Li_2O-MgO-B_2O_3-Al_2O_3-SiO_2 GLASS-CERAMIC FOR DENTAL VENEERING APPLICATION

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Abstract

Spodumene-cordierite (Li_2O-MgO-Al_2O_3-SiO_2) glass ceramic and borosilicate glass (Pyrex) are used as veneering materials due to theirbio-inertness, high thermal shock resistance, and low thermal expansion coefficient which is compatible with silicon nitride ceramic dental cores. This study has focused on the study of the phase analysis, hardness, and improved appearance of glass ceramics prepared by melting 1.9 wt% Li_2O, 3.2 wt% MgO, 7.4 wt% B_2O_3, 16.5 wt% Al_2O_3, 65.8 wt% SiO_2, 2.5 wt% ZrO_2, 1.25 wt% P_2O_5, and an addition of 2.5 wt% Na_3AlF_6 (cryolite) at 1450°C for 1 h. The glass melts were then quenched in water to make glass frits. After dry grinding with aplanetary mill at 300 rpm for 30 min, the prepared veneer powders were mixed with polyvinyl alcohol solution as a binder and were then coated on the sintered silicon nitride ceramic dental cores using a paint brush. The specimens were fired in an electrical tube furnace in the temperature range of 900-1100°C for 5 min and then soaked at 790°C for 1 h. The veneered specimen at 950°C shows a good appearance, rather white and semi-opaque, and a smooth and glossy surface without any defects or crazing. The veneering materials have a low thermal expansion coefficient of about $2.7\text{-}5.0 \times 10^{-6}$°$C^{-1}$ which is suitable for the silicon nitride ceramic dental cores. The Vickers hardness of the prepared samples is about 4.0-4.5 GPa which is close to that of human teeth.

Keywords: Spodumene-cordierite glass ceramic, borosilicate glass, silicon nitride ceramic, dental core

Introduction

Silicon nitride (Si_3N_4) has many useful properties such as high fracture toughness, hardness, strength, wear resistance, and biocompatibility. Therefore Si_3N_4 ceramics are widely used in engineering applications such as cutting tools, abrasive materials, components of engines, and bio-implant materials such as hip-joints and knee replacements (Mazzocchi and Bellosi, 2008).

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Dental materials in the past were made from metal which has a problem in that patients would suffer from toxic metal oxide and metal alloy allergy reactions with oral tissue such as inflammation, swelling, bleeding, and appearance (Schmalz and Garhammer, 2002). Consequently, ceramic restorations have been developed to fulfil patients' requirements; yttria-stabilised zirconia has been developed to be used as a dental material due to its mechanical properties but it has a problem of long-term use. Several reports indicate that water can deteriorate the zirconia lattice in a humid atmosphere. This will cause the formation of tensile stresses in the surface grains that leads to destabilization of the tetragonal phase and failure in the future (Schubert and Frey, 2005; Chevalier and Gremillard, 2009). Thus, the authors are interested in finding a new dental material and Si_3N_4 ceramicis a proper candidate because of its better mechanical and biocompatibility properties. However, Si_3N_4 ceramic has a dark or grey color which is not suitable for use as a dental material.

The authors synthesized the white colour and high density Si_3N_4 ceramics by sintering at 1650°C in a nitrogen atmosphere (Wasanapiarnpong *et al.*, 2006). From its appearance, Si_3N_4 ceramic can be a good candidate to be used as a dental core material. Moreover, Si_3N_4 has low thermal expansion. The core surface must be coated with a low thermal expansion veneering material which has thermal compatibility so that they work together as false teeth. From our previous work, (Wananuruksawong *et al.*, 2011) borosilicate glass with zirconia 5 wt% added was used as a veneer due to its chemical resistance and bio-inertness. In this study, spodumene-cordierite glass ceramics were selected to be the veneering material with low thermal expansion (Majumdar, 1998) which is close to a dental core with added borosilicate glass for non-cytotoxicity and added metal oxide for colour control of the veneer so as to be suitable for each patient (Karkhanavala and Hummel, 1953; Junlar *et al.*, 2011)

Materials and Methods

Si_3N_4 Preparation

The raw materials consist of high purity α-Si_3N_4 powders (particle size 0.8 μm, SN E-10 grade, Ube Industries Ltd., Tokyo, Japan) with Y_2O_3 (RU, Shin-Etsu Chemical Co. Ltd., Tokyo, Japan), SiO_2 (KE-P30, Nippon Shokubai Co. Ltd., Osaka, Japan), and MgO (MJ-30, surface area 31.7 m²/g, Iwatani Corp., Tokyo, Japan) as sintering aids. The Si_3N_4 dental core was mixed in the calculated ratio (the weight ratio of silica:magnesia: yttria is 3:3:5) to synthesize dense and white dental cores. Then, the powders were mixed by ball milling in a polyethylene bottle with Si_3N_4 balls in ethanol for 24 h. After drying by a rotary evaporator at 60°C for 45 min and screening through a sieve (number 100 mesh), the powders were pressed at 40 MPa into pellets and then sintered at 1650°C for 2 h in anitrogen atmosphere. The densities of the sintered Si_3N_4 were determined by water displacement technique based on the Archimedes' principle.

Veneering Preparation

Veneering materials were prepared by melting borosilicate, spodumene, and cordierite (Sp-Cor-Boro) composed of 1.9 wt% Li_2O, 3.2 wt% MgO, 7.4 wt% B_2O_3, 16.5 wt% Al_2O_3, 65.8 wt% SiO_2, 2.5 wt% ZrO_2, 1.25 wt% P_2O_5, and 2.5 wt% Na_3AlF_6 (cryolite) at 1450°C for 2 h and then quenched in water to make glass frits. After being dry-ground by planetary milling at 300 rpm for 30 min, the prepared veneer powders were mixed with 10 wt% polyvinyl alcohol solution as a binder and then were coated on sintered silicon nitride dental cores with a paint brush. The specimens were fired in an electrical tube furnace in the temperature range of 900-1100°C for 1-15 min and then cooled down to 790°C and soaked for 1 h. The thermal analysis of the veneering material was measured from room temperature to 1200°C by differential scanning calorimetry (DSC),

(STA449C, Netzsch-Gerätebau GmbH, Selb, Germany). The microstructural studies were focused on the area between the veneer layer and the dental core under a scanning electron microscope (SEM), (JSM 6480LV, JEOL Ltd., Tokyo, Japan). The hardness values of the veneering materials coated on the dental core were measured by a Vickers hardness tester (HV-50A, Laizhou Huayin Testing Instrument Co. Ltd., Laizhou, China). The coefficient of thermal expansion (CTE) of the specimens was measured with adilatometer (402C, Netzsch-Gerätebau GmbH, Selb, Germany). X-ray diffraction (XRD) analyses were performed for analysing the phase of the veneering. An X-ray diffractometer (D8-Advance, Bruker Corp., Billerica, MA, USA) was used with Cu-K$_\alpha$ radiation, and the diffraction data were collected over the 2θ range from 10 to 80° with a step size of 0.02°.

Results and Discussion

Thermal Analysis by DSC

The DSC method was used to study the thermal behaviour of the veneering material by heating from room temperature to 1200°C under air atmosphere.
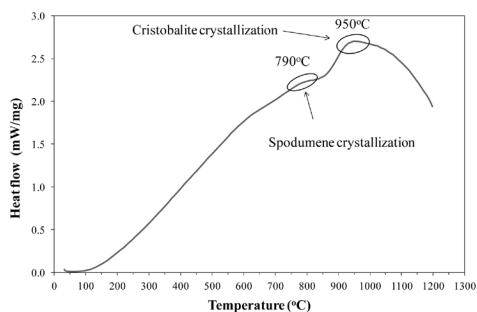
Figure 1 shows the DSC curve of spodumene-cordierite-borosilicate glass ceramic which indicates that this glass has an endothermic process around 790°C and 950°C. To study further, glass powder was coated on dental cores and fired at 790°C and 950°C and then soaked for 1 h.

Phase Identification by XRD

The XRD analysis was performed to study the crystalline phase of the veneering material. Figure 2 shows the XRD pattern of spodumene-cordierite-borosilicate glass fired at 790°C and soaked for 1 h. The XRD pattern reviews the peaks of beta-spodumene, cristobalite, and quartz. Figure 3 shows the XRD pattern of spodumene-cordierite-borosilicate glass fired at 950°C and soaked for 1 h. The XRD pattern reviews the peaks of beta-spodumene, cristobalite, and quartz. The intensity of the peaks of cristobalite and quartz are increasing which causes higher thermal expansion that leads to incompatibility between the veneering and the dental core.

Figure 4 reviews the XRD patterns of spodumene-cordierite-borosilicate glass fired at 900, 950, 1,000, 1050, and 1100°C and which was soaked for 5 min and then soaked at 790°C for 1 h. The XRD patterns review the peaks of cristobalite and quartz. With
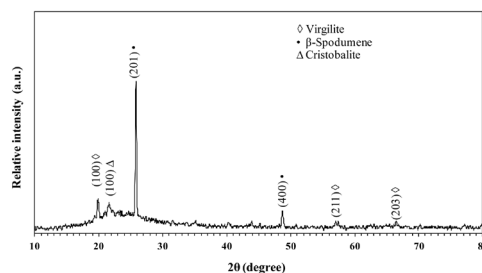

Figure 1. The thermal analysis (DSC) of SP-Cor-Boro veneering material measured from room temperature to 1200°C which shows endothermic peaks at 790°C and 950°C

Figure 2. XRD pattern of spodumene-cordierite-borosilicate glass fired at 790°C and soaked for 1 h

increasing the temperature, the intensity of the peaks of cristobalite and quartz increased. This may cause specimens to have higher thermal expansion values which lead to causing incompatibility between the veneering material and the dental core, as shown in Figure 5.

Appearance of Dental Material

Figure 5 reviews the veneered specimens coated with spodumene-cordierite-borosilicate glass ceramic which have been sintered at 950, 1000, 1050, and 1100°C, soaked for 5 min, and then soaked at 790°C for 1 h, respectively. Figure 5(a) shows a smooth and glossy surface. With increasing the temperature, the surface of the specimens shows more crazing and pinholes. Figure 5(a) shows a better appearance than the others.

Microstructure by SEM

Figure 6 shows the SEM micrograph at a magnification of × 1,000 that reviews the interface between the silicon nitride ceramic core and spodumene-cordierite-borosilicate glass veneered and fired at 950°C with a soaking time of 5 min and further soaking at 790°C for 1 h.

Figure 7 shows SEM micrographs of the specimens with a magnification at × 250 that reviews the good adhesion between the veneered layer and the dental core. When the temperature was increased, the veneer layers showed more bubbles and pinholes which may be due to over-firing of the veneering materials.

Coefficient of Thermal Expansion of Specimens by Dilatometer

Table 1 shows the CTE of the spodumene-cordierite-borosilicate glass specimens coated on silicon nitride pellets and fired and sintered at 950, 1000, 1050, and 1100°C, and which were soaked for 5 min and then soaked at 790°C for 1 h.
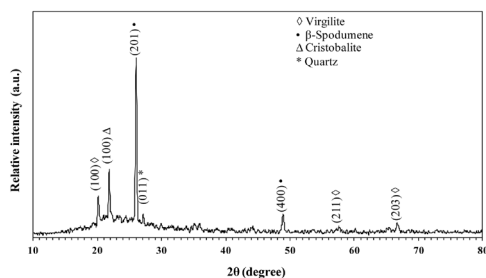
From the CTE results, the CTE values

Figure 3. XRD patterns of spodumene-cordierite-borosilicate glass fired at 950°C and soaked for 1 h
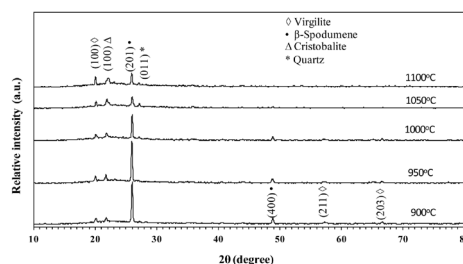

Figure 4. XRD patterns of spodumene-cordierite-borosilicate glass fired at 900, 950, 1000, 1050, and 1100°C and soaked for 5 min then cooled down to 790°C for 1 h, respectively
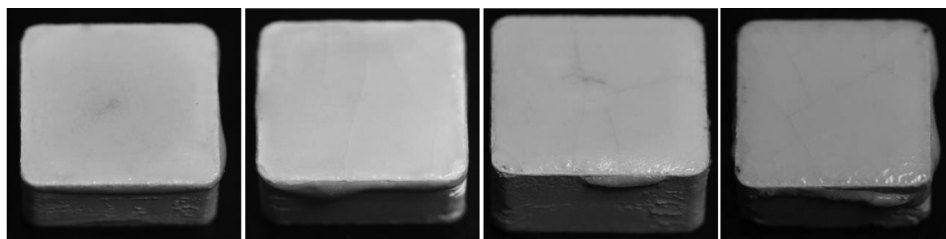

Figure 5. Veneered specimens with spodumene-cordierite-borosilicate glass fired at (a) 950, (b) 1000, (c) 1050, and (d) 1100°C which were soaked for 5 min and then cooled down to 790°C and soaked for 1 h, respectively

slightly increased when the firing temperature was increased which leads to causing incompatibility between the veneering material and Si_3N_4 dental core. The surfaces of the veneers show more crazing defects.

Hardness Value by Vickers Hardness

The hardness value of the dentures is an important property in their application. If the hardness value of dentures is higher than that of human teeth, it may cause damage or deterioration from the collision between false teeth and human teeth (Mohammad *et al.*, 2003)

The hardness value was measured with a Vickers hardness tester based on the indentation technique. This technique has been selected for the study of dental ceramics because it is suitable for specimens which have a relatively small crack growth (Seghi *et al.*, 1995). Each sample was tested 5 times at random locations by pressing the indenter at 1 kgf for 15 sec. The Vickers hardness values of each specimen were calculated by the following Equation (1).
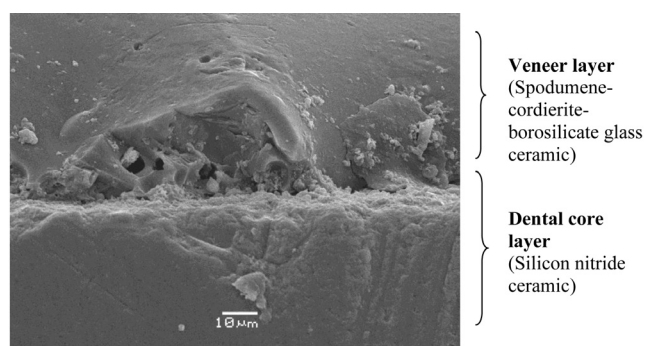

Veneer layer (Spodumene-cordierite-borosilicate glass ceramic)

Dental core layer (Silicon nitride ceramic)

Figure 6. SEM micrograph review of interface between silicon nitride ceramic core and spodumene-cordierite-borosilicate glass veneered and fired at 1100°C with soaking time of 15 min
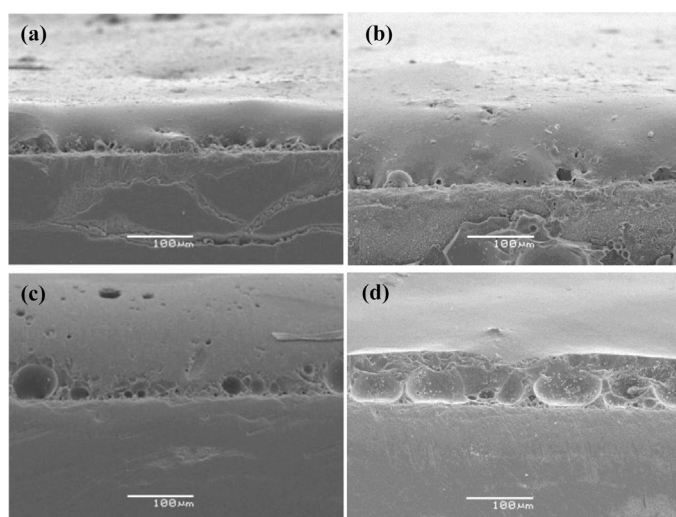

Figure 7. SEM micrographs of veneered specimens coated with spodumene-cordierite-borosilicate glass which were fired at (a) 950°C, (b) 1000°C, (c) 1050°C and (d) 1100°C soaked for 5 min and then cooled down to 790°C and soaked for 1 h, respectively

Table 1. Coefficient of thermal expansion of specimens

Veneering materials	CTE × 10⁻⁶/°C
Silicon Nitride (core : 1650°C)	3.48
Sp-Cor-Boro (950°C)	2.73
Sp-Cor-Boro (1000°C)	2.99
Sp-Cor-Boro (1050°C)	4.44
Sp-Cor-Boro (1100°C)	5.02

Table 2. Vickers hardness of specimens

Veneering materials	Vickers hardness (GPa)
VMK (standard)	4.9
Sp-Cor-Boro (950°C)	4.33
Sp-Cor-Boro (1000°C)	4.33
Sp-Cor-Boro (1050°C)	4.36
Sp-Cor-Boro (1100°C)	4.49

$$HV = \frac{1.8544(9.807P)}{d^2} \qquad (1)$$

HV is the Vickers hardness value, P is the indentation load (P = 1 kgf), and d is the average diagonal length that is calculated by the 2 diagonal lengths left by the indentation. The Vickers hardness values of veneering materials are close to human teeth (3-5 GPa). From Table 2, the Vickers hardness values of spodumene-cordierite-borosilicate glass fused at 950, 1000, 1050, and 1100°C and which was soaked for 5 min and then soaked at 790°C for 1 h, respectively, are close to VMK (a commercial veneering material) which is similar to human teeth (3-5 GPa) (Park *et al.*, 2008).

Conclusions

The spodumene-cordierite-borosilicate-glass prepared by firing at 950°C have a well-matched surface with the white sintered Si_3N_4 which was obtained by pressureless sintering at 1650°C, due to its similar CTE values. The appearance of the veneered specimens has shown whiteness, vitrification, smooth surfaces, and semi-opaqueness. The hardness values of the veneers are similar to human teeth (3 to 5 GPa). Therefore, white sintered Si_3N_4 coated with spodumene-cordierite-borosilicate-glass can be used as a dental material.

Acknowledgements

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