Original Article

Effect of a Commercial Fluorescence Liquid on 3Y-TZP Surface Microstructure: A Preliminary Study

Jing-Fen Wu, DDS, MS
Graduate Institute of Clinical Dentistry, School of Dentistry, National Taiwan University, Taipei, Taiwan

Tong-Mei Wang, DDS, MS, PhD
Graduate Institute of Clinical Dentistry, School of Dentistry, National Taiwan University, Taipei, Taiwan

Ru-Shi Liu, MS, PhD
Department of Chemistry, National Taiwan University, Taipei, Taiwan

Li-Deh Lin, DDS, PhD
Graduate Institute of Clinical Dentistry, School of Dentistry, National Taiwan University, Taipei, Taiwan

Corresponding author:
Li-Deh Lin, DDS, PhD
Graduate Institute of Clinical Dentistry, School of Dentistry, National Taiwan University, Taipei, Taiwan
No. 1, Chang-Te St, Jhongjheng Dist, Taipei City 100, Taiwan R.O.C.
Fax: +886-2-2383-1346
E-mail: lidehlin@ntu.edu.tw

Abstract

Objective

3 mol% yttrium-stabilized tetragonal zirconia poly-crystal (3Y-TZP) ceramics can be stained with a color/fluorescence liquid to match the color and fluorescence of natural teeth. However, the effects of different shading liquids and methods are still not fully known. The purpose of this study, therefore, was to evaluate the effect of a commercial fluorescence liquid on the surface microstructure of 3Y-TZP ceramics.

Material and methods

Green-stage 3Y-TZP ceramics (Zirkonzahn® Prettau Zirkon) were sectioned into disc forms and divided into 3 groups: the dip-coating (D) group, the brush-coating (B) group, and the control (C) group. The D and B groups were shaded with a commercial fluorescence liquid before sintering either by dipping or by brushing respectively. Undyed discs were used as the C group. Each disc was 10mm in diameter and 2mm in thickness after sintering. X-ray diffraction analysis (XRD) was used to analyze the crystalline forms of each group. Surface structural differences and chemical compositions were evaluated by scanning electron microscopy (SEM) and energy dispersive analysis (EDS). The mean grain size of each group was calculated by the circular intercept method (that is, Abram's Three-Circle Procedure). One-way ANOVA analysis and the Tukey test were used to analyze the data, at a significant level of P Value <0.05.

Results

The XRD results showed that each group was mainly composed of tetragonal phase and a small quantity of monoclinic phase. The SEM results revealed that the different shading methods changed the distribution of the coloring pigment, homogeneity of grain size, and mean grain size. The B group had more even and smaller grains (than the C group, whereas the D group had nonhomogeneous and larger grains). The difference was statistically significant ($p<0.05$).

Conclusion

Shading with a commercial fluorescence liquid by prolonged dipping could result in nonhomogeneous and enlarged grain sizes. It is thus recommended that shading be performed by brushing instead of prolonged dipping in clinical use.

Keywords: crystalline, fluorescence, grain size, 3Y-TZP

Introduction

Fluorescence is the emission of visible light from a substance that occurs when the substance is excited by a shorter wavelength light or radiation. In 1911, Stübel et al.[1-3] first reported that natural teeth emitted bluish fluorescence under UV light. The fluorescence properties of different parts of human teeth are heterogeneous. Human dentin and cementum display more intense fluorescence than enamel[2-4]. Fluorescence makes natural teeth look brighter and whiter[1, 5]. A restoration emitting fluorescence can return more light to the observer, lower the chroma, and hide underlying discoloration[5]. Generally, the value of a restoration decreases as the translucency of the restoration increases. For high-value cases, fluorescence emitted from the inner layer of a restoration can increase its value without decreasing its translucency[5]. In clinical practice, rare earth oxides (e.g. europium, cerium, and ytterbium) are usually added into dental porcelain powder and composite resin as phosphors for fluorescence emission[6, 7].

3 mol% yttrium-stabilized tetragonal zirconia poly-crystal (3Y-TZP) ceramics have become one of the most popular restorative materials in recent years due to the excellent mechanical properties, good biocompatibility, and tooth-like ivory/white color appearance of 3Y-TZP. However, pure 3Y-TZP ceramics are still too white and opaque to meet clinical esthetic demands. As such, the application of shading to 3Y-TZP ceramics is one solution for improving the esthetic performance of these ceramics. There are two available methods for shading 3Y-TZP ceramics[8, 9]. The first method consists of adding pigments into the ceramic powder before the powder is pressed into green-stage 3Y-TZP milling blanks. The pigments are thus homogeneously distributed in the milling blanks. The other method consists of the use of colored liquids to stain green-stage 3Y-TZP ceramics before subjecting them to the sintering process. These colored liquids can be applied by brushing or dipping. In addition to these colored liquids, some manufacturers also provide a fluorescence liquid that can be applied to 3Y-TZP ceramics to cause them to mimic the photoluminescence of natural teeth. Dental technicians can adjust the color or fluorescence by changing the painting strokes or immersion time they use when applying the liquid to the ceramics. However, the effects of different application methods and colored liquids on 3Y-TZP ceramics are still not entirely clear.

The purpose of this preliminary study is thus to evaluate the effects of a commercial fluorescence liquid and different application methods on the surface microstructure of 3Y-TZP ceramics.

Material and methods

Sample preparation

Green-stage 3Y-TZP (Zirkonzahn® Prettau Zirkon) blanks were milled into disc forms by a milling machine (Zirkonzahn® CAD/CAM System 5-TEC). A commercial fluorescence liquid (Zirkonzahn®) was then applied to some of the 3Y-TZP discs to increase their fluorescence, while one group of discs was left undyed. Each specimen that was stained was stained using just one of the following two shading methods: dipping or brushing. Thus, the discs were effectively divided into 3 groups: the control group (C) (that is, the undyed discs), the dip-coating group (D), and the brush-coating group (B). The C group discs (n=3) were, again, prepared without any shading. For the D group, the discs (n=4) were immersed in the fluorescence liquid for 10 min. For the B group, the fluorescence liquid was applied on the surface of the discs (n=4) with a metal-free brush. After the staining procedure, the specimens were dried under infra-red lamp for 45 minutes. Then the specimens were sintered in a sintering oven (Zirkonzahn®) at 1600°C for 2 hours. After the sintering process, each disc was 10mm in diameter and 2mm in thickness.

X-ray diffraction analysis

The crystalline phases of the C, D, and B groups were analyzed by X-ray diffraction analysis (XRD) using a 30kV, 10mA Cu-K α X-ray. Each scan was performed with the following settings: a 2θ angle of between 20°-90°, a step size of 0.02°, and a time step of 0.9sec (Bruker D2 PHASER).

The acquired diffraction data of the specimens were compared with the crystallographic database of the Powder Diffraction File™ (PDF®). The matched diffraction patterns were found to identify the crystalline phases of the specimens.

Scanning electron microscope

The specimens then were coated with a layer of 10 to 20 nm-thick Pt-Au before being subjected to scanning electron microscopy (SEM) examinations. The topographic images of the specimens were recorded by a field emission scanning electron microscope (JOEL JSM-6700F SEM). The average grain size was calculated by the circular intercept method (that is, Abram's Three-Circle Procedure). The data was analyzed by one-way ANOVA analysis and the Tukey test, at a significant level of P Value <0.05. The surface chemical composition of the specimens was determined by X-ray energy dispersive spectrometer (EDS).

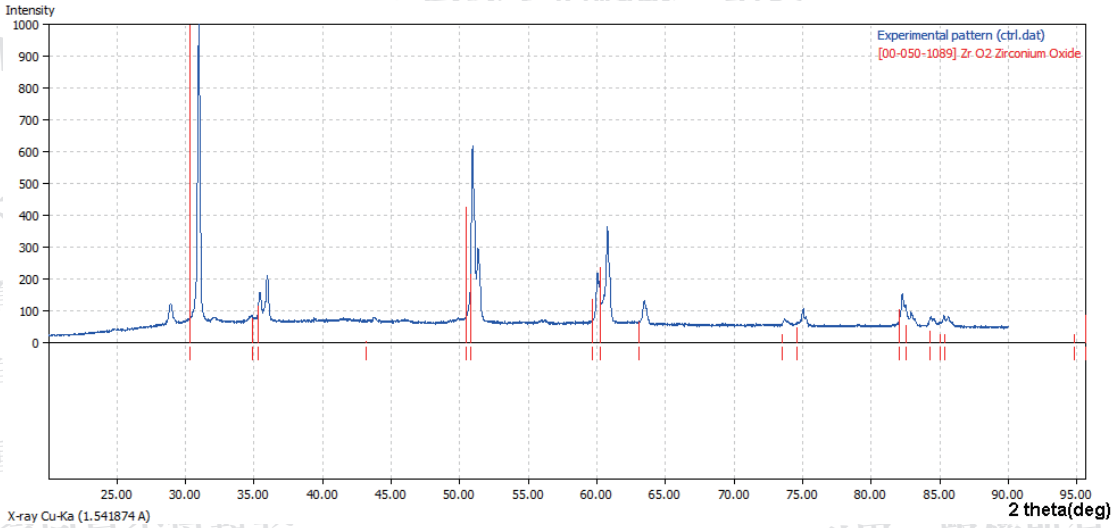

Fig. 1: XRD spectrum of undyed 3Y-TZP (C).

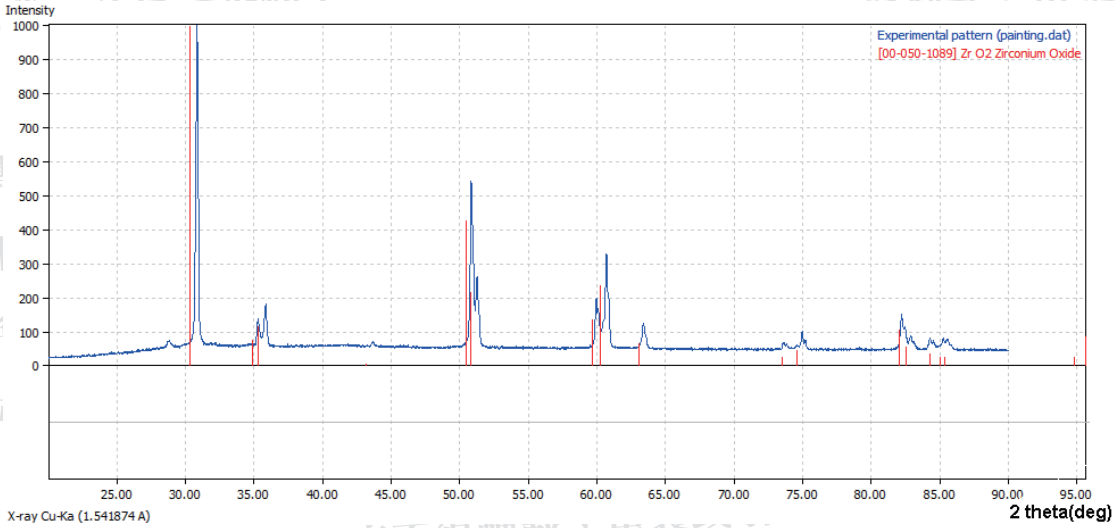

Fig. 2: XRD spectrum of 3Y-TZP shaded by brushing (B).

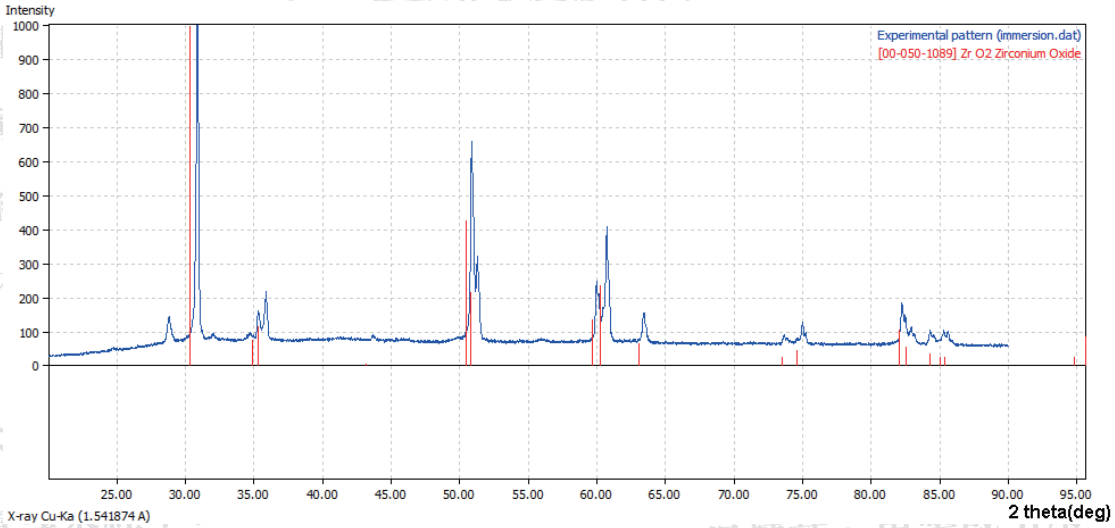

Fig. 3: XRD spectrum of 3Y-TZP shaded by dipping (D).

Results

X-ray diffraction analysis

Figures 1-3 show the individual XRD data and a matched spectrum of the C, D, and B groups. The blue line in each figure presents the diffraction data of each group. The red line indicates a matched standard diffraction spectrum for each group, and the results revealed that all the groups had the same matched spectrum – tetragonal phase. That is, the XRD data showed that the discs in all the groups were mainly composed of tetragonal phase. Compared to the C group discs, however, the diffraction peaks of the B and D groups were left shifted. This shift in the diffraction peaks indicated changes of in the lattice parameters of the B and D group discs relative to the C group discs.

For each group, there were two additional weak diffraction peaks, m(-1,1,1) and m(1,1,1,), observed at 2θ between 28° and 32° (Fig. 4), and these peaks belonged to the monoclinic phase. These weak diffraction peaks thus indicated that each group contained traces of monoclinic phase.

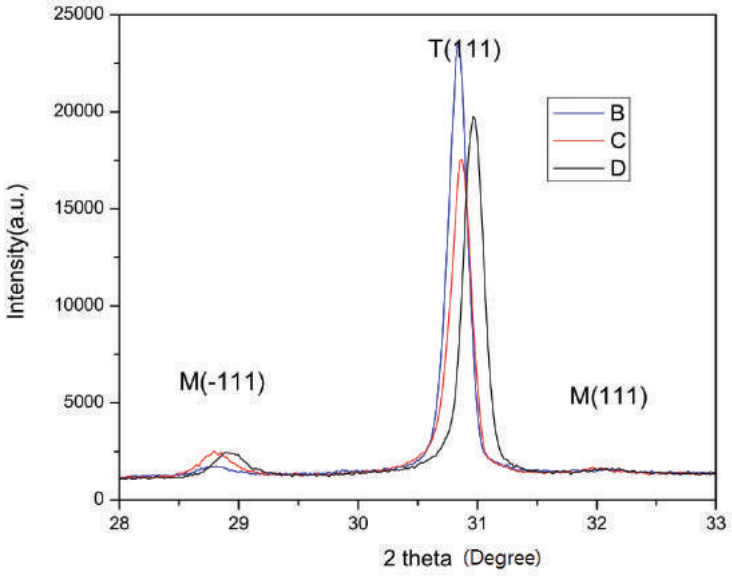

Fig. 4: Monoclinic phase contents was found in all three groups.

Scanning electron microscope

The SEM images revealed that the C group discs simply contained ZrO_2 grains of homogeneous grain size (Fig. 5). The mean grain size of the C group discs was μm. The B and D group discs (Figs. 6 and 7) were mainly composed of ZrO_2 grains, although their surfaces were covered with other particles. There were three different kinds of particles other than ZrO_2 grains noted. The grain size of the ZrO_2 grains in the B group discs was homogeneous, and the mean grain size was . The D group discs had more variable ZrO_2 grain dimensions and a mean grain size, μm, that was larger than the mean grain sizes of the C and B groups. The difference was statistically significant ($p<0.05$).

The EDS results showed that the C group discs mainly contained the elements of zirconium and oxygen. In addition to zirconium and oxygen, a remarkable amount of carbon was found in the D and B group discs.

Discussion

At atmospheric pressure, pure zirconia can exist in three different crystallographic forms – the monoclinic phase, tetragonal phase, and cubic phase - as temperature rises. The equilibrium phase at room temperature is the monoclinic phase. As the temperature rises to 1170°C, zirconium transforms into the tetragonal phase, and at 2370°C, it trans-

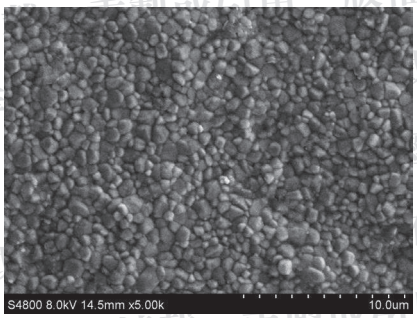

Fig. 5: SEM image of undyed 3Y-TZP (C), 5000x magnification.

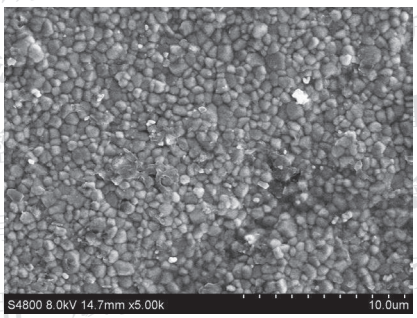

Fig. 6: SEM image of 3Y-TZP shaded by brushing (B), 5000x magnification.

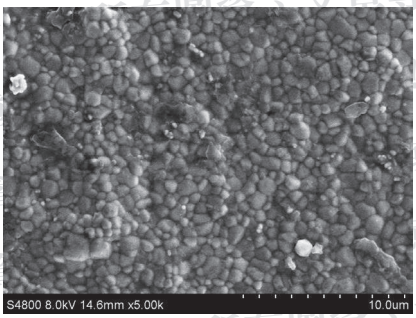

Fig. 7: SEM image of 3Y-TZP shaded by dipping (D), 5000x magnification.

forms into the cubic phase. Zirconium in its monoclinic phase has low strength and toughness. When alloying with some dopants such as MgO, CaO, and Y_2O_3, zirconium can maintain its tetragonal or cubic phase at room temperature. Under such circumstances, it is in a metastable state, and stress can break the stability and provoke its transformation. This kind of stress-induced transformation, from the tetragonal phase to the monoclinic phase, leads to an approximately 4.5% increase in the volume of the zirconium. This volume increase can result in compressive stress and prevent crack propagation. This is the phase transformation toughening (PTT) mechanism that gives dopant-stabilized tetragonal zirconia poly-crystal (TZP) ceramics their extremely excellent mechanical properties[10-12].

3Y-TZP is a material of high flexural strength and fracture toughness. It is composed of fine grain zirconia, containing both the monoclinic and tetragonal phases with a very high content of the metastable tetragonal phase. It was reported by Gupta et al. that the flexural strength of 3Y-TZP is increased as its tetragonal phase content is increased, whereas it is decreased as the monoclinic phase content is increased[13]. Lange et al. observed that the fracture toughness of 3Y-TZP is also correlated with its tetragonal phase content[14]. In summary, the mechanical properties of 3Y-TZP are directly related to its tetragonal phase content.

In this study, the XRD results revealed that the tested commercial 3Y-TZP samples in all three groups were mainly composed of tetragonal phase with a small portion of monoclinic phase, even after groups B and D were shaded with a fluorescence liquid using different methods. The fraction of monoclinic phase can be calculated using the Garvie-Nicholson formula. It showed that the group D discs had higher monoclinic phase content than the other groups. This increased monoclinic phase content after shading by prolonged dipping may be accompanied by lowered strength and toughness. However, the ability of XRD as a tool for detecting small fractions (< 5%) has certain limitations. Further investigations would thus be necessary to provide a reliable evaluation in this regard.

In humid environments, the surface of 3Y-TZP may spontaneously undergo a slow phase transformation that is known as low temperature degradation (LTD) or aging. This kind of transformation leads to surface roughening or micro-cracking. PTT and LTD are both based on the same mechanism, the transformation of a thermodynamically metastable phase. It is thus impossible to take advantage of PTT without facing the risk of LTD.

The stability of a zirconium metastable phase is affected by its grain size. As the grain size is decreased, zirconium becomes more stable in its tetragonal phase. As the grain size is increased, zirconium becomes more stable in its monoclinic phase. Lange et al. reported there was a critical grain size for fixed content yttrium-stabilized zirconia poly-crystal. Above the critical grain size, ZrO_2 had a tendency to exist in the monoclinic phase, and below that size, ZrO_2 tended to exist in the tetragonal phase[14]. This phenomenon implied that changes in grain size may be accompanied by changes in toughness. It was also observed that maximum fracture toughness occurred just below the critical grain size[14, 15]. According to the study by Lange et al., the critical grain size of 3Y-TZP was slightly smaller than 1 μm and optimum fracture toughness was obtained. However, LTD is another phenomenon of concern in clinical practice. Studies have shown that the LTD resistance of 3Y-TZP is closely related to its grain size as well. As the grain size is increased above 0.6μm, the LTD resistance decreases obviously[16]. In summary, both the fracture toughness and LTD of 3Y-TZP are critically dependent on the grain size. A balance must therefore be struck between fracture toughness and LTD resistance when deciding the grain size of 3Y-TZP.

In this study, we found that prolonged dipping with a commercial fluorescence liquid would result in enlarged and nonhomogeneous grain size. This result means that prolonged dipping with a fluorescence liquid may lead to a decrease in the LTD resistance. Such a decrease in LTD resistance would, in turn, affect the long-term survival of 3Y-TZP. However, the actual changes in LTD resistance and its implications after shading were not determined in this study. Further investigations are thus needed.

Conclusion

In this study, we found that, compared to the brushing method, shading by prolonged dipping leads to enlarged and heterogeneous grain size, and that the difference was statistically significant ($p < 0.05$). Shading by brushing is thus probably is a better method to use than dipping when seeking to maintain an adequate and even grain size of ZrO_2. However, the physical properties of 3T-TZP after it is subjected to shading with a commercial fluorescence liquid are still not fully known. Further studies are thus necessary to evaluate the effect of a commercial fluorescence liquid on 3Y-TZP.

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