Toughening of CAD/CAM all-ceramic crowns by staining slurry

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The ability of staining slurries containing silver and/or potassium compounds to enhance the mechanical properties of a leucite-reinforced glass ceramic (IPS Empress CAD) was investigated by measuring the Vickers hardness, median crack length, toughness, and compressive residual stress of specimens. A staining slurry containing potassium ions was found to increase the toughness of IPS specimens more than a staining slurry containing only silver ions when applied prior to sintering. None of the staining slurries produced any color changes. Thus, the results obtained in this study demonstrate that staining slurries increase the Vickers hardness and the fracture toughness of the surface and subsurface regions of all-ceramic IPS blocks fabricated by a CAD/CAM system without sacrificing their aesthetics.

Keywords: CAD/CAM, Staining slurry, Silver, Potassium, All-Ceramic Crowns

INTRODUCTION

Porcelain is a vitreous material that has a high permeability, is excellent for reproducing crown color, is hygienic since it is not water absorbent or soluble, and has outstanding biocompatibility\(^1\). However, unlike metals, porcelain is not malleable or ductile. Consequently, it readily cracks and breaks with virtually no deformation when an excessive occlusal force is applied. Endodontic fittings made from porcelain sometimes fracture or chip due to the application of a strong occlusal force or impact generated by bruxism, which necessitates replacing the fitting\(^2,3\).

The application of a clinically controlled occlusal force to prevent the breakage of porcelain has been investigated. This technique is partly based on the assumption that it is not possible to improve the mechanical strength of porcelain; the results obtained to date have been disappointing\(^4,5\). Another method to prevent the breakage of porcelain is \textit{in vitro} toughening of the material. One technique for realizing this involves rapid cooling, which introduces a residual surface compressive stress due to differential contraction between the treated surface and the subsurface region\(^6\). Ion exchange strengthening is a chemical process in which large alkaline ions such as potassium are substituted into porcelain surface sites that are occupied by smaller ions such as sodium\(^7,8\). Another technique is dispersion reinforcement by ceramic particles such as alumina\(^9\) and leucite\(^8,10\), which can hinder crack propagation in porcelain.

We found that incorporating silver nanoparticles in porcelain increased its fracture toughness and Vickers hardness\(^11\). Two possible mechanisms have been proposed for this toughening of porcelain by silver nanoparticles: the ductility of silver improves the toughness by crack bridging and deflection\(^12-14\) and strengthening occurs on ion exchange due to the introduction of silver ions\(^11\). The latter mechanism is supported by the observation that the introduction of silver ions into glass by a silver compound slurry strengthens the material\(^15,16\).

In this study, we compared the effects of introducing silver and potassium ions by a commercial staining slurry on the Vickers hardness and fracture toughness of CAD/CAM blocks.

MATERIALS AND METHODS

Blocks of a leucite-reinforced glass ceramic, IPS Empress CAD CEREC (Ivoclar Vivadent, Schaan, Liechtenstein; hereafter, referred to as IPS blocks (SiO\(_2\), Al\(_2\)O\(_3\), K\(_2\)O, Na\(_2\)O, CaO, the others)) were cut into 1-mm-thick plates (14×12×1) using a precision cutting machine (MPC-200, Musashino Electronics, Tokyo, Japan) and polished to #4000 using SiC waterproof abrasive paper in a polisher (Abramin, Struers, Copenhagen, Denmark). Five groups of three plates were prepared. Table 1 lists the brand names, codes, and compositions of the staining slurry in which silver carbonate and/or potassium nitrate were dispersed. For example, AgK0 contains 10 wt% Ag\(_2\)CO\(_3\) in a staining slurry consisting of a pigment, a cellulose-based resin, diethyl glycol, and terpineol (Okuno Chemical Industries Co. Ltd., Osaka, Japan). G3-5295, G3-5296, G3-5297 are trial products. In order to make them in the same condition, all the ingredients are the same, but the contents of Ag\(_2\)CO\(_3\) and KNO\(_3\) are

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different. The slurries were applied with a brush to three plates of each group. The plates were then fired in a porcelain furnace (Denken, KDF Master Summit J100, Kyoto, Japan) using the firing cycle recommended by the manufacturer (drying time: 1 h; temperature rise rate: 50°C/min; vacuum pressure: 70 cm Hg; initial temperature: 200°C; final temperature: 500°C; mooring time: 1 h; rapid cooling). Flowchart of specimen preparation is shown in Fig.1. For comparison, control specimens (Ag0K0) were produced by firing three plates that had not been treated with a staining slurry under the same conditions.

When staining slurry is used in clinically restorations, All-Ceramic Crowns which are manufactured with CAD/CAM supposed to be applied staining slurry and fired in a porcelain furnace.

Vickers hardness and crack length measurements by indentation fracture method

The each three plates used a microhardness tester (HMV, Shimadzu Co., Kyoto, Japan), a Vickers indenter was pressed into five areas on each specimen for 15 s at a load of 9.807 N and the Vickers hardness (Hv) was calculated from the diagonal length of the pressure impression. The lengths of median cracks (2a1, 2a2) (Fig.2) that extended from the edge of the pressure impression were measured by the method given in JSMS SD401 (JSMS, 2001) and the mean value of 2a was calculated.

Young modulus
To estimate the Young modulus, IPS blocks were cut into 14×4×1-mm three plates were cut using a precision cutting machine (MPC-200, Musashino Electronics, Tokyo, Japan) and polished to #800–4,000 using three water proof SiC abrasive paper. Strain gauges (KFG-1N-120-C1-11L1M2R; Kyowa Dengyo Co., Tokyo, Japan) were adhered to the central area of each specimen and connected to a dynamic strain measurement system (DSA-606B, Minebea Co., Nagano, Japan) via a bridge box (Minebea Co., Nagano, Japan). Three-point bending tests (JIS-R1602) were performed using a universal test machine (EZGraph, Shimadzu Co., Kyoto, Japan) at a cross-head speed of 0.1 mm/min and a fulcrum separation of 12 mm. It has been applied on the surface then. The Young modulus, E (GPa), was calculated from the load (N) and the strain using:

\[ E = \frac{3l(P_2 - P_1)}{2w^2(\varepsilon_{S2} - \varepsilon_{S1})} \]  (1)

where \( P \) is the load (N), \( l \) is the distance between the fulcrums (m), \( w \) is the width of the specimen, \( t \) is the thickness of the specimen, and \( \varepsilon \) is the strain.

Toughness
The toughness, \( K_{IC} \) (MPam\(^{1/2}\)), was calculated using:

\[ K_{IC} = 0.026 \frac{E^{1/2}P^{1/2}d}{a^{3/2}} \]  (2)

where \( a \) is half the crack length (m) and \( d \) is the diagonal length of the pressure impression (m).

![Flowchart showing specimen preparation.](image-url)
Residual stress
The residual stress, $\sigma$, before and after heating was calculated from the Young modulus $E$, the toughness $K_{IC}$, and the parameters $a$, $d$, and $P$ in Eq. (2) using\textsuperscript{17}

$$\sigma = \frac{K_{IC}(\pi a)^{-1/2} - 0.026(EP/\pi)^{1/2}(d/2)(a)^{-2}}{M}$$

where the correction factor $M=1.4$. Negative (positive) values of $\sigma$ indicate compressive (tensile) residual stress.

Color measurements
The colors of 1-mm-thick each three plates (14×12×1) that had been polished in the manner described above were measured. The color was determined in the range 200–780 nm according to the CIE $L^*a^*b^*$ color scale relative to a standard white tile made of barium sulfate (CIE $L^*=100$, $a^*=0$, $b^*=0$) using a spectrophotometer (UV-3600, Shimadzu Co., Kyoto, Japan) that equipped with an integrating sphere. $L^*$ is a measure of the lightness, $a^*$ is a measure of the redness (positive direction) or greenness (negative direction), and $b^*$ is a measure of the yellowness (positive direction) or blueness (negative direction) of an object. Measurements were repeated three times for the three specimens of each sintered body. To evaluate the effect of the staining slurry after sintering, the color difference ($\Delta E^*$)\textsuperscript{18} was calculated using $\Delta E^* = [(L^*_1 - L^*_2)^2 + (a^*_1 - a^*_2)^2 + (b^*_1 - b^*_2)^2]^{1/2}$, where the subscripts 1 and 2 denote sintered specimens without and with a staining slurry, respectively.

![Fig. 2](image_url) Vickers indentation with Median cracks induced (2a1, 2a2).

![Fig. 3](image_url) Vickers hardness (Hv) (a), median crack length (2a) (b), toughness ($K_{IC}$) (c), and compressive residual stress (d) of sintered specimens of A0K0, AgK0, Ag2K1, Ag1K2, and Ag0K.
Statistical analysis

The values of Hv, 2a, E, KIC, residual stress, \( \Delta E^* \) and CIE \( L^*a^*b^* \) were expressed as mean±standard deviation and evaluated by one-way analysis of variance using the Bonferroni method with a statistical significance of 0.05.

Focused ion beam milling to expose cross sections

Specimens were sputter coated with platinum (80%) and palladium (20%) to prevent charging. Carbon was coated on the area of interest to prevent it being damaged by the gallium ion beam. A “staircase” mill19) was formed to create a cross section using a focused ion beam (FIB) system (SMI2050, SII Nano Technology, Chiba, Japan) operating at an accelerating voltage of 30 kV. The staircase was approximately 20 µm×20 µm at the opening and was a few micrometers deep. It was formed by rough milling (beam current: 5300 pA; aperture width: 300 nm), milling (beam current: 1300 pA; aperture width: 100 nm), and fine milling again (beam current: 200 pA; aperture: 35 nm) to smooth and polish the cross section.

Scanning electron microscopy and energy-dispersive X-ray analysis

For AgK0 and Ag1K2, cross sections that had not been coated, were observed at a low accelerating voltage of 5 kV to prevent charging (tilt angle: 45°) using a field-emission scanning electron microscope (FE-SEM, S-4700, Hitachi Ltd., Tokyo, Japan). Some specimens were subjected to elemental analysis using a Falcon energy-dispersive X-ray (EDX) detector coupled to the FE-SEM at an accelerating voltage of 15 kV.

RESULTS

Figure 3 shows the Vickers hardness, Hv (a), median crack length (b), toughness, \( K_{IC} \) (c), and compressive residual stress (d) of the sintered specimens Ag0K0, AgK0, Ag2K1, Ag1K2, and Ag0K.

As Fig. 3(a) shows, there is no apparent relation between Hv and either the Ag content or the KNO3 content of the stain. However, AgK0 (599±39) and Ag1K2 (589±59) have significantly higher Hv than the controls, Ag0K0 (525±22) and Ag2K1 (537±31). There were no significant differences in the Vickers hardnesses of AgK0 and Ag1K2, of Ag0K0 and Ag2K1, and of Ag0K and the other specimens.

Figure 3(b) shows that both Ag and KNO3 stains reduced the crack length (the latter reduced it more than the former); the crack length decreased approximately in proportion with the KNO3 content of the stain; i.e., in the order Ag0K0 (114.1±2.9)>Ag0K1 (107.1±5.3)>Ag2K1 (83.5±1.0)>Ag1K2 (62.8±3.3)>Ag0K (60.0±1.7).

The fracture toughness, \( K_{IC} \), increased in the order Ag0K0 (1.34±0.22), Ag0K (2.41±0.74) relative to Ag0K0 were significantly smaller than \( \Delta E^* = 2.64 \), which Chang et al. considered to be the perceptibility threshold16. AgK0 (68.08±0.54), and Ag1K2 (70.53±0.20) had significantly smaller values of \( L^* \) than Ag0K0 (71.14±0.74), whereas Ag0K (73.38±0.30) had a significantly larger value of \( L^* \) than Ag0K0. Ag0K (2.59±0.16), and Ag1K2 (2.78±0.04), and Ag0K (2.73±0.05) had significantly smaller values of \( a^* \) than Ag0K0 (3.11±0.42), Ag0K0 (25.62±0.61), and Ag1K2 (25.92±0.03), and Ag1K2 (26.25±0.08) had significantly larger values of \( b^* \) than Ag0K0 (25.43±0.05), whereas Ag0K (24.78±0.1) had a significantly smaller value.

Figure 4 shows scanning electron microscopy (SEM) images of the surface of AgK0 and a cross section of Ag1K2 together with their corresponding EDX spectra showing the elements that are present. A small area (diameter: approximately 2 µm) that appeared gray in the SEM image of AgK0 was rich in Ag (as demonstrated by the EDX spectrum that contained a peak at an energy of 3 kV). However, no similar areas were observed in the cross section (data not shown) and no Ag was detected.

<table>
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<th>N</th>
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<th>SD</th>
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**p<0.01
* p<0.05
in the cross section at depths of 2 or 4 µm from the outer surface. Ag-rich areas were not observed on either the surface or the cross section of Ag1K2. A clear distinction in the potassium content was not observed because potassium was present in the CEREC block.

**DISCUSSION**

All-ceramic crowns have been fabricated by carving them out of IPS blocks or porous, hypodense sintered blocks using a CAD/CAM system, allowing glass to infiltrate the pores after processing to produce a glass-infiltrated ceramic, and then re-sintering to increase their density and strength. This is a much more efficient fabrication technique than the conventional method, which involves a technician manually aggregating powder and burning it to reproduce the form. The above-mentioned blocks have fewer internal defects and are physically more stable than a fired powder/burnt body; in the latter case, while the core is very strong, the outer layer may break as the result of the application of excessive occlusal force or bruxism, which may cause chipping or breakage to occur when an all-ceramic crown is fitted in the oral cavity. It is thus necessary to toughen the porcelain layer to increase the success rate of clinical all-ceramic crown treatment.

In a previous study, which used silver nanoparticles rather than silver ions, silver nanoparticles were found to toughen the porcelain layer. Although the color changes induced by the inclusion of silver nanoparticles are within the range acceptable for Japanese teeth, as reported by Ueda, they were significantly greater than ∆E* = 2.69, which Chang et al. considered to be the perceptibility threshold. In contrast, the inclusion of silver ions did not significantly alter the color of IPS blocks (see Table 2). Nevertheless, it did significantly increase Hv and reduce the median crack length of pressure impressions on IPS specimens (see Figs. 1(a) and (b) for AgK0).

In industry, silver-ion-containing glass, which can be easily laser processed, is called light-workable glass. In such glass, the Si–O–Si bonds of SiO₄ tetrahedrons, which are connected via the oxygen at the top and form an oxygen-bridging structure, are broken by the positively charged silver ions (Si–O–Ag⁺ for Si–O–H⁺), resulting in the formation of a non-oxygen bridging
structure. Compared with untreated glass, light-workable glass, whose surface has been subject to silver ion exchange, has a significantly reduced processing threshold; furthermore, almost no cracks or damage have been reported to occur in the treated portion. These increases in Kc and compressive residual stress are caused by the formation of a non-bridging oxygen structure that contains silver ions and ion exchange between silver and sodium ions.

Unexpectedly, the inclusion of Ag ions alone in IPS blocks did not alter the toughness, Kc, or the compressive residual stress (see Figs. 1(c) and (d)). On the other hand, the staining slurry that contained only potassium ions (i.e., Ag0K) greatly increased the toughness of IPS blocks when it was applied before firing. Since the ion concentration for potassium is three times (about eight times) greater than silver on a weight (molar) basis, this effect may simply be due altering the ion concentration.

Ag2K1 and Ag1K2 have approximately the same silver ion concentrations, whereas the potassium ion concentration is about 3.5 times higher in the latter and Ag1K2 has a significantly higher Kc. This suggests that the toughness increases as the potassium ion concentration is increased in the staining slurry through ion exchange by which sodium ions in the IPS glass are replaced by alkaline ions such as potassium that have a larger radius; this difference in ionic radius is thought to generate compressive stress at the surface. Since the radius of a potassium ion (133 pm) is slightly greater than that (126 pm) of a silver ion, K+ ions will generate greater compressive stress on the surface of an IPS block than Ag+ ions when both ions have the same ion exchange efficiency with Na+ ions (i.e., K+ for Na+ and Ag+ for Na+)30).

Since potassium was abundant in the IPS blocks, analysis of the potassium distribution in IPS blocks after treatment by a staining slurry such as Ag1K2, Ag2K1, and Ag0K would not be meaningful. Instead, the silver ion distribution was investigated. Cross sections, which were very difficult to obtain by conventional methods, were milled by a FIB system that did not introduce artifacts. However, except for a very limited area, no silver was detected (see Fig. 3). This finding may indicate that silver ions are evenly distributed on the surface of IPS blocks and that the silver concentration is below the detectable level of the EDX detector in the present study.

CONCLUSION

Treatment by a staining slurry increased the Vickers hardness of the surface of IPS blocks and inhibited crack propagation. A staining slurry containing potassium nitrate generated compressive residual stress and consequently increased the fracture toughness. No color changes were observed after sintering IPS blocks treated by the staining slurry used in the present study. This finding suggests that applying this staining slurry prior to sintering is promising for toughening the outer layer of all-ceramic crowns polished by CAD/CAM.

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