ARTICLE IN PRESS

Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International ∎ (∎∎∎∎) ∎∎∎–∎∎∎

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Bi-colored zirconia as dental restoration ceramics

Jing Zhao[a,b], Zhijian Shen[b,c], Wenjie Si[c], Xinzhi Wang[a,*]

[a]Department of Prosthodontics, Peking University School and Hospital of Stomatology, No. 22 Zhongguancun Nandajie, Haidian District, Beijing 100081, PR China

[b]Department of Materials and Environmental Chemistry, Arrhenius Laboratory, Stockholm University, Svante Arrhenius Väg 16C, Stockholm 106 91, Sweden

[c]Department of Materials Science and Engineering, State Key Lab of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, PR China

Received 6 March 2013; received in revised form 26 April 2013; accepted 10 May 2013

Abstract

Machinable zirconia blocks with gradient colors are fundamental for fabrication of full-contour esthetic dental restorations. The aim of this study was to process and evaluate bi-colored zirconia ceramics as a pilot dental material by using well-established techniques. Two commercially available partially stabilized zirconia granules, one undoped and one doped with 0.202 wt% Fe_2O_3, resulted in white and yellow colors after sintering, respectively. Bi-colored zirconia was fabricated by two-step dry pressing of both zirconia granules one above the other to form green bodies, followed by cold isostatic pressing (CIP) and, a two-step pressureless sintering finally at 1450 °C. The dilatometer results showed that the Fe_2O_3 doped zirconia sintered slightly rapid, but the difference of shrinkage between two powders was $<1\%$. Sintered bars achieved full density, 6.018 g/cm^3 (~99%TD), without cracks in the ~1 mm color gradient zone. The microstructures were characterized by scanning electron microscopy (SEM) and careful observation of both surface and interior provided no obvious structural difference of either grains or pores among the three distinct regions, comprising white, yellow and color gradient zone. Vickers hardness of bi-colored zirconia was ~13.1 GPa, with no obvious difference in the three regions. The four-point bending strength of the bi-colored zirconia bars was 745.5 ± 159.6 MPa, which appeared noticeably lower than that of the single-colored references being above 1000 MPa. Fractographic analysis revealed that in most of the cases (60%) the fracture was initiated at the color gradient zone, where large voids with high coordination numbers, agglomerates with critical size and concentration of irregular grains with porous surfaces were observed. Above all, bi-colored zirconia ceramics prepared by the improved technique could meet the basic requirements of dental materials. The ways of minimizing the defects within bi-colored blocks should be developed for the production of esthetic zirconia ceramics of high strength and reliability.

Keywords: A. Pressing; C. Color; D. ZrO_2; E. Biomedical application

1. Introduction

Imitation of natural teeth is the purpose of the artificial dental restorations. It is for the esthetics that ceramics were introduced into prosthetic dentistry. The initial application of ceramic materials was to mask the metal-core color of a crown by fusing porcelain layer by layer onside. This kind of restorations is called as Porcelain Fused to Metal (PFM) crowns [1]. PFM crowns with an opaque metal inside cannot produce the important translucent effect as natural teeth [2]. Additionally, the release of metal ions may cause gingiva discoloration, which would decrease the visual aesthetics further [3]. Besides promoting high cosmetic requirements, other beneficial properties of ceramics are the biocompatibility and chemical stability. Subsequently, the metal cores were replaced by ceramic cores and the strongest dental ceramic commercially available is 3 mol% yttria stabilized tetragonal zirconia polycrystals (3Y-TZP), shortened as zirconia below. This zirconia has become the most popular choice for the dental core and multiple units framework [4].

The porcelain veneered zirconia all-ceramic restorations once were considered as the most promising combination of strength and esthetics. However, the frequently observed chipping of veneering porcelains reduced this anticipation [5–7]. The chipping of veneers was mainly caused by poor

*Corresponding author. Tel./fax: +86 1062179977.
E-mail address: xinzwang.dent@gmail.com (X. Wang).

0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2013.05.036

Please cite this article as: J. Zhao, et al., Bi-colored zirconia as dental restoration ceramics. Ceramics International (2013), http://dx.doi.org/10.1016/j.ceramint.2013.05.036

bonding between porcelain–zirconia [8] and has not yet been solved, although improvements have been reported [9–11]. It was also observed that the veneered layer-construction decreased the strength significantly compared to the monolithic construction [12]. This behavior is expected as the strength of multilayer materials depends on the weakest component; in the veneered crowns being the brittle porcelain. The bending strength of porcelain is only around 100 MPa and porcelain has a very low toughness causing fracture under high biting load [13]. The success of traditional layer-by-layer veneering procedure is dependent on labor technicians with high technical skill and the procedure is very time-consuming. Therefore, full-contour dental zirconia restorations without a need of veneering are highly desired nowadays [14].

Color is one of the first properties to be consider for the esthetic appearance of an artificial tooth [15]. Most of the available commercial zirconia ceramics give white color upon sintering, which disagrees from most natural teeth. Although series of coloring liquids are available for dental zirconia ceramics, the final restorations will be colored homogeneously. They cannot reproduce the gradient color of the natural teeth, which is the integral effect of translucent enamel and yellow dentin [16]. In this case, the requirement of veneers for esthetic purpose can hardly be eliminated.

For mimicking the color gradient appearance of a natural tooth, one possible way is to manipulate the distribution of the coloring additives within one single zirconia block. This novel esthetic zirconia block contains several structure layers with different coloring additive arranged in desirable orders. It could be regarded as a kind of Functional Gradient Material (FGM), where the function refers to the esthetic property. Combined with the advanced CAD/CAM technique, the full-contour zirconia restorations can be shaped from such blocks and are expected to exhibit satisfied esthetic effects for direct use in the posterior regions.

The so far established process for producing machinable zirconia blocks is dry pressing of thermal-spray granulated zirconia powders into green bodies followed by partial sintering. These porous blocks can be milled, then sintered to full density and give individually shaped restorations [17]. With the development of pre-colored zirconia powders, it appeared possible to fabricate layered and differently colored esthetic zirconia blocks based on the existing equipment and processes. The aim of this study was to investigate the feasibility of the new process and evaluate the mechanical properties and microscopic features of a bi-colored zirconia pilot dental material.

2. Materials and methods

2.1. Sample preparation

Two commercial 3Y-TZP powders manufactured by Tosoh Cooperation (Tokyo, Japan) were selected, namely, TZ-3YSB-E (Lot SY301041B) and TZ-YELLOW-SBE (Lot S300033B). They will yield ceramics with two different colors after sintering. The former gives after sintering a white body and the latter one becomes yellow, due to doping with a small amount of Fe_2O_3 (0.202 wt%). Both of them are provided as thermal-sprayed granules aimed for direct dry pressing. Bi-colored 3Y-TZP discs were made by uniaxial dry pressing of the same amount of each powder in a stainless steel die one layer above another under 2 MPa pressure for 1 min, followed by cold isostatic pressing (CIP) under 200 MPa. Pressureless sintering was performed in air at 900 °C to make a partly solidified bulk that could be easily shaped by milling. Rectangular bars were cut from this bi-colored zirconia disc and then fully sintered at 1450 °C for 2 h. A color gradient zone was observed in the middle of the bars. All the experimental bars were grinded and polished to a fineness of 1 μm using a series of diamond polishing papers. The final dimensions of the test bars were $20 \times 4 \times 1.2$ mm^3 with edge chamfers suitable for four-point bending test according to ISO 6872:2008(E) [18]. The bars were ultrasonically cleaned in acetone solution and deionizer water for 5 min, respectively. Fig. 1 shows a photograph of the 20 mm long test bar of the bi-colored type. Two reference groups were made from pure white or yellow zirconia powders, respectively, through the same way as the bi-colored group but just with one dry pressing. Ten bars in each group were prepared for bending test.

2.2. Characterizations

The sintering shrinkage behavior of the two different zirconia powders was investigated by using a contact-mode dilatometer (Bähr-Thermoanalyse, Hüllhorst, Germany). The powders were sintered at a heating rate of 3 °C/min up to 1450 °C and hold for 2 h. The density of the sintered samples was determined in water by Archimedes' method. The theoretical density of 3Y-TZP is calculated to be 6.10 g/cm^3.

The microstructure of the bi-colored zirconia samples was investigated by scanning electron microscopy (SEM, JEOL JSM-7000F, Tokyo, Japan). For achieving a better contrast, the samples were thermally etched at 1250 °C for 1 h before being coated with a thin carbon layer to avoid charging effects. For evaluating the interior microstructure, one sample was cross-section polished (CP) by an ion beam polisher (JEOL SM-09010, Tokyo, Japan) at the color gradient zone. The grain sizes in three different regions (white, yellow and the color gradient zone) were measured by the lineal intercept method. The reported mean grain size was calculated according to ISO 13356:2008 [19].

Fig. 1. A photo showing a 20 mm long bi-colored zirconia test bar prepared for four-point bending test.

Please cite this article as: J. Zhao, et al., Bi-colored zirconia as dental restoration ceramics. Ceramics International (2013), http://dx.doi.org/10.1016/j.ceramint.2013.05.036