one of the major structural materials in modern fixed prosthodontics. As a material in dental medicine, zirconium-dioxide was introduced in the 1970s when different types of coverage for dental implants were investigated (1). The first use of zirconium-dioxide in fixed prosthodontics was when small amounts of aluminum-oxide (Al_2O_3), in glass-infiltrated ceramic (In Ceram, Zahnfabrik Vita, Germany), were replaced by zirconium-dioxide crystals (ZrO_2). Later on, the development of zirconium-dioxide was followed by the development and improvement of CAD/CAM technology, as the only commercial way for making restorations in fixed prosthodontics from this material. To understand the values of zirconium-oxide ceramics and its excellent mechanical properties, the development of dental ceramics in general must be considered.

Most dental ceramics consist of an amorphous part and crystals. The amount and size of crystals determine the mechanical properties. The amorphous part predominantly consists of SiO_2 (glass), which gives ceramics an esthetically pleasant and natural looking appearance (translucency), and

može osigurati dobra mehanička svojstva i funkciju dugovječnost krunica i mostova u stražnjoj regiji. Zato se ta keramika najčešće peče na metalni skelet koji osigurava mehaničku stabilnost, a istodobno je zadržana estetska komponenta. Zahtjevi da protetski radovi izgledaju estetski i prirodnije rezultirali su razvojem novih keramika s povećanom količinom kristala. Takve keramike mogu podnijeti veće žvacne sile te se upotrebljavaju kao samostalni materijal bez metalne konstrukcije. To su staklom infiltrirane keramike koje su uglavnom kristalni sustavi (najčešće aluminijev oksid – Al_2O_3) s dodanim stakлом, te staklokeramike koje su većinom staklo s dodanim kristalima. Međutim, zbog njihovih i dalje ograničenih mehaničkih svojstava mogu se upotrebljavati maksimalno za tročlane mostove u premolarnoj regiji. Zato su proizvedene i polikristalne keramike kao što su aluminij-oksidna i cirkonij-oksidna. Obje se sastoje samo od kristala i nemaju amorfni dio.

Cirkonijev dioksid ima odlična mehanička svojstva jer mu je savojna čvrstoća od 900 do 1200 MP i tvrdoća od 1200 HV (2) (tablica 1.). Te su vrijednosti gotovo istovjetne onima legura za metal-keramičke radove i znatno su veće od vrijednosti svih ostalih keramika kojima se koristimo u dentalnoj medicini. Osim što nema amorfni dio, razlog za tako izvrsna mehanička svojstva jest i svojstvo cirkonijeva dioksida pri stresu kada se pukotina zatvara i zaustavlja. Kod ostalih keramika, ako nastane pukotina u materijalu zbog djelovanja vanjskih sila, ona se ne zaustavlja nego se širi pa materijal s vremenom pukne.

insures chemical bond with resin cements. Basic types of ceramics, such as feldspathic ceramic, predominantly consist of glass, and only have small amounts of crystals, which cannot insure good mechanical properties and functional longevity for crowns and bridges in posterior region. Because of this, these ceramics have been veneered on metal framework, which insures mechanical stability while the esthetics of ceramic remains. Demands for better esthetics and natural looking appearance led to development of new ceramics with increased amount of crystals that could withstand greater forces and can be used as a single material without metal framework. These were glass-infiltrated ceramics, that are crystalline-based systems (mostly alumina, Al_2O_3) with added glass, and glass-ceramics, that are glass-based systems with added crystals. But, due to its limited mechanical properties, they could only be used in up to three-unit bridges in premolar region. Because of this, new polycrystalline ceramics, such as aluminum-oxide and zirconium-oxide ceramics were introduced. These ceramics consist only of crystals and do not have an amorphous part.

Zirconium-dioxide has excellent mechanical properties, with flexural strength of 900-1200 MPa and hardness of 1200 HV (2) (Table 1). These values are almost the same as of metals used for metal-ceramic restorations, and significantly higher than values of all other ceramics used in dentistry. Apart from the absence of an amorphous part, the reason for such good mechanical properties lies in the behavior of the zirconium-dioxide under applied stress. Unlike other ceramics, which develop cracks due to applied loads leading to material fracture, after the crack formation in zirconium ceramics, those cracks are constricted and stopped and do not progress further.

Tablica 1. Mehanička svojstva cirkonijeva dioksida
Table 1 Mechanical properties of zirconium-dioxide

Gustoća • Density	g/cm ³	>6
Poroznost • Porosity	%	<0.1
Savojna čvrstoća • Traction resistance	MPa	900-1200
Tlačna čvrstoća • Compression resistance	MPa	2000
Youngov modul • Young modul	GPa	210
Otpornost na pucanje K_{IC} • Fracture toughness K_{IC}	MPa/m	7-10
Koeficijent toplinskog širenja • High thermal expansion	K^{-1}	11×10^{-6}
Provodljivost topline • Thermal conductivity	Wm/K	2
Tvrdoća • Hardness	HV0.1	1200

Struktura cirkonijeva dioksida

Da bismo shvatili svojstva cirkonijeva dioksida moramo razumjeti njegovu osnovnu strukturu. Cirkonijev dioksid je polikristalni materijal i nalazi se u prirodi kao mineral s monoklinskom kristalnom strukturom. Zagrijavanjem na 1170 °C prelazi u tetragonsku fazu, a nakon 2370 °C u kubnu. Transformacije između kristalnih faza reverzibilne su, pa hlađenje uzrokuje povratak u monoklinsku fazu. Pri promjeni faza mijenja se i volumen kristalnih zrna i upravo ta promjena bitna je za shvaćanje mehaničkih svojstava cirkonij-dioksidne keramike. Za korištenje u dentalnoj medicini taj se ma-

Structure of zirconium-dioxide

To understand excellent mechanical properties of zirconium-dioxide the basic structure must be understood. Zirconium-dioxide is a polycrystalline material that can be found in nature in mineral that has monoclinic crystalline structure. By heating it up to 1170°C, zirconium-dioxide transforms into tetragonal phase; and by heating it up to 2370°C it transforms into the cubic phase. This transformation between crystalline phases is reversible and cooling causes the return into monoclinic phase. With the phase transformation, the volume of crystalline grains is changed, and exactly

terijal zagrijava do tetragonske faze i stabilizira dodavanjem tri do pet posto Y_2O_3 . Te male količine itrijeva oksida sprječavaju prijelaz tetragonske u monoklinsku fazu ispod 1170 °C i omogućuju tetragonsku fazu na sobnoj temperaturi. Ta faza samo je djelomično stabilizirana i, zbog djelovanja stresa na površinu, može se transformirati u monoklinsku. Zbog toga se taj materijal zove *cirkonij-dioksid djelomično stabiliziran itrijem* (Y-PSZ) (3,4). Stabilnost faze i mehanička svojstva ovise o veličini kristalnih zrna. Ako su prevelika materijal je nestabilan i nastaje spontana preobrazba u monoklinsku fazu, a ako su premala sprječavaju transformaciju i tako smanjuju lomnu čvrstoću (5). Kako je već spomenuto, stres koji djeluje na površinu keramike uzrokuje pukotinu, a posljedica je lom materijala. Kada se pojavi pukotina u cirkonij-oksidnoj keramici oko nje nastaje transformacija tetragonske u monoklinsku fazu s povećanjem volumena kristalnih zrna za otprilike 4,5 posto. Upravo to povećanje volumena uzrokuje zatvaranje pukotine i jačanje materijala (6 – 8) (slika 1.).

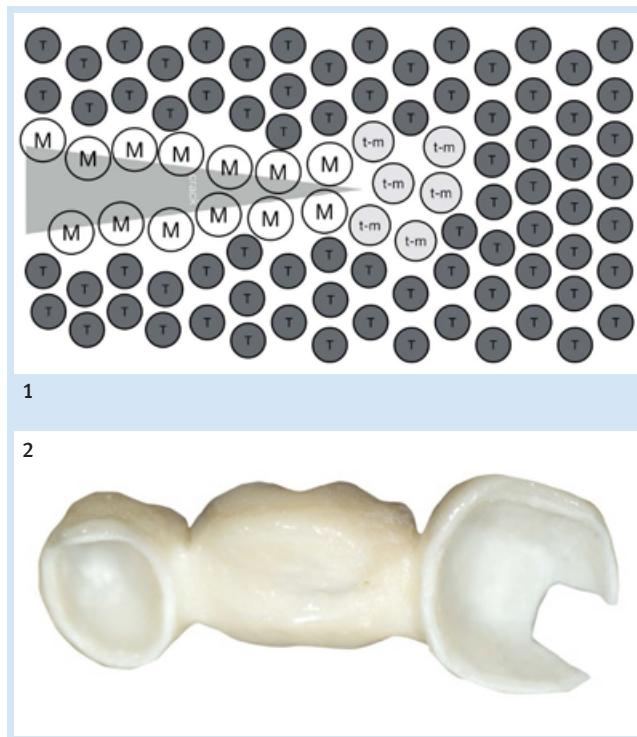
Nakon što se počela upotrebljavati u medicini zbog izvrsne biokompatibilnosti i bijele boje, cirkonij-oksidna keramika smatrala se idealnim materijalom za kliničku upotrebu (umjetni kukovi). No poslije početnog oduševljenja pojavili su se problemi jer su kukovi neobjašnjivo pucali (9, 10). Otkriveno je da je sterilizacija uzrokovala *starenje* materijala i spontani prijelaz iz tetragonske u monoklinsku fazu, što je oslabjelo materijal i prouzročilo pucanje. Na *starenje* cirkonij-dioksa zajedno utječu koncentracija i distribucija itrijeva oksida, veličina zrna, broj pukotina prije kliničke upotrebe, način proizvodnje i završna obrada (7, 11).

Završna obrada u dentalnom laboratoriju ili ordinaciji te kvaliteta materijala najviše pridonose funkcionalnoj trajnosti cirkonijeve keramike. Zato što nije translucentan, cirkonij-dioksid nije bio korišten kao samostalni materijal za dentalne radove nego je zahtijevao slojevanje gliničnom keramikom ili staklokeramikom. Za upotrebu u fiksnoj protetici cirkonij-oksidna keramika proizvodi se individualno ili se nabavlja kao gotov tvornički proizvod poput kolčića za nadogradnje ili suprastruktura za implantate. Ako se proizvodi individualno, cirkonij-dioksid upotrebljavamo za krunice, mostove i suprastrukturu na Zubima i implantatima, a dobiva se tehnologijom CAD/CAM. Većina cirkonij-oksidsnih keramika danas se gloda u predsinteriranoj fazi zato što je materijal mekan i ima konzistenciju krede, što olakšava proizvodnju jer dopušta lagano glodanje bez brzog trošenja svrdala i mogućeg oštećenja materijala. Ako se pri gladanju koristi sinterirani cirkonij-dioksid, mehanička svojstva završnog rada niža su od deklariranih (12 – 14). Taj fenomen nastaje zbog površinskih mikropukotina i pukotina koje se pojavljuju poslije takvih tretmana (15). Predsinterirani radovi otprilike su 30 posto veći jer sinteriranje smanjuje volumen i postizanje jednolične tetragonske strukture bez pukotina. Oprez je potreban ako se završna restauracija mora dodatno prilagoditi. Naime, tada se mogu stvoriti nove pukotine i transformacije zbog zatvaranja pukotina, pa dobivamo rad s lošijim mehaničkim svojstvima. To je važno jer, unatoč činjenici da transformacija oko pukotine ojačava materijal, taj se fenomen može dogoditi samo jedanput. Ako se dogodi očvrsnuće prije stavljanja rada u usta, cirkonijev dioksid više se ne mo-

this volume change was used for getting excellent mechanical properties. To get the stable material that can be used in dentistry, and medicine in general, the zirconium-dioxide is stabilized by adding 3-5% Y_2O_3 in tetragonal phase. These small amounts of Y_2O_3 inhibit tetragonal to monoclinic transformation below 1170° allowing the presence of tetragonal phase at the room temperature. This tetragonal phase is only partially stabilized, and under stress applied to the surface can transform into monocline phase. That is why this material is called yttrium-partially-stabilized zirconium-dioxide (Y-PSZ) (3, 4). The zirconium-dioxide is stabilized in tetragonal phase, because in the tetragonal phase the material is white in color and has excellent mechanical properties. The phase stability and mechanical properties depends on crystalline grain size. Crystals which are too large cause unstable material and spontaneous transformation into monoclinic phase, whereas crystals which are too small inhibit transformation, leading to reduced fracture toughness (5). As mentioned, stress applied to the surface of ceramic causes crack formation leading to the fracture of the material. Unlike other ceramic systems, when cracks initiate in the zirconium-ceramic phase the transformation from tetragonal to monocline which occurs around the crack with the volume increase of crystalline grains of approximately 4.5%. This volume increase causes constriction of crack and hardening of the material (6-8) (Figure 1).

When introduced in medicine, zirconium-ceramic, with its excellent biocompatibility and white color was considered an ideal material for clinical practice (hip replacement). However, after the promising start, problems arose and hips started to fracture unexplainably (9, 10). It was discovered that sterilization causes "aging" of material and spontaneous transformation from tetragonal to monoclinic phase, which weakens the material and causes fracture under very small loads. Concentration and distribution of yttrium-oxide, grain size, the amount of cracks present before clinical use, manufacturing process and finishing procedures all affect aging of zirconium-dioxide (7, 11).

The final production in dental laboratory or dental office, and the quality of material contributes the most to the functional longevity of zirconium-ceramic in the mouth. Due to absence of translucency, zirconium-dioxide cannot be used as a single material for dental restorations and needs veneering with feldspathic or glass-ceramic. For the use in fixed prosthodontics, zirconium-ceramic is manufactured individually or comes as industrially made final products such as posts or implant abutments. If custom made, zirconium-dioxide is used for crowns, bridges and supra-structures on teeth and implants, and manufactured using CAD/CAM technology. Today, most zirconium-ceramics are milled in pre-sintered phase, because the material is very soft, of chalk consistency, which simplifies the production, allowing easy milling without excessive wear of the burs and possible damage of the material. Apart from this, if sintered, zirconium-dioxide is produced using CAD/CAM technology, the mechanical properties of final restorations are poorer than the declared ones (12-14). This phenomenon occurs due to surface microcracks and fractures that appear after such treatment (15).



1

2



3

**Slika 1.** Fazna transformacija oko pukotine**Figure 1** Phase transformation around crack**Slika 2.** Puknuće cirkonij-oksidnoga skeleta zbog loše manipulacije**Figure 2** Zirconium framework fracture caused by inappropriate laboratory treatment**Slika 3.** HT cirkonij-dioksid (Zenostar Zr Translucent Pure, Wieland Dental, Njemačka)**Figure 3** HT zirconium-dioxide (Zenostar Zr Translucent Pure, Wieland Dental, Germany)

že transformirati i nastaju nove pukotine, što rezultira pučanjem cijelog rada (slika 2.). Zbog toga se cirkonij-dioksid obrađuje drukčije negoli metal – vodenim hlađenjem i specijalnim svrdlima. Pjeskarenje s Al_2O_3 pod velikim pritiskom i upotrebu prevelikih čestica treba izbjegavati jer također mogu potaknuti površinsku fazu transformacije (16).

The pre-sintered restorations are approximately 30% bigger, because sinterization causes volume shrinkage, and achieves equal tetragonal structure without cracks. Caution is required if the final sintered restoration needs to be adjusted to avoid crack formation before placing the restoration into the mouth, and transformation into monoclinic phase which could decrease its mechanical properties and cause fracture. This is important, because despite the fact that this phase transformation around the crack causes strengthening of the material, this phenomenon can occur only once. If it occurs before placing the restoration in the mouth, the zirconium-dioxide does not have ability for new transformation, and if new crack appears under occlusal loads the fracture could not be stopped any more and would lead to the fracture of the material (Figure 2). Consequently, zirconium-dioxide is treated differently than metal, using water-cooling and special burs. Sandblasting with Al_2O_3 under high pressure and using particles which are too large should be avoided, because it can also induce surface phase transformation (16).

Površinska otkrhnuća (*chipping*)

Osnovni problem u kliničkoj praksi jest otkrhnuće vanjske keramike ili *chipping*. Općenito gledano, takvo oštećenje može biti malo i veliko. Ako je malo ne utječe na estetiku i funkciju rada i u većini slučajeva zahtijeva samo poliranje ili popravak kompozitom, a velika otkrhnuća stvaraju lomove s izloženim cirkonijevim skeletom. Zaostatni stres u obloženoj keramici može se smatrati najvažnijim čimbenikom u nastanku otkrhnuća, ali stvarni uzrok toga stresa još uvejk je nepoznat. Zaostatni stres može biti tlačni i vlačni. Tlačni poboljšava mehanička svojstva materijala, a vlačni uzrokuje njezino pučanje (17, 18). Termička svojstva cirkonij-oksidnog skeleta i obložne keramike te svojstva samoga spoja između

Chipping problems

The main problem of zirconium-dioxide restorations in clinical practice has become fracture of veneering ceramic or chipping. In general, chipping can be classified as minor and major chipping. Minor chipping does not compromise esthetics and function of the restoration, and in most cases requires only polishing or composite repair, while major chipping implies bigger fractures with zirconium framework exposed. The residual stresses in the veneer ceramic can be considered the most important factor in the chipping phenomenon, but the exact origin of these stresses is still unknown. Residual stresses can be compressive and tensile. Compressive stresses improve mechanical properties of

cirkonij-oksida i spomenute keramike, smatraju se najvažnijim čimbenicima koji utječu na nakupljanje zaostatnog stresa u obložnoj keramici.

Cirkonij-dioksid i keramike kojima se koristimo za slojevanje imaju drukčiji koeficijent termičke ekspanzije (CTE). Ta razlika u CTE-u slična je kao kod metal-keramičkih radova i stvorena je namjerno da bi se postigla otprilike jednaka mehanička svojstva. Unatoč tomu laboratorijski rezultati pokazuju vlačni stres u dubokim slojevima vanjske keramike, za razliku od metal-keramičkih radova kod kojih je zabilježen samo tlačni stres (19 – 22). Osim toga, cirkonij-dioksid provodi toplinu sporije nego vanjska keramika (23, 24). Kao rezultat toga, hlađenje i grijanje tijekom slojevanja mogu dodatno utjecati na različitosti u termičkim svojstvima između ta dva materijala i povećati zaostatni stres u vanjskoj keramici. Testovi *in vitro* pokazali su da radovi su otporniji na pucanje ako je usporeno zagrijavanje i hlađenje tijekom pečenja vanjske keramike (24, 25). S druge strane, pak, posljednja istraživanja distribucije stresa unutar vanjske keramike upotrebom FIB nanotomografije, pokazala su prisutnost vlačnoga stresa u dubokim slojevima vanjske keramike izložene usporenom hlađenju (18). Znajući da vlačni stres potiče pucanje materijala, ova istraživanja oprečna su ranijim rezultatima *in vitro* (24, 25). Kako je već spomenuto, različite obrade površine cirkonijeva skeleta mogu uzrokovati promjene faze i veličine površinskih kristala. Osim što smanjuje mehanička svojstva, ta transformacija uzrokuje nakupljanje stresa unutar površine skeleta pa naknadno može rezultirati zaostatnim stresom u vanjskoj keramici (26). Uz to, monoklinski cirkonij-dioksid ima znatno manji CTE, što dodatno utječe na nakupljanje stresa u tim područjima (27). Osim što štiti od površinskih promjena, dobra veza između skeleta i obložne keramike osigurava homogenost strukture i distribuciju stresa od skeleta na spojni sloj i završno na obložnu keramiku. Ako je taj spoj oštećen različitim površinskim promjenama, stres se prenosi izravno na vanjski sloj i povećava se katkad i do 12 puta negoli kod homogenog spoja (28).

Ponavljanja okluzalna opterećenja tijekom funkcije na obložni sloj, s nakupljanjem zaostatnoga vlačnoga stresa, može rezultirati nastankom pukotine i lomom vanjskog sloja. Da bi se riješio taj problem, predložene su nove keramike za slojevanje i tehnike slojevanja. Umjesto slojevanja samo gliničnom keramikom, cirkonij-oksidni skelet slojevao se staklokeramikom. Osim toga, ispitana je tehnika prešanja kod koje se cijeli obložni sloj staklokeramike u komadu preša na cirkonij-oksidni skelet. Ta keramika industrijski je pripremljena i postojane je kvalitete. Tako su isključene moguće pogreške tijekom pripreme i slojevanja koje mogu uzrokovati pukotine i artefakte koji naknadno uzrokuju pucanje obložnog sloja (29). Osim toga, modifikacija cirkonij-oksidnog skeleta prema anatomskom obliku dovodi do različite debljine čvrstog skeleta i jednakе debljine vanjske keramike. Kako cirkonij-oksidni skelet ima sjajna mehanička svojstva, različita debljina neće na njih znatno utjecati, nego će osigurati jedinstvenu potporu za slabiju vanjsku keramiku i bolje kliničke rezultate s manje otkrnuća (30).

Svi ti čimbenici moraju se uzeti u obzir ako se želi smanjiti neuspjeh kod cirkonij-dioksidnih radova. Štoviše, najno-

material, while tensile stresses cause material fracture (17, 18). Thermal characteristics of zirconium framework and veneering ceramic and zirconium/veneer interface characteristics are considered the most important factors that influence generating of residual stresses in the veneer ceramic.

Zirconium-dioxide and ceramics used for veneering have different coefficient of thermal expansion (CTE). This mismatch in CTE is similar to metal-ceramic restorations, and was designed on purpose in order to achieve the similar mechanical properties. Despite that, laboratory results showed the presence of tensile stresses in the deep layers of veneer ceramic, unlike metal-ceramic restorations where only compressive stresses were recorded (19-22). Apart from this, zirconium-dioxide conducts heat slower than veneering ceramic (23, 24). As a result, heating and cooling processes during veneer firing can additionally influence thermal characteristic differences between these two materials and increase residual stresses within veneer ceramic. *In vitro* tests showed that when slow heating and cooling during firing of the veneer ceramic were applied, the restorations achieved better fracture resistance (24, 25). On the other hand, latest observations of stress distribution within veneer ceramic using focus ion beam nanotomography (FIB-nt), showed the presence of tensile stress in the deep layers of veneer ceramic submitted to slow cooling (18). Knowing the fact that tensile stresses lead to material fracture, these findings are contrary to previous *in vitro* results (24, 25). Apart from thermal characteristics, the interface between framework and veneering ceramic can also induce the presence of residual stresses. As mentioned, different surface treatments on zirconium framework can cause the change of phase and size of surface crystals. Apart from decreasing of mechanical properties, this transformation causes generation of stresses within framework surface that could secondly cause development of residual stresses in the veneer ceramic (26). Apart from this, monoclinic zirconium-dioxide has much lower CTE, which further influences the generating of stresses in these areas (27). In addition to surface changes, a good bond between framework and veneer insures homogenous structure and stress distribution from framework to the bond layer and finally to the veneer. If this bond is affected by different surface changes the stress is distributed directly to the veneer, causing increased stress, which can be up to 12 times bigger than in homogenous interface (28).

Repeated occlusal loads on the veneer during function, with generated residual tensile stresses, can lead to crack formation and veneer fracture. To try to overcome this problem, new veneering ceramics and techniques have been proposed. Instead of veneering only with weak feldspathic ceramic, zirconium framework is veneered with glass-ceramic. Apart from this, the over-pressing technique has been introduced, where the whole veneer is over-pressed to the zirconium framework at once. This ceramics is industrially prepared, has always the same quality and the possible procedure mistakes during layering that can lead to potential flaws and artefacts which could then lead to veneer fracture are excluded (29). Apart from veneering ceramics and application technique, anatomically designed framework and veneer/frame-

vije tehnike omogućuju proizvodnju cijeloglo obložnog sloja od litij-disilikatne staklokeramike tehnikom CAD/CAM koji se tada cementiranjem spaja na cirkonij-oksidni skelet. Te restauracije imaju još bolja mehanička svojstva u odnosu prema onima od cirkonijeva oksida koje su slojevane ili na koje je prešan vanjski sloj (31, 32). Najnovije dostignuće u proizvodnji cirkonijeva dioksida jest transparentni (HT) cirkonij-dioksid koji omogućuje izradu potpuno oblikovanih monolitnih restauracija bez vanjskog slojevanja i bez opasnosti od otkrhnuća (slika 3.). Te se restauracije trebaju samo obojiti kako bi se postigla veća prirodnost. No razvoj HT cirkonij-dioksida još uvijek nije napredovao dovoljno da bi se postigla savršena estetika te su zato njegove indikacije još uvijek u stražnjoj regiji, a za prednje zube koristimo se slojevanom cirkonij-oksidnom keramikom.

work thickness ratio, with lower ratio, also contribute to better clinical performance of zirconium-ceramic restorations and decreased chipping. Modification of zirconium framework design to anatomical shape leads to uneven thickness of strong framework and equal veneer thickness. Since the zirconium framework has excellent mechanical characteristics, they would not be greatly influenced by uneven thickness, but would insure uniform support for weak veneer ceramic and better clinical performance (30).

All these factors must be taken into account to minimize the failures of these restorations. Moreover, the newest techniques include CAD/CAM production of whole veneer from lithium-disilicate ceramics, which is then joined with zirconium framework. These restorations show much better mechanical properties compared to layered or over-pressed zirconium restorations (31, 32). The latest development in production of zirconium-dioxide is high-translucency (HT) zirconium-dioxide, which allows production of full-contoured monolithic restorations without need for veneer and risk of chipping (Figure 3). These restorations are stained to get better esthetics, but the development of HT zirconium still has not progressed sufficiently to achieve excellent esthetics, and therefore its indications are still in the posterior region, whereas for the anterior teeth the veneered zirconium-ceramic is used.

Kliničke studije

Kliničke studije o pouzdanosti i trajnosti cirkonij-oksidnih keramičkih radova podudaraju se sa studijama *in vitro* (33 – 48). Lom vanjske keramike glavna je komplikacija, ali učestalost velikih i malih otkrhnuća teško je točno odrediti jer ne postoji standardizirana kategorizacija. S druge strane, cirkonij-oksidni skelet vrlo rijetko pukne. Anatomski oblik cirkonijeva skeleta smanjuje mogućnost otkrhnuća i osigurava bolja klinička svojstva (36, 38 – 40). Različite tehnike slojevanja također utječu na pouzdanost takvih restauracija, a veliko poboljšanje postiglo se kad se obložna keramika počela prešati na anatomski oblikovani cirkonij-oksidni skelet (38). Unatoč problemima, postotak uspješnosti cirkonij-oksidnih keramičkih radova vrlo je visok jer je većina zabilježenih puknuća vanjske keramike mala i jednostavno se popravljuju u ustima. Pritom se ne kompromitira ni estetika ni funkcija.

Clinical studies

Clinical studies regarding reliability and longevity of zirconium-ceramic restorations are in the correlation with the *in vitro* studies (33-48). Fracture of the veneer ceramic is the main complication, but the incidence of major and minor chipping is hard to strictly determine since there is no standardized fracture categorization. On the other hand, zirconium framework fracture occurs very rare. Anatomical design of zirconium framework decreases the possibility of chipping and leads to better clinical performance (36, 38-40). Different veneering techniques also affect the reliability of zirconium restorations, with the greatest improvements when veneer ceramic was over-pressed to the anatomically designed zirconium framework (38). Nevertheless, the survival rate of zirconium-ceramic restorations is very high, because most of the reported veneer fractures are minor ones, and are easy to repair in the mouth without compromising the esthetics and function.

Conclusion

After great expectations from zirconium-ceramics, the clinical use has shown imperfections of this material. There is still no standardized technical procedure in manufacturing of fixed restorations, which leads to great discrepancies in reliability of zirconium-ceramics. From its introduction, it has undergone many improvements, but further enhancements are needed for it to become the gold standard in dental medicine.

Zaključak

Nakon velikoga uzbudjenja i očekivanja od cirkonij-oksidne keramike, klinička upotreba pokazala je nesavršenosti toga materijala. Još uvijek nema standardizirane tehnike proizvodnje fiksno-protetskih radova, pa je pouzdanost cirkonij-oksidne keramike različita. Otkako se počeo proizvoditi, cirkonijev oksid znatno je poboljšan, što je bilo nužno da bi taj materijal postao *zlatni standard* u dentalnoj medicini.

Abstract

Dental ceramics represents a major structural material in fixed prosthodontics. Increasing demands for esthetics led to development of new ceramic materials in order to eliminate the use of metal framework and for all ceramic restorations with mechanical properties to withstand high occlusal forces. Out of all the present ceramic materials, zirconium-ceramic has the best mechanical properties, and is the only material that can be used for longer span fixed dental restorations. Despite its excellent mechanical properties, to achieve great esthetics, due to absence of translucency, zirconium-dioxide cannot be used as a single material and needs veneering with more esthetic ceramic. When introduced in dental medicine, it was considered an almost ideal material for fixed prosthodontics, but clinical use and *in vivo* and *in vitro* studies showed many problems which still persist despite the improvements. This review aims to reveal new developments in zirconium-ceramics and technical procedures which could increase clinical performance and longevity of these restorations.

Received: February 25, 2015

Accepted: May 22, 2015

Address for correspondence

Marko Jakovac DMD, PhD
University of Zagreb
School of Dental Medicine
Department of Prosthodontics
Gundulićeva 5, 10 000 Zagreb
Tel:+ 385 1 4802 123
jakovac@sfzg.hr

Key words

Denture, Partial, Fixed; Dental Porcelain; zirconium oxide; Dental Veneers; translucency

References

1. Cranin AN, Schnitman PA, Rabkin SM, Onesto EJ. Alumina and zirconia coated vitalium oral endosteal implants in beagles. *J Biomed Mater Res.* 1975 Jul;9(4):257-62.
2. ISO TC 150/SC 1. Implants for surgery-ceramic materials based on yttria-stabilized tetragonal zirconia (Y-TZP). ISO/DIS 13356, 1995.
3. Rieth PH, Reed JS, Naumann AW. Fabrication and flexural strength of ultra-fine grained yttria-stabilised zirconia. *Bull Am Ceram Soc.* 1976;55:717.
4. Gupta TK, Bechtold JH, Kuznickie RC, Cadoff LH, Rossing BR. Stabilization of tetragonal phase in polycrystalline zirconia. *J Mater Sci.* 1978;13:1464-66.
5. Denry I, Kelly JR. State of the art of zirconia for dental applications. *Dent Mater.* 2008 Mar;24(3):299-307.
6. Garvie RC, Hannink RH, Pascoe RT. Ceramic steel?. *Nature.* 1975;258:703-4.
7. Piconi C, Maccauro G. Zirconia as a ceramic biomaterial. *Biomaterials.* 1999 Jan;20(1):1-25.
8. Kelly JR, Denry I. Stabilized zirconia as a structural ceramic: an overview. *Dent Mater.* 2008 Mar;24(3):289-98.
9. Maccauro G, Piconi C, Burger W, Pilloni L, De Santis E, Muratori F, et al. Fracture of a Y-TZP ceramic femoral head, analysis of a fault. *J Bone Joint Surg Br.* 2004 Nov;86(8):1192-6.
10. Piconi C, Maccauro G, Pilloni L, Burger W, Muratori F, Richter H G. On the fracture of a zirconia ball head. *J Mater Sci Mater Med.* 2006 Mar;17(3):289-300.
11. Kosmač T, Kocjan A. Aging of dental zirconia ceramics. *J Eur Ceram Soc.* 2012;32(11):2613-2622.
12. Jakovac M. Utjecaj toplinske obrade na mikrostruktturne promjene i ostala svojstva cirkonijeve keramike [dissertation]. Zagreb:Stomatološki fakultet; 2008.
13. Luthardt RG, Rieger W, Musil R. Grinding of zirconia-TZP in dentistry-CAD/CAM-technology for the manufacturing of fixed dentures. In: Sedel, L; Rey, C - editors. 10th International Symposium on Ceramics in Medicine Bioceramics 10, Paris: Elsevier; 1997. p. 437-40.
14. Luthardt RG, Sandkuhl O, Reitz B. Zirconia-TZP and alumina-advanced technologies for the manufacturing of single crowns. *Eur J Prosthodont Rest Dent.* 1999;7:113-9.
15. Luthardt RG, Holzhüter MS, Rudolph H, Herold V, Walter MH. CAD/CAM-machining effects on Y-TZP zirconia. *Eur J Prosthodont Restor Dent.* 1999 Dec;7(4):113-9.
16. Turp V, Sen D, Tunceli B, Goller G, Özcan M. Evaluation of air-particle abrasion of Y-TZP with different particles using microstructure analysis. *Aust Dent J.* 2013 Jun;58(2):183-91.
17. Baldassarri M, Stappert CJF, Wolff MS, Thompson VP, Zhang Y. Residual stresses in porcelain-veneered zirconia prostheses. *Dent Mater.* 2012 Aug;28(8):873-9.
18. Mainjot AK, Douillard T, Gremillard L, Sadoun MJ, Chevalier J. 3D-characterization of the veneer-zirconia interface using FIB nanotomography. *Dent Mater.* 2013 Feb;29(2):157-65.
19. Mainjot AK, Schajer GS, Vanheusden AJ, Sadoun MJ. Residual stress measurement in veneering ceramic by hole-drilling. *Dent Mater.* 2011 May;27(5):439-44.
20. Mainjot AK, Schajer GS, Vanheusden AJ, Sadoun MJ. Influence of cooling rate on residual stress profile in veneering ceramic: measurement by hole-drilling. *Dent Mater.* 2011 Sep;27(9):906-14.
21. Mainjot AK, Schajer GS, Vanheusden AJ, Sadoun MJ. Influence of zirconia framework thickness on residual stress profile in veneering ceramic: measurement by hole-drilling. *Dent Mater.* 2012 Apr;28(4):378-84.
22. Mainjot AK, Schajer GS, Vanheusden AJ, Sadoun MJ. Influence of veneer thickness on residual stress profile in veneering ceramic: measurement by hole-drilling. *Dent Mater.* 2012 Feb;28(2):160-7.
23. Swain MV, Johnson L, Syed R, Hasselman D. Thermal diffusivity, heat capacity and thermal conductivity of porous partially stabilized zirconia. *J Mat.* 1986;5(8): 799-802.
24. Tan JP, Sederstrom D, Polansky JR, McLaren EA, White SN. The use of slow heating and slow cooling regimens to strengthen porcelain fused to zirconia. *J Prosthet Dent.* 2012 Mar;107(3):163-9.
25. Rues S, Kröger E, Müller D, Schmitter M. Effect of firing protocols on cohesive failure of all-ceramic crowns. *J Prosthet Dent.* 2012 Mar;107(3):163-9.
26. Lughí V, Sergio V. Low temperature degradation -aging- of zirconia: A critical review of the relevant aspects in dentistry. *Dent Mater.* 2010 Aug;26(8):807-20.
27. Stawarczyk B, Ozcan M, Roos M, Trottmann A, Sailer I, Hämmele CHF. Load-bearing capacity and failure types of anterior zirconia crowns veneered with overpressing and layering techniques. *Dent Mater.* 2011 Oct;27(10):1045-53.
28. Rocha EP, Anchieta RB, Freitas AC, de Almeida EO, Cattaneo PM, Chang Ko C. Mechanical behavior of ceramic veneer in zirconia-based restorations: a 3- dimensional finite element analysis using microcomputed tomography data. *J Prosthet Dent.* 2011 Jan;105(1):14-20.
29. Baldassarri M, Zhang Y, Thompson VP, Rekow ED, Stappert CJF. Reliability and failure modes of implant-supported zirconium-oxide fixed dental prostheses related to veneering techniques. *J Dent.* 2011 Jul;39(7):489-98.
30. Guess PC, Bonfante EA, Silva NRFA, Coelho PG, Thompson VP. Effect of core design and veneering technique on damage and reliability of Y-TZP-supported crowns. *Dent Mater.* 2013 Mar;29(3):307-16.
31. Beuer F, Schweiger J, Eichberger M, Kappert HF, Gernet W, Edelhoff, D. High-strength CAD/CAM-fabricated veneering material sintered to zirconia copings--a new fabrication mode for all-ceramic restorations. *Dent Mater.* 2009 Jan;25(1):121-8.
32. Schmitter M, Mueller D, Rues S. Chipping behaviour of all-ceramic crowns with zirconia framework and CAD/CAM manufactured veneer. *J Dent.* 2012 Feb;40(2):154-62.
33. Raigrodski AJ, Chiche GJ, Potiket N, Hochstedler JL, Mohamed SE, Billiot S, et al. The efficacy of posterior three-unit zirconium-oxide-based ceramic fixed partial dental prostheses: a prospective clinical pilot study. *J Prosthet Dent.* 2006 Oct;96(4):237-44.
34. Sailer I, Fehér A, Filser F, Gauckler LJ, Lüthy H, Hämmeler CH. Five-year clinical results of zirconia frameworks for posterior fixed partial dentures. *Int J Prosthodont.* 2007 Jul-Aug;20(4):383-8.
35. Edelhoff D, Beuer F, Weber F, Johnen C. HIP zirconia fixed partial dentures--clinical results after 3 years of clinical service. *Quintessence Int.* 2008 Jun;39(6):459-71.
36. Molin MK, Karlsson SL. Five-year clinical prospective evaluation of zirconia-based Denzir 3-unit FPDs. *Int J Prosthodont.* 2008 May-Jun;21(3):223-7.

37. Tinschert J, Schulze KA, Natt G, Latzke P, Heussen N, Spiekermann H. Clinical behavior of zirconia-based fixed partial dentures made of DC-Zirkon: 3-year results. *Int J Prosthodont.* 2008 May-Jun;21(3):217-22.
38. Beuer F, Edelhoff D, Gernet W, Sorensen JA. Three-year clinical prospective evaluation of zirconia-based posterior fixed dental prostheses (FDPs). *Clin Oral Investig.* 2009 Dec;13(4):445-51.
39. Sailer I, Gottnerb J, Kanelb S, Hammerle CH. Randomized controlled clinical trial of zirconia-ceramic and metal-ceramic posterior fixed dental prostheses: A 3-year follow-up. *Int J Prosthodont.* 2009 Nov-Dec;22(6):553-60.
40. Schmitt J, Holst S, Wichmann M, Reich, S, Gollner M, Hamel J. Zirconia posterior fixed partial dentures: a prospective clinical 3-year follow-up. *Int J Prosthodont.* 2009 Nov-Dec;22(6):597-603.
41. Schmitter M, Mussotter K, Rammelsberg P, Stober T, Ohlmann B, Gabbert O. Clinical performance of extended zirconia frameworks for fixed dental prostheses: two-year results. *J Oral Rehabil.* 2009;36:610-5.
42. Wolfart S, Harder S, Eschbach S, Lehmann F, Kern M. Four-year clinical results of fixed dental prostheses with zirconia substructures (Cercon): end abutments vs. cantilever design. *Eur J Oral Sci.* 2009 Dec;117(6):741-9.
43. Beuer F, Stimmelmayr M, Gernet W, Edelhoff D, Guth J, Naumann M. Prospective study of zirconia-based restorations: 3-year clinical results. *Quintessence Int.* 2010 Sep;41(8):631-7.
44. Roediger M, Gersdorff N, Huels A, Rinke S. Prospective evaluation of zirconia posterior fixed partial dentures: four-year clinical results. *Int J Prosthodont.* 2010 Mar-Apr;23(2):141-8.
45. Christensen RP, Ploeger, BJ. A clinical comparison of zirconia, metal and alumina fixed-prosthesis frameworks veneered with layered or pressed ceramic: a three-year report. *J Am Dent Assoc.* 2010 Nov;141(11):1317-29.
46. Peláez J, Cogolludo P, Serrano B, Lozano JFL, Suárez MJ. A prospective evaluation of zirconia posterior fixed dental prostheses: Three-year clinical results. *J Prosthet Dent.* 2012 Jun;107(6):373-9.
47. Raigrodski AJ, Yu A, Chiche GJ, Hochstedler JL, Mancl LA, Mohamed SE. Clinical efficacy of veneered zirconium dioxide-based posterior partial fixed dental prostheses: five-years results. *J Prosthet Dent.* 2012 Jun;107(6):373-9.
48. Rinke S, Gersdorff N, Lange K, Roediger M. Prospective evaluation of zirconia posterior fixed partial dentures: 7-year clinical results. *Int J Prosthodont.* 2013 Mar-Apr;26(2):164-71.