Evaluation of Brittleness of Porcelain Fused to Pure Titanium by Fracture Toughness, Hardness and Fracture Energy

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To elucidate the cause of brittleness of porcelain fused to pure titanium (PFPT) which leads to chipping and cracking similar to that of conventional porcelain in clinical use, fracture toughness KIc, hardness (Hv and Hk) and fracture energy G reflecting the bonding energy of atoms were evaluated. In KIc there were no differences between PFPT and conventional porcelain, nor for Hv and Hk, but for the G of PFPT calculated from the KIc and the Young modulus measured by the resonance method there was less than that of conventional porcelain. These results indicate that mechanical properties such as KIc and hardness cannot always substantiate the brittleness of PFPT experienced in practical use. However, a comparatively small G of PFPT may suggest a fatigue crack growth as a more likely phenomenon as it occurs more easily than the conventional one in oral.

Key words: Porcelain for pure titanium-ceramics, Fracture toughness, Fracture energy

INTRODUCTION

A requirement for restoring aesthetics to prosthetics has recently increased in importance. It is especially important that, a dental porcelain fulfill this requirement. Above all, a porcelain fused to pure titanium (PFPT) is best because titanium used as a core metal has good anti-corrosive characteristics, is very biocompatible, and can even be applied to patients with metal allergies.

Based on feed from a basis of follow-up survey, however, Kaus et al. reported that the breakage of facing porcelain frequently occurred in bridges, and so, proposed that PFPT be limited to use in a single crown. Our clinical follow-up survey also indicated that a chipping at the edge and cracking occur more frequently than with a conventional porcelain during clinical use. Bonding ruptures between porcelain and Ti have been also observed, but the mechanical properties of PFPT itself seem to be inferior to those of the conventional one in oral use.

The purpose of this study was to find the cause of clinical brittleness in PFPT.
Of mechanical properties, fracture toughness (KIC) is the most important and appropriate parameter in evaluating resistance against catastrophic fractures. The KIC of most dental porcelains\(^5\) has been measured using an indentation fracture (IF) method. The IF method is quite excellent for inter-comparisons\(^6\) of materials with a homogeneous structure, but it is considered that the values will be affected by a microstructure in composite materials like that of dental porcelain. Furthermore, the basic equation for calculating KIC is a semi-empirical one. In this study, a measurement of the absolute value of KIC was carried out using chevron notched beam (CNB) specimens. Vickers (HV) and Knoop (HK) hardness was also measured for comparison. In addition, to calculate the fracture energy \(\Gamma\) from KIC and Young modulus (E), elastic stiffness constants (\(C_{ij}\), \(i, j=1 \sim 6\)) were measured using the rectangular parallelepiped resonance (RPR) method\(^7\).

**MATERIALS AND METHOD**

**Preparation of specimen**

Descriptions of two PFPT (Duceratin, Ducera Co., Germany, and Titanium porcelain, Vita Co., Germany) and one conventional porcelain (Vintage halo, Shofu Co., Kyoto, Japan) used in this study are given in Table 1. A mixture of porcelain powder and water was put into a metal mold (12×15×50 mm) and condensed. After being dried in air, the porcelain powder cake was fired at times listed on the schedules shown in Table 2 in a porcelain furnace (KDF Master, Denken Co., Kyoto, Japan). These sintered blocks were cut into four rectangular parallelepiped bars (width B=3 mm, height W=4 mm and length 50 mm) and their surfaces and edges were finished according to JIS R-1607 Specimen I\(^9\). The crystal phases before and after firing were examined using an X-ray powder diffraction apparatus (RINT2000, 60kv, 300mA, Ni-filtered CuKa, Rigaku Co., Tokyo, Japan).

| Table 1 Descriptions of materials used in this study |
|---|---|---|---|
| Code | Materials | Manufacturers | Lot No. |
| DU | Duceratin | Ducera | 991319 |
| TP | Titanium porcelain | Vita | 6156K |
| VH | Vintage halo | Shofu | 069913 |

| Table 2 Firing schedule |
|---|---|---|
| Specimen | Start temperature (°C) | Final temperature (°C) | Temperature rise rate (°C/min) |
| DU | 450 | 710 | 10 |
| TP | 400 | 770 | 10 |
| VH | 680 | 930 | 10 |

Firing pressure<99KPa
Measurement of fracture toughness using the chevron notched beam method

The chevron notched beam (CNB) method does not require the making of a pre-crack in advance because the crack initiates at the tip of triangle during loading as shown in Fig. 1. The chevron notch was machined with a diamond notch blade 0.1 mm thick by use of a specimen holder for notching chevrons. The notch angles \( \theta \) and \( \alpha_i \) were set to 60 degrees and \( W \), respectively. The fracture load \( P_{\text{max}} \) was measured with a universal testing machine (Autograph AG-5000C, Shimadzu Co., Kyoto, Japan) using a 4-point-bend mode (upper span \( S_1=10 \text{ mm} \), lower span \( S_2=30 \text{ mm} \)) at a cross head speed of 0.1 mm/min. During measurement, the Ar gas atmosphere was maintained so that a so-called slow crack growth (SCG) did not occur. After testing, \( a_0 \) and \( a_1 (\div W) \) on the fracture surface were measured with a micrometer attached to a stereoscopic microscope. The \( K_{IC} \) was calculated by Equation (1) according to the method of Munz et al.:

\[
K_{IC} = \frac{P_{\text{max}} \cdot Y^{*\min}}{B \cdot W^{1/2}}
\]

where \( B \) (3 mm) and \( W \) (4 mm) are the thickness and the height of the specimen, respectively. \( Y^{*\min} \) is the minimum value of shape factor \( Y^* \) expressed by Equation (2) when the crack length is \( a \):

\[
Y^{*} = \left[ \frac{1}{2} \left( \frac{\partial C^*}{\partial a} \right) \left( \frac{a - a_0}{a - a_0} \right) \right]^{1/2}
\]

where \( a_0 = a_i/W, \) \( a_1 = a_0/W, \) \( a = a/W, \) and \( C^* = E^*BC \) is the dimensionless compliance given by \( E^* = E/(1 - \nu^2) \), where \( E \) is Young modulus and \( \nu \) is Poisson's ratio. The catastrophic fracture starts at \( P_{\text{max}} \) and \( Y^{*\min} \), and the crack length \( a_c \) at this point is obtained analytically. In this study, "C* of the specimen with the chevron notch was calculated by Bluhm's slice model in which a specimen with a trapezoidal crack was divided into \( n \) slices of uniform thickness regarded itself as a straight-through-crack. \( Y^{*\min} \) increased as the slice number increased and reached a constant. The present \( K_{IC} \) was calculated with \( n=5000 \). The number of specimens was five for each type of porcelain.

Measurement of hardness

Vickers hardness (Hv) and Knoop hardness (Hk) of the rectangular parallelepiped
bars were measured with a micro hardness tester (HMV-2000, Shimadzu Co., Kyoto, Japan) under a load of 200 g for 30 sec. 10 places on each porcelain specimen were then measured and averaged.

Elastic constants measurement using the rectangular parallelepiped resonance (RPR) method and calculation of fracture energy

According to the elastic theory, elastic moduluses such as young modulus are expressed by the elastic stiffness constants C_{ij} (i, j = 1~6). In this experiment, the rectangular parallelepiped resonance (RPR) method \(^7\) was employed to measure the C_{ij}. A rectangular parallelepiped specimen with edge lengths L_k (k = 1 to 3) was cut from a bar specimen prepared for KIc measurement. The mth observed resonance frequency, \(f_{m}^{\text{obs}}\) of specimens is written in a functional form as Equation (3):

\[
f_{m}^{\text{obs}} = f_{m}(C_{ij}, L_k, \rho)
\]

where \(\rho\) is specimen bulk density. As the values of L_k and \(\rho\) are measurable, the \(f_{m}^{\text{obs}}\) can be expressed using a Taylor series with respect to \(\Delta C_{ij} = C_{ij} - C_{ij}^t\) as Equation (4):

\[
f_{m}^{\text{obs}} = f_{m}^{\text{cal}} + \sum (\frac{\partial f_{m}^{\text{cal}}}{\partial C_{ij}}) \Delta C_{ij}
\]

where \(C_{ij}^t\) is the set of trial elastic constants and \(f_{m}^{\text{cal}}\) is the mth resonance frequency calculated using \(C_{ij}^t\) stated in the theory by Ohno et al. \(^7\). By minimizing \(|f_{m}^{\text{obs}} - f_{m}^{\text{cal}}|^2\) using the least squares method, \(\Delta C_{ij}\) can be determined as the amount of corrections from the trial value \(C_{ij}^t\). The series of \(f_{m}^{\text{obs}}\) were measured by a device as illustrated in Fig. 2. The specimen was supported by two transducers. A radio frequency signal was fed to the specimen via one transducer and the resonance vibration of the specimen was picked up by the other. The previous data \(^13\) was used as the first trial value for calculating \(f_{m}^{\text{cal}}\) and \(\frac{\partial f_{m}^{\text{cal}}}{\partial C_{ij}}\). A few alterations were made until further change in \(C_{ij}\) did not decrease the differences between \(f_{m}^{\text{obs}}\) and \(f_{m}^{\text{cal}}\).

![Diagram for resonance frequency measurement of rectangular parallelepiped specimen.](image-url)
Fracture energy $\Gamma$ can be computed by Equation (5) using $K_{Ic}$ and $E$ according to the fracture mechanics:

$$\Gamma = \frac{1}{2}K_{Ic}^2/E$$

(5)

where $E = E/(1 - \nu^2)$ in the plane strain. $E$ and $\nu$ are given by the isotropic elastic stiffness constants $C_{ij}$ from Equations (6) and (7), respectively.

$$E = \frac{(C_{11} - C_{12})(C_{11} + 2C_{12})}{(C_{11} + C_{12})}$$

(6)

$$\nu = \frac{C_{12}}{(C_{11} + C_{12})}$$

(7)

Observation of polished-etched surface and fracture surface

After measurement of $K_{Ic}$, the fracture surfaces were observed with SEM (JSM-35C, Japan electron Co., Tokyo, Japan). A mirror-like polished and etched surface was also observed with an optical microscope (VH-6300, KEYENCE Co., Osaka, Japan). The surface became mirror-like by being polished with 0.3 $\mu$m lapping film (3M Imperial Co., Tokyo, Japan) after being grinded with waterproof grinding paper up to #2000 (Sankyo Rikagaku Co., Saitama, Japan). The etching was done using a 5 wt% HF solution, so that the cracks formed around the leucite crystals could be clearly confirmed.

RESULTS

Fracture toughness and hardness

$K_{Ic}$ of the three porcelains are shown in Table 3, and illustrated in Fig. 3. Fig. 4 shows the Hv and Hk. A multiple comparison by Bonferroni/Dunn on these proper-

Table 3 Fracture toughness $K_{Ic}$ (MPa·m$^{1/2}$) of three porcelains

<table>
<thead>
<tr>
<th>Specimen</th>
<th>DU</th>
<th>TP</th>
<th>VH</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_{Ic}$ (MPa·m$^{1/2}$)</td>
<td>1.30±0.21</td>
<td>1.31±0.10</td>
<td>1.38±0.08</td>
</tr>
</tbody>
</table>

(): Deviation

Table 4 Mechanical properties of three porcelains

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{44}$</th>
<th>$\nu$</th>
<th>$E$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DU</td>
<td>86.3</td>
<td>34.6</td>
<td>27.2</td>
<td>0.286</td>
<td>66.5</td>
</tr>
<tr>
<td></td>
<td>(0.9)</td>
<td>(0.9)</td>
<td>(0.02)</td>
<td>(0.004)</td>
<td>(0.7)</td>
</tr>
<tr>
<td>TP</td>
<td>85.0</td>
<td>23.1</td>
<td>31.2</td>
<td>0.214</td>
<td>75.1</td>
</tr>
<tr>
<td></td>
<td>(0.6)</td>
<td>(0.8)</td>
<td>(0.05)</td>
<td>(0.002)</td>
<td>(0.9)</td>
</tr>
<tr>
<td>VH</td>
<td>74.8</td>
<td>22.4</td>
<td>27.7</td>
<td>0.230</td>
<td>64.5</td>
</tr>
<tr>
<td></td>
<td>(0.8)</td>
<td>(0.9)</td>
<td>(0.05)</td>
<td>(0.001)</td>
<td>(0.7)</td>
</tr>
</tbody>
</table>

$C_{11}$, $C_{12}$ and $C_{44}$: Elastic stiffness constants
$\nu$: Poisson's ratio, $E$: Young modulus
$E = (C_{11} - C_{12})(C_{11} + 2C_{12})/(C_{11} + C_{12})$, $\nu = C_{12}/(C_{11} + C_{12})$
Fig. 3 Fracture toughness $K_{Ic}$ measured by chevron notched beam method.

Fig. 4 Vickers hardness $Hv$ and Knoop hardness $Hk$ of three porcelains.

Fig. 5 Fracture energy $\Gamma$ calculated from fracture toughness and Young modulus. Vertical lines denote standard deviation.

Fig. 6 X-ray diffraction patterns of three porcelains before and after firing.
ties were performed at a 5% level to examine the statistical difference between the
three porcelains, but the results did not reveal any significant differences in $K_{IC}$, Hv and Hk ($p>0.05$).

**Elastic constants and fracture energy**

Table 4 shows $C_{ij}$, $E$, and $v$. Fig. 5 shows the comparison of $\Gamma'$ for the three porce-
lains. The standard deviations of $\Gamma'$ were calculated using those of $K_c$ and $E$. The
large deviation of DU resulted from the deviation of $K_{IC}$ because the elastic con-
stants were determined using a single specimen, statistical comparisons of $\Gamma'$ were
not performed, but the value of conventional porcelain was regarded to be larger
than that of PFPT.

**X-ray powder diffraction patterns before and after firing**

Fig. 6 shows the X-ray powder diffraction patterns of the three porcelains before and
after firing. TP indicates the typical amorphous pattern in either case. Before being
fired, DU was also indicated to be amorphous like TP, but some small peaks, attrib-
utable to the leucite crystal, were detected after firing. In contrast, the conventional
porcelain VH had diffraction peaks characteristic of a leucite crystal in both cases.
Obviously, for the PFPT used in this study, leucite crystals were not added as
Nagayama et al.\textsuperscript{14} reported that the crystalline component was minimal in the PFPT.

**Polished-etched surface and fracture surface**

Fig. 7 shows optical microscopic photographs taken of the specimens' polished-etched
surfaces. Particle materials were found in both DU and TP, and cracks appeared
around the large particles. In particular, clear cracks developed in TP.

Fig. 8 shows scanning electron microscopic photographs taken of the fracture
surface. Two PFPT had smooth surfaces compared with VH, which contained the
leucite crystals, and DU had the most flat fracture surfaces.

**DISCUSSION**

**Evaluation of fracture toughness and hardness**

To measure the $K_{IC}$ of ceramics, the single edge pre-cracked beam (SEPB)\textsuperscript{15} method,
which requires initiation of the pop-in pre-crack in advance into a notched specimen,
was standardized using JIS R-1607-1995\textsuperscript{9}). Once an initiated pre-crack is closed,
interlockings or bridgings occur between the opposed surfaces. These effects are en-
hanced by increasing the pre-crack length. Moreover, as it is impossible to make all
pre-crack lengths the same, the $K_{IC}$ increases in an increment relative to the pre-
crack length in a phenomenon known as R-curve behavior\textsuperscript{16,17}).

The most advantageous characteristic of the CNB method is that there is no need
to make a pre-crack, although it takes a little labor to make a chevron notch. As
the crack generates automatically at the tip of triangle and never closes once it is
opened, R-curve behavior is not a problem. Therefore, the measured $K_{IC}$ was
regarded as an intrinsic value. However, the fact that there were no differences between the Kic's of the three porcelains as well as their hardnesses indicates that we cannot explain the brittleness of PFPT in clinical use using instantaneous mechanical properties.

**Possibility of slow crack growth (SCG) in clinical use**

The optical microscopic observations of polished-etched surfaces indicated that the
particle materials were in every porcelain. According to the X-ray diffraction analysis, they were amorphous materials in DU and TP, and crystals in VH. In addition, every thermal expansion coefficient was regarded to be larger than that of the glass matrix because the cracks seemed to have generated during cooling. Considering that the fracture surface of PFPT, DU and TP was smooth (Fig. 8), it was evident that a transgranular fracture had occurred and that the mechanical strength of amorphous particles would be almost the same as that of the matrix. The rough fracture surface found with VH indicates that an intergranular fracture would result, and hence a larger $\Gamma$ for VH than DU and TP can be attributed to the intergranular fracture. These facts may indicate that PFPT causes a fatigue crack growth, that is, a slow crack growth (SCG) without difficulty in clinics compared with a conventional one.

On the basis of linear fracture mechanics, the stress intensity factor $K_I$ is expressed by Equation (8):

$$K_I = Y \cdot \sigma \cdot a^{1/2}$$

where $Y$ is the shape factor, $\sigma$ is the tensile stress applied to the direction perpendicular to the crack surface at the crack tip, and $a$ is the crack length. When $K_I$ reaches $K_{IC}$, an unstable fracture (i.e., a catastrophic fracture) occurs. Under normal masticatory force, $K_I$ will never exceed $K_{IC}$. However, if $a$ becomes larger due to an SCG, $K_I$ will be over $K_{IC}$ even with a little $\sigma$. In industrial silicate glass, it is well known that the SCG can progress under a small $K_I$ when there is water\(^{18}\). The SCG of dental porcelains has still not been clinically confirmed, but it is considered that the water used orally might also play a key role in advancing the SCG as indicated from an experiment in vitro\(^{10}\).

According to the proposed mechanism\(^{19,20}\), when the strained Si-O-Si bond at the crack tip is attacked by a water molecule, the bond is easily cut off through the following chemical reaction:

$$\text{Si-O-Si} + \text{H}_2\text{O} \rightarrow \text{Si-OH} + \text{HO-Si}$$

In this reaction, both stress and water are essential because the water seldom interacts with the bond which is not deforming at all. As masticatory force and water make a pair, the SCG of porcelain may be a common phenomenon. From these considerations, the brittleness of PFPT observed in clinics can be attributed to the time effect. It must be concluded that the SCG of PFPT would be much faster than that of a conventional one. From Equation (8), the $K_I$ depends on both the masticatory stress and the crack length, and the larger the crack length is, the smaller the necessary masticatory stress. As a result, a crack can grow without being noticed while the $K_I$ is small, but when the crack length reaches a value high enough to rupture, the catastrophic fracture would occur with normal masticatory force. To confirm this, an experiment predicting the lifetime of porcelain will be required.
CONCLUSION

The instantaneous mechanical properties such as fracture toughness, Vickers and Knoop hardness could not explain the clinical brittleness of porcelain fused to pure titanium. However, from the fact that their fracture energies were smaller than that of conventional porcelain, it was concluded that porcelain fused to pure titanium causes a slow crack growth comparable to conventional ones in clinical use.

REFERENCES

542  BRITTLENESS OF PORCELAIN FUSED TO PURE TITANIUM


