Acta Odontologica Scandinavica, 2008; 66: 262–267

informa healthcare

ORIGINAL ARTICLE

Effect of shading the zirconia framework on biaxial strength and surface microhardness

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Abstract

Objective. Zirconia ceramics for frameworks of fixed partial dentures can be color shaded to better match the shade of veneering porcelain. The aim of this study was to evaluate the effect of color shading the green-stage zirconia ceramic on some mechanical properties. ***Material and Methods.*** Zirconia disks (diameter 19 mm, thickness 0.8 mm) were divided into 10 groups of 10 disks each according to the color shade of the zirconia ceramic. The disks were shaded with the same color liquid using either the recommended shading time (3 s) or prolonged shading time (60 s). Nine control disks were tested without color. Composition of the color liquids was determined with EDX analysis. All the disks were sintered at 1500°C and their biaxial flexural strength was measured dry and at room temperature. Surface Vickers microhardness was measured. Data were evaluated using ANOVA analysis. ***Results.*** Disks of shade D4 (Vita Classic-scale) revealed the highest strength (1007 MPa) of the shaded disks, but the strength did not differ statistically from that of the control group (1132 MPa). Other color shades had values of A3: 898 MPa, B1: 918 MPa, C4: 885 MPa, and D2: 897 MPa. Prolonging the shading time from 3 s to 60 s lowered the strength even more. Shading time had no effect on microhardness, but there were some differences among the different color shade groups ($p<0.05$). EDX analysis showed slight differences between compositions of different color liquids. ***Conclusions.*** Some variation was found in strength and surface hardness of zirconia that had been color shaded to different shades.

Key Words: *Biaxial flexural strength, color shade, mechanical properties, zirconia*

Introduction

Yttrium partially stabilized zirconium dioxide, zirconia (ZrO_2), is a durable and tough novel dental ceramic. It has been used by adding 50 wt% ZrO_2 to glass porcelain, resulting in bending strength and fracture toughness 20–80% higher than porcelain alone [1]. Zirconia has since proved to be stronger than other dental ceramic materials [2–8]. In many studies, zirconia has shown flexural strength values [9–11] of over 1000 MPa. Some treatments, for example sandblasting, significantly increase the static strength of zirconia [12]. As well as with single-cycle loading, zirconia has proved to be stronger than other dental ceramics in terms of contact fatigue with multi-cycle loading [13]. When the long-term failure probability of ceramic bridges was predicted by computational techniques, the zirconia bridges showed very high mechanical long-term reliability [14].

Pure zirconia is white in color. To achieve more natural looking properties for the veneering of fixed partial dentures and crowns, the zirconia frameworks can be shaded before sintering. Some colorant oxides of Fe, Cu, Co, Mn and opacifying oxides of Sn, Zn, Al, Zr, and Ti are added to dental ceramic materials [15]. There is some evidence that the color of the framework affects the color of the veneered crown [16]. Zirconia is more opaque than other dental ceramic materials [17]. To our knowledge, there are only a few studies about color shade effects on zirconia. When white and yellowish shades of zirconia were compared, the yellowish specimens had higher flexural strength. The higher strength might be related to components that were added to obtain different shades of zirconia, such as CeO_2,

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(Received 21 November 2007; accepted 4 June 2008)

ISSN 0001-6357 print/ISSN 1502-3850 online
DOI: 10.1080/00016350802247123

Fe_2O_3, and Bi_2O_3 [18]. Pittayachawan et al. [11] tested shaded and unshaded LAVA zirconia and found that color shading had no effect on the flexural strength.

The aim of this study was to determine whether the color shade affected the mechanical properties of yttrium partially stabilized green-stage zirconium dioxide. The study hypothesis was that the color shading does not weaken the zirconium dioxide.

Material and methods

Preparation of the samples

Yttrium partially stabilized green-stage zirconium dioxide blocks (ICE Zirkon, Zirkonzahn, Sand in Taufers, Italy) were cut into disks with a low-speed diamond saw (Leitz 1600). After cutting, a total of 109 disks were ground with 800 and 4000 grit (FEPA) silicon carbide grinding paper (Struers, Copenhagen, Denmark) to a thickness of 1 mm. The disks were divided into 11 groups of 10 disks each, except for the control group, where there were 9 disks. Each test group was shaded with color liquid shades (Zirkonzahn) according to the Vita Classic scale: A3, B1, C4, D2, and D4. There were two different subgroups for each color shade: normal color shading for 3 s in accordance with the manufacturer's instructions and prolonged color shading for 1 min. The disks (except the controls) were dipped into the color liquid with plastic pincers, held there for the predetermined time (either 3 s or 60 s), and dried under a warming lamp for 30 min. After shading, all the disks were sintered at 1500°C in a sintering oven (ZirkonZahn) using a temperature rise time of 3 h and the temperature kept at 1500°C for 2 h before cooling.

Mechanical testing

The thickness and diameter of the sintered disks were measured with a digital micrometer (Mitutoyo, Andover, England) before the fracture test. Mean thickness of the disks was 0.8 mm and diameter 19 mm. The biaxial flexural strength test was carried out adapted from the ISO Standard 6872 [19] used for determining biaxial fracture strength values (Figure 1). The disks were tested dry at room temperature with a universal testing machine (Model LRX; Lloyd Instruments, Fareham, UK); they rested on three symmetrically based balls and the load was applied to the center of the top surface by the piston (diameter 1.60 mm) until fracture occurred. Cross-head speed of the piston was 1.0 mm/min. Results were recorded with PC software (Nexygen; Lloyd Instruments). Surface microhardness of the disks was determined by the indentation technique [20] to determine the Vickers hardness number (VHN) of the disks using a load of 9.81 N.

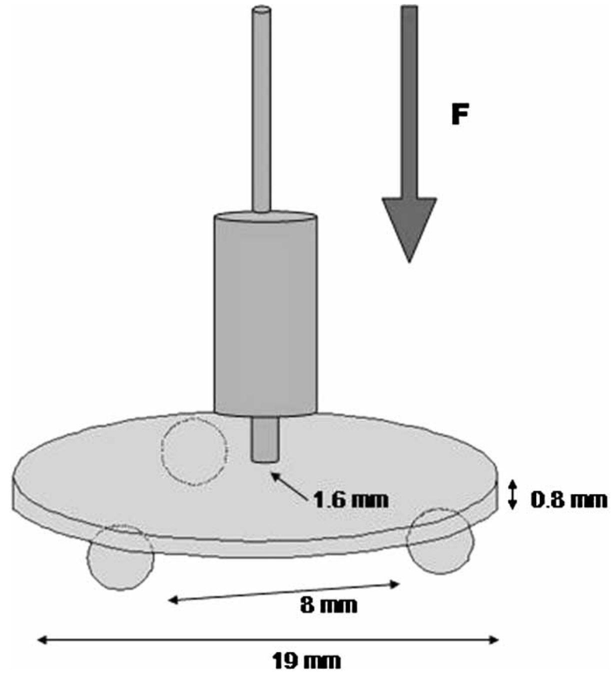

Figure 1. Biaxial flexural strength testing machine. The tested disks rested on three symmetrically based balls, and the load (F) was applied to the center of the top surface by the piston (diameter 1.60 mm) until fracture occurred.

There were 15 randomly selected indentations per subgroup.

Scanning electron microscope

Energy-dispersive X-ray analysis (EDX; Princeton Gamma-Tech Instruments, East Princetown, N.J., USA) was performed by scanning electron microscope (JEOL 5500, Tokyo, Japan) to determine the elemental composition of the shaded ceramics and the color liquids. Fractured disks were cleaned ultrasonically and covered with carbon (Bal-Tec SCD 050; Balzers, Germany) before analysis. Four sample bases with a diameter of 2 cm and a thickness of 1 cm were cut from the PMMA tube with a saw (FOX, Haguenau, France). Small holes for color liquids were drilled into each sample base with a carborundum drill. A small drop of the tested color liquids A3, B1, C4, D2, and D4 was put into the hole in the sample base with a clean pipette and allowed to dry at room temperature for a couple of days. The samples were covered with carbon and the EDX analysis was carried out using an acceleration voltage of 20 kV and a magnification of 50 ×. A 120 s spectra collection time was used to determine the elemental composition of the solidified substructure from the color liquid. One recording was made for each sample. The wt% of elements was analyzed with EDX computer software (Spirit, PGT, Princeton; Princeton Gamma-Tech Instruments, East Princetown, N.J., USA) of the color liquids.

X-ray diffraction analysis

The relative amount of the monoclinic phase after color shading was determined by X-ray diffraction (XRD) analysis (Philips PW 1830 Generator; Philips, Eindhoven, The Netherlands) using 40 kV and 30 mA and Cu Kα-1 radiation [21]. XRD analysis was performed to shaded and sintered disks that had not yet been mechanically tested. Unshaded zirconia disks were used as control.

Determination of dimensional changes

Additionally, seven disks (thickness 1 mm) per five groups were prepared using the same procedure as described previously. According to mechanical tests, the weakest and strongest color shades were chosen to determine dimensional changes. Shading times for the groups were 3 s and 1 min. One group was used as a control. All the disks were weighted using balance (Mettler Toledo AB54-S; Greifensee, Switzerland), and diameter was measured using a micrometer screw (Mitutoyo, Kawasaki, Japan) before and after the color shading and after sintering.

Statistical analysis

The data were analyzed using one-way analysis of variance (ANOVA), followed by Tukey's HSD test at a significance level of $p < 0.05$.

Results

Summaries of biaxial flexural strength and surface microhardness values according to different color shades and coloring times are given in Table I. The ANOVA analysis revealed a statistically significant difference ($p < 0.05$) in flexural strength between the groups. Disks of shade D4 revealed the highest strength of the shaded disks, but did not differ statistically from the control group. The disks, shaded for 3 s, were statistically significantly weaker than the disks of the control group. Prolonged color shading time (60 s) further decreased the strength of the disks statistically significantly ($p < 0.05$). Only group D4, which was shaded for 1 min had biaxial flexural strength on the same level as the 3-s-shaded disks (A3, B1, C4, D2). The color liquid penetrated the entire disk regardless of shading time. Surface Vickers microhardness varied between 1352 and 1481. Color shading time did not influence the surface microhardness, but there were some differences between the groups of different color shades. Disks shaded with A3 and D4 had lower microhardness than disks in the other shaded groups ($p < 0.05$).

Table I. Summary of biaxial flexural strength (MPa) and surface Vickers microhardness (VHN) of zirconia disks according to different color shades and shading times

Parameters	Flexural strength MPa (SD)	Stat. diff.*	VNH (SD)
Control	1132 (162)	a	1501 (194)
D2, 3 s	897 (95)	b,c	1426 (50)
D4, 3 s	1007 (121)	b	1454 (88)
B1, 3 s	918 (81)	b,c	1442 (72)
C4, 3 s	885 (91)	c	1481 (65)
A3, 3 s	898 (116)	c	1454 (89)
D2, 1 min	812 (106)	b,c	1437 (76)
D4, 1 min	934 (89)	b	1407 (127)
B1, 1 min	809 (88)	b,c	1419 (93)
C4, 1 min	793 (159)	c	1422 (87)
A3, 1 min	798 (84)	c	1469 (87)

*Groups with same letter indicate no statistical differences ($p > 0.05$, Tukey).

Analysis of the surface elemental composition of the disks demonstrated that they consisted mainly of zirconium (Zr), yttrium (Y), and hafnium (Hf), with no clear signs of the elements of color liquids to be seen. In the EDX analyses of the plain color liquids, it was found that oxygen, chlorine, and iron were the predominant elements of the dried liquids (Table II). Minor quantities of (<1.0%) chromium, erbium, aluminum, cobalt, and sulfur were detected, but were close to the detection limit. A minor quantity of calcium was seen only with shade D4.

X-ray diffraction analysis did not reveal any changes from tetragonal to monoclinic phase in zirconia disks after color shading. The prolonged shading time did not affect the phase change either.

Groups D4 and C4 were chosen for determination of dimensional changes, as these were seen to be the strongest and the weakest color shade group according to mechanical tests. All the shaded disks revealed 15% higher weight after dipping in color liquid. After sintering, the weight of the control disks had decreased 0.12 wt% more than the weight of the shaded disks (Figure 2), which is wt% of color pigment of zirconia. The difference was statistically significant ($p < 0.05$). Sintering shrinkage in diameter of the shaded disk varied between 19.4% and 19.5%, whereas shrinkage of the unshaded disk was higher (19.8%) and was statistically significant ($p < 0.05$) (Figure 3). As an absolute value in millimeters, the average difference in diameter was 0.08 mm between control and shaded disks.

Table II. Elemental composition (%) of solidified remnants of color liquids determined by energy dispersive X-ray analysis (EDX)

Element	A3	B1	C4	D2	D4
Oxygen, O	73.7	54.4	65.3	56.6	52.2
Chloride, Cl	19.0	26.8	23.6	25.4	27.5
Iron, Fe	5.3	15.3	9.9	15.5	18.0
Chromium, Cr	0.5	0.7	–	0.1	–
Erbium, Er	0.8	–	0.1	0.2	0.1
Aluminum, Al	0.6	0.4	0.3	0.2	0.1
Cobalt, Co	–	1.3	0.6	1.2	1.5
Sulphur, S	–	1.2	0.2	0.7	0.2
Calcium, Ca	–	–	–	–	0.5

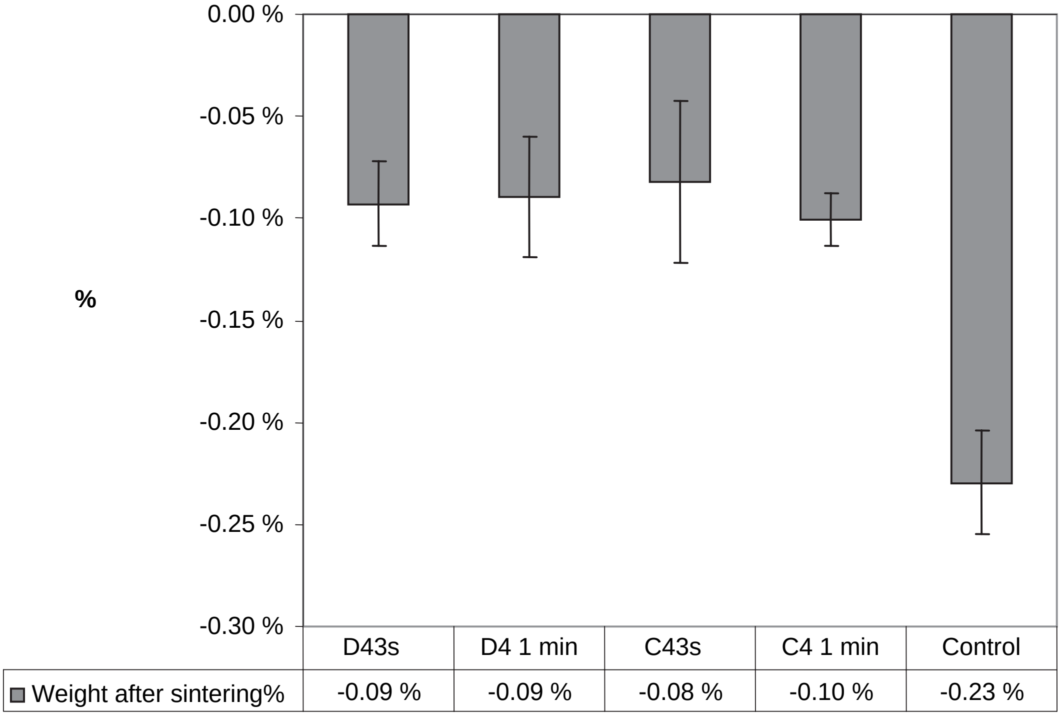

Figure 2. Change in weight (%) after sintering of shaded zirconia disks. Control disks were unshaded. Vertical lines mark standard deviation within the groups.

Discussion

This study was undertaken to evaluate changes in biaxial flexural strength of zirconia framework material when it has been shaded before sintering in green-stage form. This has been of interest to us because a tooth-shaded framework can provide a more natural looking final shade for the tooth than the pure white zirconia framework.

The study disks were tested using the biaxial flexural strength test, a static loading test where the specimen is loaded until fracture occurs. There is some evidence of different results in the flexural strength of zirconium dioxide between the static test and the static test after cyclic loading in a wet environment [22]. Itinoche et al. [23] found some differences, although not statistically significant.

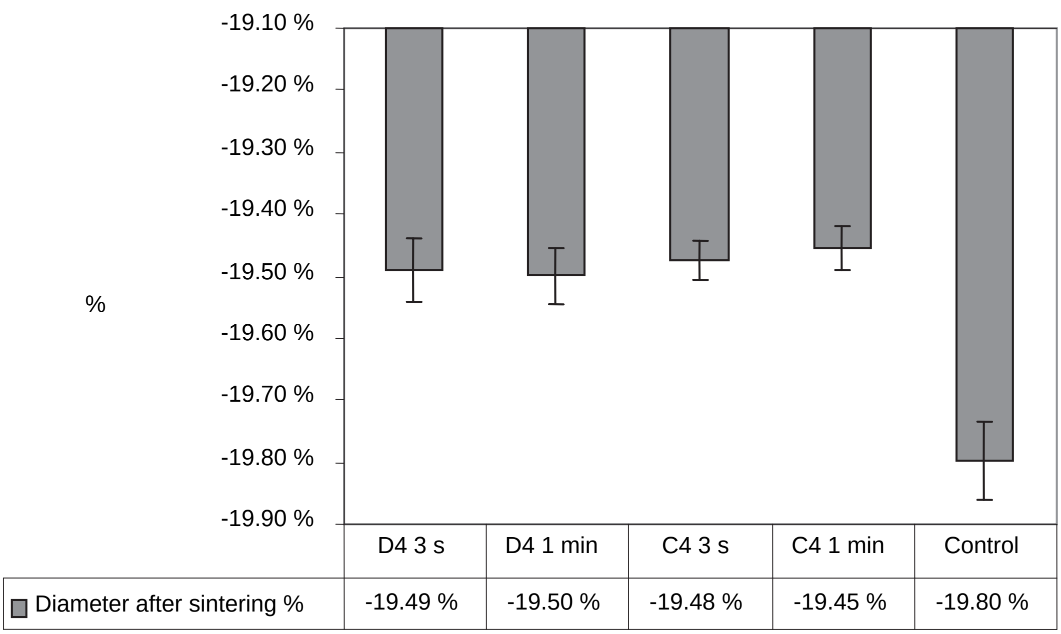

Figure 3. Sintering shrinkage in diameter (%) after sintering of shaded zirconia disks. Control disks were unshaded. Vertical lines mark standard deviation within the groups.

The results of the present study revealed that the biaxial flexural strength of zirconia disks is influenced by shading. This has also been suggested by Ardlin et al. [18], who found a higher strength with a yellowish shade. On the other hand, there is also a report about LAVA zirconia material, where no changes were observed between the groups of material shaded with different color shades [11]. In our study, an interesting observation was that shade D4 did not result in a major reduction in strength, unlike other color shades. However, all the shaded disks revealed an increased reduction in strength when the shading time was prolonged. Elemental analysis of the shaded and sintered disks did not provide a clear explanation for this. The detection limit of the SEM-EDX system was not high enough, and the components of the color liquids were not observed from the sintered disks. However, the elemental analysis of solidification remnants of the liquid itself provided some information on the composition of coloring agents. Liquid of shade D4 contained some calcium (Ca), which was not found in any other color liquids. It can be speculated that the color shading oxides of shade D4 did not affect the grain structure of yttrium partially stabilized zirconium dioxide, which might have been the case with the oxides used in other shades of the coloring agents. The other color shade liquids would probably have caused swelling of during liquid immersion. This could have caused lower density and more porosity in the material during the sintering process. However, possible changes in crystal structure require further investigation.

As the color liquid penetrated the entire disk regardless of shading time, the disks could be treated as uniform material and the biaxial flexural strength was counted using the equation in ISO standard no. 6872 for dental ceramics [19]. If the material is multilayered, the equation suggested by Hsueh et al. [24] can be used instead for evaluating biaxial flexural strength.

XRD analysis revealed that color shading has no effect on the phase change in yttrium partially stabilized zirconium dioxide. No coloring agents were seen with XRD analysis on the surface of shaded disks. As well as EDX analysis of sintered disks, this too proved that the color liquid dispersed as nanoparticles inside the grain structure of zirconium dioxide.

As the dimensional changes were determined, it could be seen that weight of the shaded disks increased dramatically right after the shading procedure. During the drying and further sintering process, major parts of the color shading liquid had evaporated. Additionally, after sintering, unshaded disks lost more weight after sintering than shaded disks. Shading also statistically significantly diminished the shrinkage of the zirconia material during sintering. This can have clinical effects for the marginal fit and cement thickness of the zirconia frameworks if the shaded zirconia does not shrink as much as unshaded frameworks.

The present study showed that the surface microhardness (VNH) was in the range 1352–1481. The control material had a slightly greater hardness than the other groups. In general, these results are in accordance with the previous studies [11,25,26].

The hypothesis that the shading procedure does not weaken the zirconia was rejected. The results confirmed the decrease of zirconia in strength and this was related to shading time. This emphasizes the importance of following the manufacturer's instructions and not using longer color shading times. When making the decision to shade the zirconia material in green-stage form, the weakening of the material needs to be taken into consideration.

In conclusion, some reduction was found in the strength and microhardness of zirconia after being color shaded in green-stage form. Also color shading of green-stage zirconia material caused some dimensional changes which may be important when manufacturing fixed partial dentures and crowns.

Acknowledgments

This study was supported by the Finnish Dental Society Apollonia. Mikko Jokinen is acknowledged for his help during the study, which was undertaken as part of the program of the Center of Excellence by the Academy of Finland and the Biocity Turku Biomaterials Research Program.

Declaration of interest: The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the paper.

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