The Effect of Aging on Composition and Surface of Translucent Zirconia Ceramic

Utjecaj starenja na sastav i površinu translucentne cirkonij-oksidne keramike

Introduction

For several years, zirconia based ceramics has been the material of choice in the fabrication of fixed partial dentures (FPD), especially for the more strain-prone posterior region of dental arch, because of its good mechanical properties (flexural strength 900-1,200 MPa, hardness HV0.1 1200) (1). Due to insufficient translucency, it has been shown that it is not able to meet high esthetic criteria for usage in the restoration of the anterior part of dental arch (2). For that reason, it has been veneered with ceramic materials that have better optical properties (glass and feldspathic ceramics) (1-3).

Two problems have arisen in the clinical application of this material. One problem is common to all bilayer systems and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material of choice in the fabrication of fixed partial dentures. This material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material is caused by a discord in the thermal expansion coefficient between the veneering material and the core material. One problem is common to all bilayer systems and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material. One problem is common to all bilayer systems and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material. One problem is common to all bilayer systems and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core material and is caused by a discord in the thermal expansion coefficient between the veneering material and the core materia-
Aging Effect on ZrO₂ Ceramic

Belgrade, Serbia

Abstract

The aim of this research was to investigate how aging protocols affect the chemical composition (in particular, the share of stabilizing yttrium oxide), phase composition and the manifestation of tetragonal-to-monoclinic transformation as well as surface state (as conveyed by surface gloss and surface roughness) of zirconia ceramics. The following hypotheses were tested: the new generation of zirconia ceramics contains a share of yttrium oxide and increases the share of transformation-resistant crystals in the monoclinic phase, which may result in the enhancement of optical properties and improve the material's mechanical and esthetic properties. Improving the esthetic quality of zirconia ceramics could be achieved by increasing the share of transformation-resistant cubic crystalline structure.

Keywords:
- Zirconia ceramics
- Aging
- Chemical composition
- Phase composition
- Surface state

Introduction

The importance of surface state and microstructure of zirconia materials while maintaining their good properties. Through multi-parameter experimental protocols, they have endeavored to examine the long-term behavior of materials in the oral cavity as realistically as possible by analyzing both mechanical and esthetic properties. Improving the esthetic quality of these materials extends their application to the anterior region of dental arch. The most recent research studies indicate that optical properties of zirconia ceramics could be improved by increasing the share of transformation-resistant cubic crystalline structure.

The following hypotheses were tested: the new generation of zirconia ceramics contains a share of yttrium oxide that correlates with structural stability, i.e. the absence of tetragonal-to-monoclinic transformation of zirconia material contains a share of yttrium oxide, phase composition and the manifestation of tetragonal-to-monoclinic transformation as well as surface state (conveyed as surface gloss and surface roughness).

The following hypotheses were tested: the new generation of zirconia ceramics contains a share of yttrium oxide that correlates with structural stability, i.e. the absence of tetragonal-to-monoclinic transformation of zirconia material contains a share of yttrium oxide, phase composition and the manifestation of tetragonal-to-monoclinic transformation as well as surface state (conveyed as surface gloss and surface roughness).
tragonal-to-monoclinic phase transformation. Experimental aging protocols will cause neither phase transformation nor a decrease in the share of stabilizing yttrium oxide in the material. Experimental aging protocols will have an effect on the surface gloss of the specimens. Experimental aging protocols will have an effect on the surface roughness of the specimens.

Material and methods

Specimen Preparation

The material employed in this research was a monolithic zirconia based ceramics KATANA-Zirconia Super Translucent Multi Layered - STML (Kuraray Noritake Dental Inc., Tokyo, Japan), shade A2. Using the CAD/CAM technology (Zenotec Easy Wieland Dental, Pforzheim, Germany), 18 disc-shaped specimens (11 x 11 x 1.5 mm with ±5% tolerance) were fabricated. The specimens were sintered in a furnace (Wieland, Pforzheim, Germany) at 1,550 °C for two hours according to manufacturer's instructions. The temperature was increased until the sintering temperature was reached and then decreased in the cooling process after the final sintering at a rate of 10 °C/min. The specimens were divided into two groups, according to the final surface treatment applied: eight specimens were glazed following the manufacturer's instructions (G1-G8), whereas eight specimens were polished with rubber (Ceragloss, EDENTA AG, Switzerland) accompanied by water cooling (P1-P8). The remaining two specimens served as control specimens in the research and received no surface treatment (K1, K2) (Figure 1).

Measurements and Analyses

All measurements and analyses of the specimens were conducted in two phases: before and after experimental aging protocols.

Two specimens (K1, P2) were analyzed using Energy Dispersive X-ray Fluorescence (EDXRF) (Ruder Bošković Institute, Zagreb, Croatia). A Philips W X-ray tube (Philips Co., Amsterdam, Netherlands) was utilized as a source. The specimens were irradiated by the secondary Mo target in rectangular geometry. The signal was detected using a semiconductor SiLi detector (Canberra Packard, Vienna, Austria) with 30 mm² of active surface area and a thickness of 3 mm. The thickness of beryllium window of the detector was 0.025 mm and the resolution at 5.9 keV was 170 eV (FWHM). The working parameters were 35 kV and 5 mA in a 100-bar vacuum. The measurement period was 100 s. The samples were analyzed for Y₂O₃, ZrO₂, HfO₂ as well as Sr and Zn. Relative errors of measurement, defined as slope coefficient errors for correlation lines were as follows: Y₂O₃ – 2.11%, ZrO₂ – 1.84%, HfO₂ – 2.50%, Zn and Sr – 0.1%. Minimum detection limits (MDL) were: Y₂O₃ – 0.11%, ZrO₂ – 1.35%, HfO₂ – 0.10%, Zn and Sr – 0.01%.

X-ray diffraction (XRD) was performed on two polished specimens (P1, P5) with a diffractometer (Philips PW 1820, Philips Co., Amsterdam, Netherlands) in order to attain the initial crystal structure. These two specimens (P1, P5) were subjected to CuK-alpha radiation in the space between 10° and 70° of the 2theta angle, with a step size of 0.02° and step u materijalu. Eksperimentalni protokoli starenja utjecat će na sjaj površine uzoraka. Eksperimentalni protokoli starenja utjecat će na hrapavost površine uzoraka.

Mjerenja i analize

Sva mjerenja i analize na uzorcima provedeni su u dvije faze – prije eksperimentalnih protokola starenja i poslije njih.

Dva uzorka (K1, P2) analizirana su metodom energetska disperzivna fluorescencije X-zraka (EDXRF) (Institut Ruder Bošković, Zagreb, Hrvatska). Kao izvor korištena je Philipsova W rendgenska cijev (Philips Co., Amsterdam, Nizozemska). Uzorci su ozračivani sekundarnim Mo zračenjem u pravokutnoj geometriji. Korišten je poluvodički SiLi detektor (Canberra Packard, Beč, Austrija), aktivne površine 30 mm² i debljine 3 mm. Debljina beriljeva prozora iznosi 0,025 mm, a rezolucija na 5,9 keV iznosi 170 eV (FWHM). Radni parametri za ozračivanje meta iznosili su 35 kV i 5 mA uz vakuum od 10° bara tijekom 100 s. U uzorcima su analizirani Y₂O₃, ZrO₂, HfO₂, Sr i Zn. Relative pogreške mjerenja određene su kao pogreška koeficijenta nagiba korelacije, a iznosile su: Y₂O₃ – 2,11 %, ZrO₂ – 1,84 %, HfO₂ – 2,50 %, Zn i Sr – 0,1 %. Minimalni detekcijski limiti (MDL) iznosili su: Y₂O₃ – 0,11 %, ZrO₂ – 1,35 %, HfO₂ – 0,10 %, Zn i Sr – 0,01 %.

Na dva polirana uzorka (P1, P5) učinjena je difrakcijska analiza X-zrakama (XRD) na difraktometru (Philips PW 1820, Philips Co., Amsterdam, Nizozemska) radi dobivanja početne kristalne strukture, uz pretpostavku da je ona ista u svim uzorcima na početku istraživanja. Dva uzorka (P1, P5) mjerenja su na CuKα zračenju u području 2θ kuta: od 10 do 70°, u koraku od 0,02° i vremenom prikupljanja od 1s/step.
time of 1 s/step, because it was assumed that the initial phase composition of all specimens was identical.

A glossmeter (Elcometer 407, Elcometer Inc., Michigan, USA) was utilized in null measurements of the surface gloss on the specimens. Elcometer is a multangle glossmeter, meaning that light is reflected (detected) off a surface at 20°, 60° and 85° angles (60° being the reference angle). Ten measurements were conducted on each specimen (Faculty of Graphic Arts, University of Zagreb, Croatia).

Ten roughness profiles were recorded on specimens G3, G6, P3 and P6 using stylus instrument Perthometer S8P (Perthen Mahr, Göttingen, Germany) under the following conditions:

- Gauss filter: \( l = 0.8 \) mm
- Tip radius: \( r = 5 \) µm
- Evaluation length: \( l_n = 4 \) mm.

Roughness parameters \( R_a \) and \( R_z \) were calculated on the recorded profiles. The traceability of measurement results was ensured by Croatian national roughness standards.

Two experimental protocols were conducted in this research. A three-hour hydrothermal degradation was carried out in an autoclave (SKO 7, Faro, Italy) at a temperature of 134 °C and under a pressure of 2 bars (six 30-minute cycles), with distilled water. On the other hand, chemical degradation was carried out in a corrosive medium (four-percent acetic acid (CH₃COOH), pH 2.49) at 80 °C over a sixteen-hour period (ISO 6872). The specimens were divided into four subgroups according to the experimental protocol they were subjected to. Four glazed specimens (G1-G4) (first subgroup) and four polished specimens (P1-P4) (second subgroup) were sterilized in an autoclave, whereas the remaining four glazed specimens (G5-G8) (third subgroup) and the remaining four polished specimens (P5-P8) (fourth subgroup) were immersed into a corrosive medium in a 1,000-mL glass measuring flask. Instead of being subjected to experimental protocols, control specimens (K1, K2) were kept at a standard temperature of 20 °C and under a standard pressure of 1 atm (101,325 Pa) throughout the study.

The same measurements and analyses from the beginning of the research were made after the aging protocols. One specimen from each subgroup (G2, G6, P2, P6) and control specimen K1 were analyzed using the EDXRF methodology so as to identify the chemical composition of the specimens after aging protocols. The phase composition was determined with a post-aging XRD analysis of one specimen from each subgroup (G1, G5, P1, P5). Surface gloss was measured on all specimens. Post-aging surface roughness was analyzed on the same specimens as at the start of the research.

Analysis of Results

The results of the research are displayed in tables (chemical composition) and figures (diffraction analyses). In order to statistically analyze the results of surface gloss measurements, a Bonferroni test and an ANOVA (Analysis of Variance) test with a 95 % confidence interval were employed. All \( p \) values under 0.05 were considered to be statistically significant. The values of roughness parameters \( R_a \) and \( R_z \) are expressed as arithmetical means of 10 recorded profiles, with

- \( p \) values under 0.05 were considered to be statistically significant.
- The significance test was conducted with a 95% confidence interval.

Učinjena su i nulta mjerenja staja površine svih uzoraka (G1-G4) (prva podskupina) i četiri polirane uzorke (P1-P4) (druga podskupina) bili su izloženi sterilizaciji u autoclavu, a preostala četiri glazirana (G5-G8) (treća podskupina) i četiri polirana uzorak (P5-P8) (četvrta podskupina) postavljeni su u staklenu mjeru tīka među 1000 mL, te im je dodan korozivni medij do potpunog uranjanja uzoraka. Kontrolni uzorci nisu izlagani eksperimentalnim protokolima starenja, nego su tijekom istraživanja čuvani na standardnoj temperaturi od 20 °C pri standardnom tlaku od 1 atm/SA (101 325 Pa).

Nakon protokola starenja na uzorcima su provedena identična mjerenja i analize kao i na početku istraživanja. Za određivanje kemijskog sastava nakon protokola starenja metodom EDXRF analiziran je po jedan uzorak iz svakog podskupina (G2, G6, P2, P6) i kontrolni uzorak K1. Za određivanje faznog sastava metodom XRD nakon protokola starenja analiziran je po jedan uzorak iz svakog podskupina (G1, G5, P1 i P5). Mjerenja staja obavljena su na svim uzorcima. Za određivanje površinske hravosti nakon protokola starenja analizirani su isti uzorci kao i na početku istraživanja.

Analiza dobivenih rezultata

Rezultati ovog istraživanja prikazani su tabelarno (kemijski sastav) i grafički (difrakcijske analize). Za statističku analizu rezultata mjerenja staja koristena je ANOVA – analiza vijanje s 95-postotnom poudažnošću te Bonferronijev test. Sve \( p \) vrijednosti manje od 0,05 smatrane su statistički značajnim. Vrijednosti parametara hravosti \( R_a \) i \( R_z \) iskazane su kao aritmetičke sredine tih parametara ostvarenih na 10 snimljenih profila te one-way-ANOVA-om.
the addition of a one-way ANOVA.

Results

The pre-aging examination of chemical composition on specimens K1 and P2 (Table 1) yielded the following shares (arithmetic mean ± standard deviation) of chemical compounds: yttrium oxide 11.97 ± 0.13%; zirconium oxide 85.87 ± 0.19%; hafnium oxide 2.16 ± 0.15%. Multiple specimens were not analyzed because the chemical composition of all specimens was found to be identical at the start of the research.

The results of chemical composition after hydrothermal degradation in an autoclave (specimens P2, G2) and chemical degradation in a corrosive medium (specimens P6, G6) are displayed in Table 2. The difference in the share of chemical elements before and after aging protocols is not a significant one. On the glazed side of glazed specimens, the difference is more pronounced (10.90 ± 0.30 %) compared to unglazed areas (11.85 ± 0.00 %).

Rezultati

Rezultati ispitivanja kemijskog sastava na početku istraživanja na uzorcima K1 i P2 (tablica 1.) pokazuju sljedeće udjelove kemijskih spojeva (aritmetička sredina ± standardna devijacija): itrijev oksid 11.97 ± 0.13 %; cirkonijev oksid 85.87 ± 0.19 %; hafnijev oksid 2.16 ± 0.15 %. Nije analizirano više uzoraka jer je kemijski sastav isti u svim uzorcima na početku istraživanja.

Rezultati kemijskog sastava nakon hidrotermalne degradacije u autoklavu (uzorci P2, G2) i kemijske degradacije u korozivnom mediju (uzorci P6, G6) prikazani su u tablici 2. Dobivena razlika u udjelu elemenata prije eksperimentalnih protokola i poslije nih nije značajna. Nešto veća razlika u udjelu itrijeva oksida uočena je na glaziranoj strani glaziranih uzoraka (10.90 ± 0.30 %) u odnosu prema neglaziranoj strani glaziranih uzoraka (11.85 ± 0.00 %). Neglazirane strane glaziranih uzoraka imaju gotovo identične udjеле spojeva kao i ostali uzorci.
Table 7 Statistical analysis of roughness parameters Ra and Rzz before and after aging protocols on G3, G6, P3 and P6 specimens.

\[(\text{One-way-ANOVA, } p < 0.05).\]

**FIGURES**

**Figure 1**
HD – hydrothermal degradation; CD – chemical degradation

**Figure 2**

GLAZED SPECIMENS
G1-G8

POLISHED SPECIMENS
P1-P4

CONTROL SPECIMENS
K1, K2 (NO SURFACE TREATMENT)

NO AGING PROTOCOL / NEGATIVE CONTROL

HYDROTHERMAL DEGRADATION
(AUToclave: 134°C, 2 BARS, 3 HOURS)

CHEMICAL DEGRADATION
(CORROSIVE MEDIUM: 4% ACETIC ACID, 80°C, 16 HOURS)

**Figure 3**
X-ray diffraction analysis of polished specimens P1 and P5 before aging protocols.

**Figure 4**
X-ray diffraction analysis after chemical degradation in a corrosive medium for glazed specimen G5 (4A) and polished specimen P5 (4B).

**Figure 1** Graphic division of groups of specimens.
Slika 1. Grafički prikaz podjele skupina uzoraka

**Figure 2** X-ray diffraction analysis of polished specimens P1 and P5 before aging protocols.
Slika 2. Difrakcijska analiza X-zrakama poliranih uzoraka P1 i P5 prije protokola starenja

**Figure 3** X-ray diffraction analysis after aging in an autoclave for glazed specimen G1 (3A) and polished specimen P1 (3B).
Slika 3. Difrakcijska analiza X-zrakama glaziranog uzorka G1 (3A) i poliranog uzorka P1 (3B) nakon starenja u autoklavu

**Figure 4** X-ray diffraction analysis after chemical degradation in a corrosive medium for glazed specimen G5 (4A) and polished specimen P5 (4B).
Slika 4. Difrakcijska analiza X-zrakama glaziranog uzorka G5 (4A) i poliranog uzorka P5 (4B) nakon kemijske degradacije u korozivnom mediju
Pre-aging surface gloss measurements have manifested significantly higher gloss values (arithmetic mean (AM) = 22.6 GU) in glazed specimens (G1-G8) than in polished specimens (P1-P8) (AM = 19.77 GU; p<0.05). After aging protocols, a statistically significant reduction in gloss value

Snimka uzoraka (P1 i P2) na kojima je provedena difrakcijska analiza X-zrakama prije protokola starenja prikazuje dijagram maksimum tetragonskog cirkonijeva oksida s pozičijom oko 30°2Theta, te pikove kubične faze (slika 2.). Udjeli faza prikazani su u postotcima: tetragonske 62.7%, kubične 37.3%. Analize faznih sastava uzoraka izloženih hidrotermalnoj degradaciji u autoklavu (glazirani G1, polirani P1) (slika 3.) pokazuju da je kubična faza posve prešla u tetragonsku. Fazni sastav ostao je gotovo nepromijenjen na uzorcima izloženima kemijskoj degradaciji u korozivnom mediju (G5, P5) (slika 4.).

Snimka uzoraka (P1 i P2) na kojima je provedena difrakcijska analiza X-zrakama prije protokola starenja prikazuje dijagram maksimum tetragonskog cirkonijeva oksida s pozičijom oko 30°2Theta, te pikove kubične faze (slika 2.). Udjeli faza prikazani su u postotcima: tetragonske 62.7%, kubične 37.3%. Analize faznih sastava uzoraka izloženih hidrotermalnoj degradaciji u autoklavu (glazirani G1, polirani P1) (slika 3.) pokazuju da je kubična faza posve prešla u tetragonsku. Fazni sastav ostao je gotovo nepromijenjen na uzorcima izloženima kemijskoj degradaciji u korozivnom mediju (G5, P5) (slika 4.).
occurred in both specimen groups (glazed AM = 18.54 GU; polished AM = 14.89 GU). With regard to the aging protocols applied, gloss change (∆G) was larger in the subgroup of glazed specimens subjected to chemical degradation (G5-G8) (∆G_{avg} = -4.38 GU) than in the subgroup subjected to hydrothermal degradation (G1-G4) (∆G_{avg} = -3.08 GU) (Table 4). In polished specimens, surface gloss reduction after both aging protocols was nearly identical (average gloss change after hydrothermal degradation (P1-P5): ∆G_{avg} = -4.65 GU; after chemical degradation (P5-P8): ∆G_{avg} = -4.97 GU) (Table 4). Control specimens displayed low gloss values from the beginning of the research as they received no surface treatment and their average gloss change ∆G_{avg} = -1.37 GU was not statistically significant.

The arithmetic means of roughness parameters R_{a} and R_{z} on polished specimens P3 and P6 obtained after experimental aging protocols were higher than the values obtained on (G5 – G8): ∆G_{med} = -4.38 GU in odnosu prema podskupini izloženoj hidrotermalnoj degradaciji (G1 – G4): ∆G_{med} = -3.08 GU (tablica 4.). Na poliranim uzorcima nastupilo je podjednako smanjenje sjaja površine pri oba provedena protokola; hidrotermalna degradacija dovela je do srednje promjene sjaja (P1 – P4): ∆G_{med} = -4.65 GU, a kemijska degradacija rezultirala je srednjom promjenom sjaja (P5 – P8): ∆G_{med} = -4.97 GU (tablica 4.). Kontrolni uzorci imaju nizak sjaj od početka istraživanja jer nisu površinski obradivani, a srednja promjena sjaja ∆G_{med} = -1.37 GU nije značajna.

Aritmetičke sredine parametara hrapavosti R_{a} i R_{z} na poliranim uzorcima P3 i P6 poslije eksperimentalnih protokola starenja nešto su viših vrijednosti u odnosu prema ostvarenim vrijednostima na istim uzorcima prije provedenog protokola starenja (tablica 5.).

Statistička analiza one-way-ANOVA testom (tablica 7.) pokazala je statistički značajno povećanje procijenjenih vrijednosti srednjih mjerenja na poliranim uzorcima P3 i P6 poslije eksperimentalnih protokola starenja nešto su viših vrijednosti u odnosu prema ostvarenim vrijednostima na istim uzorcima prije provedenog protokola starenja (tablica 5.).

| Table 5 | Values of parameters R_{a} and R_{z} on polished specimens (P3 and P6) before and after aging protocols. | Tablica 5. Vrijednosti parametara hrapavosti R_{a} i R_{z}poliranih uzoraka (P3 i P6) prije i poslije protokola starenja |
|---|---|---|
| Measurement No. • Mjerenje br. | Polished specimens before aging • Polirani uzorci prije starenja | Polished specimens after aging • Polirani uzorci nakon starenja |
| Specimen P3 • Uzorak P3 | Specimen P6 • Uzorak P6 | Specimen P3 • Uzorak P3 | Specimen P6 • Uzorak P6 |
| R_{a}, µm | R_{z}, µm | R_{a}, µm | R_{z}, µm | R_{a}, µm | R_{z}, µm |
| 1 | 0.73 | 4.5 | 0.52 | 3.26 | 0.71 | 4.39 |
| 2 | 0.56 | 3.77 | 0.55 | 3.64 | 0.65 | 4.45 |
| 3 | 0.71 | 4.19 | 0.53 | 3.67 | 0.58 | 3.9 |
| 4 | 0.7 | 4.11 | 0.56 | 3.68 | 0.62 | 4.32 |
| 5 | 0.62 | 3.83 | 0.54 | 3.5 | 0.69 | 4.47 |
| 6 | 0.61 | 3.86 | 0.58 | 3.66 | 0.63 | 3.89 |
| 7 | 0.67 | 3.84 | 0.6 | 3.78 | 0.63 | 4.2 |
| 8 | 0.57 | 3.22 | 0.57 | 3.41 | 0.72 | 4.4 |
| 9 | 0.69 | 4.45 | 0.65 | 4.16 | 0.66 | 4.28 |
| 10 | 0.67 | 4.52 | 0.54 | 3.7 | 0.69 | 4.75 |
| $R_{a}$, $R_{z}$ | 0.65 | 4.03 | 0.56 | 3.65 | 0.66 | 4.31 |
| $s$, nm | 59 | 408 | 39 | 239 | 44 | 260 |

| Table 6 | Values of parameters R_{a} and R_{z} on glazed specimens (G3 and G6) before and after aging protocols. | Tablica 6. Vrijednosti parametara hrapavosti R_{a} i R_{z}glaziranih uzoraka (G3 i G6) prije i poslije protokola starenja |
|---|---|---|
| Measurement No. • Mjerenje br. | Glazed specimens before aging • Glazirani uzorci prije starenja | Glazed specimens after aging • Glazirani uzorci nakon starenja |
| Specimen G3 • Uzorak G3 | Specimen G6 • Uzorak G6 | Specimen G3 • Uzorak G3 | Specimen G6 • Uzorak G6 |
| R_{a}, µm | R_{z}, µm | R_{a}, µm | R_{z}, µm | R_{a}, µm | R_{z}, µm |
| 1 | 1.05 | 3.72 | 1.01 | 3.35 | 0.52 | 1.83 |
| 2 | 0.64 | 2.43 | 1.16 | 3.18 | 0.47 | 1.79 |
| 3 | 0.92 | 3.8 | 1.16 | 3.93 | 0.53 | 2.07 |
| 4 | 0.78 | 2.67 | 0.76 | 2.87 | 0.71 | 4.27 |
| 5 | 0.82 | 2.94 | 0.79 | 2.72 | 0.7 | 2.54 |
| 6 | 0.95 | 3.76 | 0.83 | 3.33 | 0.64 | 2.98 |
| 7 | 1.22 | 4.89 | 0.89 | 3.03 | 0.88 | 3.28 |
| 8 | 0.68 | 2.31 | 0.89 | 2.92 | 0.66 | 2.66 |
| 9 | 0.86 | 2.49 | 0.97 | 3.12 | 0.76 | 3.23 |
| 10 | 0.64 | 2.24 | 0.82 | 3.19 | 0.89 | 2.93 |
| $R_{a}$, $R_{z}$ | 0.86 | 3.13 | 0.93 | 3.16 | 0.68 | 2.76 |
| $s$, nm | 187 | 876 | 144 | 335 | 144 | 759 |
Utjecaj starenja na ZrO2 keramiku

Mešić i sur.

The results of one-way ANOVA point to a statistically significant increase in the values of estimated standard deviations for roughness parameters \( R_a \) and \( R_z \) on polished specimen P6 (Table 6).

The arithmetic means of roughness parameters \( R_a \) and \( R_z \) on glazed specimen G3 obtained after the aging protocol were lower than before the aging protocol was performed. An increase in the values of roughness parameters \( R_a \) and \( R_z \) after the aging treatment was present on glazed specimen G6 (Table 7).

The results of one-way ANOVA point to a statistically significant change in the values of estimated standard deviations for roughness parameter \( R_z \) on glazed specimens G3 (decrease) and G6 (increase) as well as for roughness parameter \( R_a \) on glazed specimen G6 (increase) (Table 7).

### Discussion

Various aging protocols provide an insight into the possible behavior of the constituent material in the mouth over a lengthy period of time. This research comprised several contemporary and costly protocols. A three-hour period was chosen for exploring hydrothermal degradation in an autoclave because it corresponded to a restoration usage period of 10-15 years (29-31), which should be the expected restoration usage period both from a therapist’s and a patient’s point of view. Submersing specimens into a medium of low pH value (pH 2.49) at a temperature of 80 °C for 16 hours (ISO 6872) is a method of examining the stability of material in a controlled environment. Furthermore, these testing methods were employed using very expensive, sophisticated apparatus and methods which would have obtained the results relevant even on a small number of specimens. It is to be expected that the small number of specimens before aging protocols were performed (Table 5).

The results of one-way ANOVA point to a statistically significant increase in the values of estimated standard deviations for roughness parameters \( R_a \) and \( R_z \) on polished specimen P6 (Table 6).

The arithmetic means of roughness parameters \( R_a \) and \( R_z \) on glazed specimen G3 obtained after the aging protocol were lower than before the aging protocol was performed. An increase in the values of roughness parameters \( R_a \) and \( R_z \) after the aging treatment was present on glazed specimen G6 (Table 7).

The results of one-way ANOVA point to a statistically significant change in the values of estimated standard deviations for roughness parameter \( R_z \) on glazed specimens G3 (decrease) and G6 (increase) as well as for roughness parameter \( R_a \) on glazed specimen G6 (increase) (Table 7).

### Table 7

| Specimen • Uzorak | Protocol • Protokol | \( Ra \) AM ± SD before \( Ra \) AS ± SD prije | \( Ra \) AM ± SD after \( Ra \) AS ± SD poslije | \( P \) | \( R_z \) AM ± SD before \( R_z \) AS ± SD prije | \( R_z \) AM ± SD after \( R_z \) AS ± SD poslije | \( P \) |
|-------------------|---------------------|---------------------------------|---------------------------------|------|---------------------------------|---------------------------------|------|
| G3                | HD                  | 0.86 ± 0.035                    | 0.68 ± 0.02                     | 0.03 | 3.13 ± 0.77                     | 2.76 ± 0.58                     | 0.33 |
| G6                | CD • KD             | 0.93 ± 0.02                     | 1.26 ± 0.05                     | 0.001| 3.16 ± 0.11                     | 4.03 ± 0.06                     | 0.005|
| P3                | HD                  | 0.65 ± 0.004                    | 0.66 ± 0.002                    | 0.834| 4.03 ± 0.166                    | 4.31 ± 0.07                     | 0.09 |
| P6                | CD • KD             | 0.56 ± 0.001                    | 0.63 ± 0.002                    | 0.003| 3.65 ± 0.06                     | 3.94 ± 0.1                      | 0.03 |

### Rasprava

Različiti protokoli starenja daju uvid u moguće ponašanje gradivnog materijala u ustima tijekom duljeg razdoblja. Ovo istraživanje obuhvatio je više suvremenih i skupih protokola. Za ispitivanje hidrotermalne degradacije u autoklavu odabrano je vrijeme od 3 sata, što odgovara razdoblju od 10 do 15 godina korištenja nadomjeska u ustima (29 – 31). To bi trebalo biti očekivano razdoblje primjene nadomjeska za terapeuta i pacijenta. Uranjanje uzoraka u medij niske pH vrijednosti (pH 2,49) na temperaturi od 80 °C tijekom 16 sati (ISO 6872), način je ispitivanja kemijske postojanosti materijala u uvjetima konstantnih promjena pH vrijednosti i temperature kakva je u usnoj šupljini (30 – 32). Plak koj adhiera na površine tvrdih zubnih tkiva, pa tako i nadomjestaka, u svojoj dubini ima pH vrijednost vrlo sličnu pH vrijedno-

ti korištene kiseline u ovom istraživanju, čime se i taj utjecaj simulira (33). Broj uzoraka za ovo istraživanje definiran je nakon pilot-studije u dogovoru sa suradnicima/stručnjacima pod čijim su nadzorom provedena testiranja. Za dio testiranja (EDXRF, XRD, površinska hrapavost) bio je dovoljan te-
stirani broj uzoraka jer je riječ o materijalu proizvedenom u kontroliranim uvjetima. Osim toga, korištene metode testiranja provedene su na vrlo skupim i sofisticiranim uredažima postupcima čiji su rezultati testiranja relevantni i na malom broju uzoraka. Može se očekivati da će mali broj uzoraka biti reprezentativan za određenu vrstu testiranja te da će dobiti rezultati biti ponovljivi i primjenjivi na većem broju uzoraka. Za neka testiranja (XRD, površinska hrapavost) svakako bi bilo poželjno imati više uzoraka, ali potrebno je usetiti u obzir iznimno visoku cijenu testiranog materijala, vrlo skupu...
pected that a small quantity of specimens would be representative of a certain test type and that the obtained results could be repeated and applied to a greater number of specimens. It would have certainly been desirable to have more specimens for other tests (XRD, surface roughness), but one ought to take into account the extremely high price of the tested material, great costs for specimen manufacture as well as the cost and delicacy of measuring instruments.

At room temperature, pure zirconia exists in the monoclinic phase and great tension inside the material renders it unusable in the field of dental medicine, i.e. fixed prosthodontics (14). Yttrium oxide is the most frequently used stabilizer in zirconia ceramics (8-12, 14). When its share is 3-8%, it is possible to stabilize the tetragonal phase of zirconia ceramics, the result being so-called Y-TZP (yttrium-stabilized tetragonal zirconia polycrystal material). In the present study, the post-aging share of yttrium oxide (polished specimens 11.88 ± 0.07%, control specimens 11.75 ± 0.01%, glazed specimens 10.90 ± 0.30% - 11.85 ± 0.00%) was not significantly lower than the pre-aging share (11.97 ± 0.13%), i.e. the chemical composition of the specimens was not significantly altered (Table 2). A somewhat lower share of yttrium oxide on the glazed side of glazed specimens (10.90 ± 0.30%) can be explained by the presence of strontium and zinc in the glaze. Tested specimens manifested the stability of their chemical composition after being subjected to both hydrothermal degradation in an autoclave and chemical degradation in acetic acid. So far, there has been no mechanism for which one could say with certainty that it ages zirconia, although there have been some theories that could account for that phenomenon. A theory by Lange et al., based on an analysis of SEM images, suggests that water reacts with Y2O3, creating yttrium hydroxide (Y(OH)3), a chemical compound that prompts the loss of stabilizers in the surrounding grains and a tetragonal-to-monoclinic transformation (34). According to Yoshimura, water evaporation causes the bond between zirconium and oxygen in zirconia ceramics to break; the newly-free -OH ions exert stress and strain on the material and the outcome is a tetragonal-to-monoclinic transformation (35). Chevalier et al. believe that free oxygen radicals O2-, formed as a consequence of water dissociation, destabilize the structure of Y-TZP and trigger LTD (36). It has been proven that a tetragonal-to-monoclinic transformation starts on the surface of the material and progresses into its interior (8-14). This transformation leads to an increase in the volume of surface grains, which rise above the rest of the surface, create micro-cracks and open up the way for water and thereby the transformation to penetrate deeper into the material. Under the strain of e.g. masticatory force in the mouth, a restoration will ultimately crack (37-39). A greater post-aging share of stabilizing yttrium oxide calculated in this study (up to 12%) suffices for maintaining the stability of the crystal structure of specimens (15-17), i.e. for preventing a phase transformation. The first hypothesis is thus confirmed.

At the start of the present study, two phases were found to co-exist in specimens: tetragonal (approx. 63%) and cubic (approx. 37%). After being exposed to hydrothermal degradation in an autoclave, the crystal structure of the specimens
fully transitioned to a tetragonal structure (100%). Unlike the first aging protocol, degradation in a corrosive medium did not bring about a change in the crystal structure of the specimens, i.e. tetragonal and cubic structures continued to co-exist in nearly the same ratio as at the start of the research. These analyses did not establish a phase (tetragonal-to-monoclinic) transformation of monolithic zirconia specimens; therefore the second hypothesis is accepted. A monoclinic phase in monolithic zirconia with a mixed tetragonal-cubic microstructure was not manifested in a study by Muñoz et al., although the share of the cubic phase increased after hydrothermal degradation (39). Kolakarnprasert et al. did not prove the manifestation of a monoclinic phase in the material after exposing specimens submerged in water to a temperature of 120 °C for a twelve-hour period; their findings correspond to the results of this study (15).

Long-term stability, smoothness and gloss of a restoration are important from a hygienic (20-23, 28), tribological (20, 21, 23) and esthetic point of view (19, 22, 40). Surface roughness and final surface treatment on FPD affect the color stability of dental materials (40). Discoloration of dentures, caused by beverages such as coffee and tea, has been described in literature (41). In the present study, zirconia ceramic was subjected to two types of final surface treatment – polishing and glazing. Glazing is a standard surface finishing treatment which closes any pores left after sintering, allows for a better aesthetic impression of the restoration and reduces the accumulation of biofilm (42). In this research, surface state was expressed in terms of two parameters – surface gloss and surface roughness. In the imitation of a natural tooth in fixed prosthodontic therapy, a lot of emphasis is placed on the successful reproduction of surface texture (22). An enamel-like texture is attained by manually spreading a thin layer of glaze over a finished restoration (22). Because of divergences in the refraction of light, differences in texture generate differences in color perception. In this study, both experimental protocols brought about a statistically significant reduction of surface gloss in both specimen groups (G1-G8, P1-P8), which prompts the acceptance of the third hypothesis (p<0.05). From the beginning, glazed specimens manifested significantly higher surface gloss values than polished specimens. This study established that the surface gloss of specimens was reduced regardless of the final surface treatment applied, with both subgroups of polished specimens (P1-P4, P5-P8) having a higher mean gloss change \( \Delta G \) than glazed specimens (G1-G4, G5-G8). It needs to be noted that surface gloss reduction in an oral cavity would unfold at a slower pace than during experimental protocols. Control specimens (K1, K2) did not manifest significant surface gloss reduction in this research, although their gloss values were low from the onset because they were not subjected to any surface treatment. Gloss reduction in glazed specimens is most likely a result of congruent dissolution of glaze during experimental protocols, especially during chemical degradation in a corrosive medium, which is confirmed by the results relating to surface roughness. A glazed specimen subjected to aging in an autoclave (G3) recorded a decrease of parameters \( R_z \) (p=0.03) and \( R_s \) (p=0.33), while a specimen submerged in a corrosive medium as a početku istraživanja. Ovim analizama nije utvrđena fazna (t-m) transformacija u uzorcima monolitne cirkoni-oksidne keramike, čime je prihvadena druga hipoteza. Muñoz i suradnici u monolitnom cirkonijskom oksidu tetragonsko-kubične struktura također nisu dokazali pojavu monokline faze, ali se u njihovoj studiji, pri hidrotermalnoj degradaciji, pojavio veći udjel kubične u odnosu prema tetragonskoj fazi (39). Kolakarnprasert i suradnici, pri izlaganju uzoraka temperaturi od 120 °C tijekom 12 sati u vodi, također nisu dokazali prisutnost monokline faze u materijalu, što je u skladu s rezultatima ove studije (15).

Površina nadomjesta koja je dugoročno stabilna, glatka i sa stajanjem važna je s higijenskog (20 – 23, 28), trilobolško (20, 21, 23) i estetskog aspekta (19, 22, 40). Hrapavost površine i načini završne obrade površine nadomjesta utječu na stabilnost boje dentalnih materijala (40). U literaturi su opisane diskolorencije nadomjesta pićima poput kave i čaja (41). U ovom istraživanju površina cirkonijsk-oksidne kerami ke završno je obrađena na dva načina – poliranjem ili glaziranjem. Glaziranje je standardni način završavanja keramičke restauracije kojima se zatvaraju pore koje su eventualno zavlaknale nakon procesa sinteriranja, omogućujući bolji estetski dojam nadomjesta, ali i reducirajući akumulaciju biofilma (42). Stanje površine u ovom istraživanju prikazano je dvama mjerama – sjajem i hrapavcima površine. Pri oponašanju izgleda prirodog zuba u fiksni proizvodni terapiji, velik naglasak se stavljala na uspješnu reprodukciju površinske teksture (22). Tekstura nalik na zubnu kalkinu postiže se ručnim nanošenjem tankog sloja glazure na gotovi nadomjestak (22). Zbog različitog loma svjetlosti razlike u teksturi i razliku u percepciju boje. U ovom istraživanju statistički značajno smanjenje sjaja površine nastalo je tijekom obaju eksperimentalnih protokolaca u obje skupine uzoraka (G1 – G8, P1 – P8) u odnosu prema početnim mjerama, što dovodi do prihvaćanja treće hipoteze \( p < 0.05 \). Glazirani uzorci su već na početku istraživanja imali statistički značajno veću vrijednost sjaja površine od poliranih. U ovom istraživanju dokazano je smanjenje sjaja površine uzoraka bez obziira na način završne obrade, s tim da je veća srednja promjena sjaja \( \Delta G \) nastupila u objema skupina podskupinama poliranih uzoraka (P1 – P4, P5 – P8) u odnosu prema glaziranim uzorcima (G1 – G4, G5 – G8). Vazno je istaknuti da bi proces smanjenja sjaja površine nadomjesta u usnoj slučajnosti bio mnogo gostiji u odnosu prema eksperimentalnim protokolima. Kontrolni uzorci u ovom istraživanju također pokazuju smanjenje sjaja površine koje nije statistički značajno, iako je sjaj površine nizak od početka jer nisu završno obradivani. Smanjenje sjaja glaziranih uzoraka (G1 – 4, G5 – 8) vjerovatno je rezultat kongruentnog otapanja sloja glazure pri eksperimentalnim protokolima, osobito pri kemijskoj degradaciji u korozivnom mediju, što potvrđuju rezultati površinskih hravosti. Na glaziranom uzorku podvrgnutom postupku starenja u autoklavu (G3) zabilježeno je smanjenje vrijednosti parameutra \( R_z \), koje je značajno \( p = 0.03 \) i parametra \( R_s \) koje nije značajno \( p = 0.33 \), a na uzorku unorenjenom u korozivni medij (G6) uočeno je značajno povećanje parametara hrapavosti \( R_z \) i \( R_s \) \( p < 0.05 \). Glazura kao amorfniji materijal nije otporna na agresivne vanjske utjecaje niti je kemijski stabilna, odno-
Conclusions

Within the limitations of this study, it can be concluded that experimental aging protocols do not reduce the share of stabilizing yttrium oxide and consequently do not generate a tetragonal-to-monoclinic phase transformation, i.e. aging of translucent multilayer zirconia ceramic.

Sno inertna. Iz glazure u agresivnom mediju gube se površinski ioni, čime se stvaraju površinske nepravilnosti koje povećavaju hrpavost, što je u skladu s istraživanjima Maniconea i suradnika (1) te Milledinga i suradnika (43, 44). Smanjenje parametara hrpavosti \( R_s \) i \( R_t \) nastalo na glaziranom uzorku koji je stario u autoklavu (tablica 6.), govori u prilog da je proces starenja u autoklavu rezultirao zaglađivanjem površine uzoraka, zbog čega je i srednja promjena sja \( \Delta G \) kod tih uzoraka (G1 – G4) manja u odnosu prema poliranim uzorcima (P1 – P4). Utjecaj hidrotermalne degradacije u autoklav kod glaziranih uzoraka (G1 – G4) smanjen je zbog zaštitne prevlake na površini (glazure), čime se bilo kakva penetracija vode u materijal, odnosno degradacija osnovnog materijala neće događati, za razliku od uzoraka koji nemaju zaštitnu prevlaku. Tu tvrdnju potvrđuju Palla i suradnici koji su dokazali da se kroz površinu neglaziranog staklokeramičkog nadomjesta u materijal infiltrira voda, što rezultira dezintegracijom strukture (45). Campisilvan i suradnici sugerišu nanošenje glazure na sve nadomjeste cirkonij-oksidne keramike kako bi se spriječilo utjecaj hidrotermalnog protokola starenja na površinu materijala (46). Na poliranim uzorcima (P1 – P8) utvrđeno je smanjenje sja površine uz veću promjenu sja \( \Delta G \) u odnosu prema glaziranim uzorcima (G1 – G8), što bi se moglo pripisati povećanju vrijednosti mjernih parametara hrpavosti pri oba eksperimentalna protokola (tablice 5. i 7.). Štefančić u svojoj disertaciji također potvrđuje te navode (47). Povećanje hrpavosti nije značajno za uzorak izložen hidrotermalnoj degradaciji (P3) u odnosu prema uzorku izloženom kemijskoj degradaciji (P6), ali je zasigurno utjecalo na opće smanjenje sja površine poliranih uzoraka (47). Na temelju rezultata parametara hrpavosti može se gortoriti o djelomičnom prihvaćanju četrtnih hipoteza jer je značajna promjena hrpavosti površine nastala na uzorcima G6 i P6 koji pripadaju podskupinama glaziranih i poliranih uzoraka izloženih kemijskoj degradaciji u korozivnom mediju (\( p < 0.05 \)). Na kontrolnim uzorcima nije provedeno mjerenje hrpavosti površine profilometrijom jer nisu površinski obrađeni ni jednom metodom, čime je hrpavost površine velika i nema svrhe raditi usporedbu s hrpavoću površine poliranih, odnosno glaziranih uzoraka.

Pregledom relevantne literature može se zaključiti da sve vrste zubnih keramika (silikatne i oksidne) pokazuju kemijsku reaktivnost u vodnome mediju tako da ne postoji posebno inertni keramički materijal (1, 43, 44, 47). Polikristalničine, oksidne keramike, za razliku od onih silikatnih, također otpuštaju ione, ali u mnogo manjoj količini (43, 44, 47).

Zaključak

Unatoč ograničenjima ove studije može se zaključiti da eksperimentalni protokoli starenja ne rezultiraju redukcijom udjela stabilizatora itrijeva oksida, što posljedično ne dovodi do tetragonsko-monoklinsko fazne transformacije, odnosno do starenja translucentne multilayered cirkonij-oksidne keramike.

Eksperimentalni protokoli starenja dovode do značajnog smanjenja sja površine svih uzoraka, bez obzira na način po-
Utjecaj starenja na ZrO₂ keramiku

Mešić i sur.

Utjecaj starenja na ZrO₂ keramiku

Regardless of the surface treatment applied, surface gloss on all specimens was significantly reduced by experimental aging protocols, with surface gloss reduction being somewhat greater in polished specimens. The reduction of the gloss of specimens is an indicator of possible repercussions on the esthetic properties of dentures, particularly in polished specimens.

In contrast to the changes in the value of roughness parameters in glazed specimens subjected to aging in an autoclave (decrease) and glazed specimens submerged in a corrosive medium (increase), a significant increase in the value of roughness parameters in polished specimens following both aging protocols is a signal of substantial unwanted changes in surface state caused by polishing.

Glazing will have better esthetic, hygienic and tribological effects on the surface of a FPD than polishing.

Conflict of interests

The authors report no conflict of interests.

Acknowledgements

Science project: Defining the Possibility of Using Mini Dental Implants: the results in “in vitro” and in clinical prospective studies. (No 1218) Funded by Croatian Science Foundation, by Professor Asja Čelebić, DMD, MSc, PhD

Author’s contribution

K.M. – designed the research as a part of her doctoral thesis, conducted all experimental phases of the research, wrote the article; I.M. – assisted in gloss measurements and the interpretation of the results in that experimental part of the research; J.O. – assisted in the analysis of the specimens’ chemical composition and the interpretation of the results in that experimental part of the research; G.B. – assisted in surface roughness measurements and the interpretation of the vršinske obrađe, s nešto većim smanjenjem sjaja na uzorcima obrađenima poliranjem. Smanjenje sjaja uzoraka upućuje na moguće reperkusije na estetiku nadomjesta, osobito kod uzoraka obrađenih poliranjem.

Promjene u vrijednostima parametara hrapavosti na glaziranim uzorcima izloženima starenju u autoklavu u obliku smanjenja, te na glaziranim uzorcima izloženim korozivnom mediju u obliku povećanja u odnosu prema poliranim uzorcima kod kojih je nastupilo povećanje vrijednosti parametara hrapavosti u oba protokola, upućuju na veće neželjene promjene stanja površine na uzorcima završno obrađenima prosjecom poliranjem.

Završnom obradom nadomjesta glaziranjem ostvarit će se manji estetski, higijenski i tribološki defekt površine nadomjesta u odnosu prema završnoj obradi poliranjem.

Sukob interesa

Autori izjavljuju da nisu bili ni u kakvom sukobu interesa.

Zahvala

Objavljeni rezultati dio su projekta pod naslovom Definiranje mogućnosti uporabe mini dentalnih implantata (MDI) i njihovi rezultati u in vitro i u kliničkim prospektivnim istraživanjima pod vodstvom prof. dr. sc. Asje Čelebić.

Projekt je financirala Hrvatska zaklada za znanost No. 1218.

Doprinos autora

K. M. – osmišlja istraživanje koje je dio vlastite doktorske disertacije, provela sve eksperimentalne faze istraživanja, napisala članak; I. M. – pomogao pri provedbi mjerenja sjaja površine uzoraka i interpretaciji rezultata tog dijela istraživanja; J. O. – pomogla pri provedbi analize kemijskog sastava uzoraka i interpretaciji rezultata tog dijela istraživanja; G. B. – pomogla pri provedbi mjerenja površinske hrapavosti i interpretaciji rezultata tog dijela istraživanja; K. M. – mentor, savjetnik u svim fazama provedbe i pisanja ovoga rada.
References that experimental part of the research; K.M. was a recipient of a scholarship for a Ph.D. study, and during all stages of the article:

1. Manicone P, Iommetti P, Raffaelli L. An overview of zirconia ceramic: Basic properties and clinical applications. J Dent Assoc 2004 Apr;70(4):230.
2. Gordan VV, Abu-Hanna A, Möjr IA. Esthetic dentistry in North American dental schools. J Can Dent Assoc 2004 Apr;70(4):230.
3. Gorman CM, E McDevitt W, Hill RG. Comparison of two-pressed all-ceramic dental materials. Dent Mater 2000 Nov;16(6):389-95.
4. Heintze SD, Rousson V. Survival of zirconia- and metal supported fixed dental bridges: a systematic review. Int J Prosthodont Nov-Dec 2010;23(6):493-502.
5. Stawarczyk B, Jahn D, Becker I, Fischer J, Hämmerle CHF. Influences of the Gerüstdesigns upon the Bruchlast of ZrO₂-Kronen. [Influence of the framework design on the breaking load of ZrO₂ crowns]. Quintessenz Zahntechn. 2008;34(10):1246-54.
6. Pjetursson BE, Saugier I, Zwahlen M, Hämmerle CH. A systematic review of the survival and complication rates of all-ceramic and metal-ceramic reconstructions after an observation period of at least 3 years. Part 1: Single crowns. Clin Oral Implant Res 2007;18 Suppl 3:73-85.
7. Kohorn R, Borowiec L, Stremler J. Low-temperature degradation of different zirconia ceramics for dental applications. Acta Biomater 2012 Mar;8(3):1213-20.
8. Kawai Y, Uo M, Wang Y. Phase transformation of zirconia ceramics by hydrothermal degradation. Dent Mater 2011;30(3):286-92.
9. Chevalier J, Cales B, Drouin JM. Low temperature aging of Y-TZP ceramics. J Prosthodont 2015 Dec;24(6):286-92.
10. Lugi V, Sorge V. Low temperature degradation -aging of zirconia: a critical review of the relevant aspects in dentistry. Dent Mater 2010 Aug;26(8):807-20.
11. Papanagiotou HP, Morgano SM, Giordano RA, Pober R. In vitro evaluation of low-temperature aging effects and finishing procedures on the flexural strength and structural stability of Y-TZP dental ceramics. J Prosthodont 2006 Sep;96(3):154-64.
12. Kim JW, Covel NS, Guess PC, Rekow ED, Zhang Y. Concerns of hydrothermal degradation in CAD/CAM zirconia. J Dent Res 2010 Jan;89(1):91-5.
13. Zhengan L, Danyu J, Lei H, Guoqiang Z, Qiang L, Cheng Z. Low temperature degradation of yttria stabilized zirconia. Mater 2007;336-8:1188-9.
14. Starwarczyk B, Keul C, Eichberger M, Figge D, Edelhoff D, Lammert N. Three generations of zirconia: From veneered to monolithic. Part I. Quintessence Int 2017;48(5):369-380.
15. Kolakanprasert N, Kaizer MR, Kim DK, Zhang Y. New multi-layered zirconias: Composition, microstructure and translucency. Dent Mater 2019;35(5):797-806.
16. Zhang F, Inokoshi M, Batuk M, Hadermann J, Naert I, VanMeerbeeck B, et al. Strength, toughness and aging stability of highly translucent Y-TZP ceramics for dental restorations. Dent Mater 2016 Dec;32(12):e327-e337.
17. Tong H, Tanaka CB, Kaiser MR, Zhang Y. Characterization of three commercial Y-TZP ceramics produced for their high translucency. Ceram Int. 2016 Jan;42(1 Pt B):1077-1085.
18. Fathy S, El-Falall A, El-Negy S, El-Bedawy AB. Translucency of monolithic and core zirconia after hydrothermal aging. Acta Biomater Odontol Scand. 2015 Dec 23;1(2):84-92.
19. Sarikaya I, Yerliyurt K, Hayran Y. Effect of surface finishing on the colour stability and translucency of dental ceramics. BMC Oral Health. 2018 Mar 13;18(1):40.
20. Al-Wahadni AM, Martin DM. An in vitro investigation into the wear effects of stained, unfinished and relieved dental porcelain on an opposing material. J Oral Rehabil. 1999 Jun;26(6):538-46.
21. Ritter AV, Resendiz CV, Henson BR, Culp L, Donovan TE, Amaya-Pajares SP. Effect of finishing and polishing on the surface roughness of four ceramic materials after occlusal adjustment. J Esthet Restor Dent. 2016 Nov 12;28(6):392-96.
22. Ancowitz S, Torres T, Rostami H. Texturing and polishing: The final attempt at value control. Dent Clin North Am. 1998 Oct;42(4):607-12, viii.
23. Passos SP, Torrealba Y, Major P, Linke B, Flores-Mir C, Ny chka A. In vitro wear behavior of zirconia opposing enamel: a systematic review. J Prosthodont 2014 Dec;23(6):593-601.
24. Sripretchandon J, Leevailoj C. Wear of human enamel opposing monolithic zirconia, glass ceramic, and composite resin: an in vitro study. J Prosthodont Jun 2004;13(2):93-99.
25. Han GL, Kim JH, Lee MA, Chae SY, Lee YH, Cho BH. Performance of a novel polishing rubber wheel in improving surface roughness of feldspathic porcelain. Dent Mater J 2014;33(6):739-48.
26. Stober T, Bermejo JL, Rammelsberg P, Schmitter M. Enamel wear caused by monolithic zirconia crowns after 6 months of clinical use. J Oral Rehabil. 2016 Apr;43(4):314-22.
27. Mundhe K, Jain V, Pruthi G, Shah N. Clinical study to evaluate the wear of natural enamel antagonist to zirconia and metal ceramic crowns. J Prosthodont Dent 2015 Sep;114(3):358-63.
28. Weitmann RT, Eames WB. PLAque accumulation on composite surfaces after various finishing procedures. J Am Dent Assoc. 1975 Jul;91(1):101-6.
29. Chevalier J, Grandjean S, Kuntz M. On the kinetics and impact of tetragonal to monoclinic transformation in an alumina/zirconia composite for arthroplasty applications. Biomaterials. 2009 Oct;30(29):5279-82.
30. Kawai Y, Uo M, Wang Y. Phase transformation of zirconia ceramics by hydrothermal degradation. Dent Mater J 2011;30(3):286-92.
31. Anusavice KJ. Degradability of dental ceramics. Adv Dent Res. 1992 Sep;9(2):82-9.
32. Jakovac M, Zivko-Babic J, Curkovic L, Aurer A. Chemical durability of dental ceramic material in acid medium. Acta Stomatol Croat. 2006;40(1):65-7.
33. Šutalo J. Patologija i terapija tvrdih zubnih tkiva. 1st ed. Zagreb: Zadro; 1994.
34. Yoshimura M, Toma N, Kawabata K, Somiya S. Role of water on the degradation process of Y-TZP. J Mater Sci: Mater Med. 1998;9(1):23-30.
35. Lange FF, Dupeyron C, Davis BL. Degradation during ageing of transformation toughened ZrO₂ – Y₂O₃ material at 250 °C. J Am Ceram Soc. 1986;69:237-40.
36. Chevalier J, Gremillard L, Virkar AV, Clarke DR. The tetragonal-monoclinic transformation in zirconia: lessons learned and future trends. J Am Ceram Soc. 2009;92:1901-22.
37. Lee JK, Kim H. Surface crack initiation in 2Y-TZP ceramics by low temperature aging. Ceram Int. 1994;20:413-18.
38. Piconi C, Burger W, Richter HG, Ciudadina A, Maccauro G, Covacci V, et al. Y-TZP ceramics for artificial joint replacements. Biomaterials. 1998 Aug;19(16):1489-94.
39. Muñoz EM, Longhini D, Gutierrez Antonio S, Adabo GL. The effects of mechanical and hydrothermal aging on microstructure on biaxial flexural strength of an anterior and a posterior monolithic zirconia. J Dent 2017 Aug;63:94-102.
40. Um CM, Ruyter IE. Staining of resin-based veneering materials with coffee and tea. Quintessence Int. 1991 May;22(5):377-86.
41. Luse FF, Dupéryon C, Davis BL. Degradation during ageing of transformation toughened ZrO₂ – Y₂O₃ material at 250 °C. J Am Ceram Soc. 1986;69:237-40.
42. Al-Wahadni A, Martin DM. Glazing and finishing dental porcelain: a literature review. J Can Dent Assoc. 1999;65(4):580-3.
43. Mileding P, Karlsson S, Nyborg L. On the surface elemental composition of noncorroded and corroded dental ceramic materials in vitro. J Mater Sci: Mater Med. 2003 Jun;14(6):557-66.
44. Mileding P, Wannerberg A, Alaeedini S, Karlsson S, Simon E. Surface corrosion of dental ceramics in vitro. Biomaterials. 1999 Jan;20:733-46.
45. Palla ES, Kontonasaki E, Kanirianis N, Papadopoulos L, Zorba T, Parakevopoulos KM, et al. Color stability of lithium disilicate ceramics after aging and immersion in common beverages. J Prosthod Dent 2018 Apr;119(4):632-642.
46. Camposilvan E, Leone R, Gremillard L, Sorrentino R, Zorba T, Ferrari M, et al. Aging resistance, mechanical properties and transluency of different yttria-stabilized zirconia ceramics for monolithic dental crown applications. Dent Mater 2018 Jun;34(6):879-890.
47. Štefančič S. Utjecaj korozivnog medija na strukturu i svojstva dentalnih keramika (dissertation). Zagreb: Stomatološki fakultet; 2013.