Original paper

Estimation of Residual Stress in Dental Porcelain by Laser-Raman Spectroscopy

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Residual stress in the surface of dental porcelain was estimated using laser Raman spectroscopy. Sixteen different magnitudes of residual stress were generated in commercial porcelain disks by tempering, ion exchange, and slow cooling. The specimens were analyzed using a laser-Raman spectrometer with an Ar+ laser. The Raman shift of the largest peak near 500 cm⁻¹ originating from silica was used as an indicator of the level of residual stress. For comparison, the residual stress in the specimen was estimated by the indentation micro-fracture method. The Raman shift of the porcelain increased with increasing residual stress at 3.7 × 10⁻² cm⁻¹/MPa (R²=0.89). The increase in the Raman shift corresponded to the increase in compressive stress. In addition, the value of full width at half maximum on the peak corresponded to the residual stress (−1.57 × 10⁻¹ cm⁻¹/MPa: R²=0.82). These results revealed that the increase of residual stress in porcelain clearly appears on the Raman spectrum as an increase in the Raman shift. It is thus feasible to estimate residual stress in porcelain by laser-Raman spectroscopy.

Key words: Dental porcelain, Residual stress, Laser-Raman spectroscopy

INTRODUCTION

Residual compressive stress is generated in the surface of glassy materials such as dental porcelain by rapid cooling after firing. In addition, stress is generated at the interface between porcelain and dental alloy due to the mismatch of their coefficients of thermal expansion. The fit of the margin of a porcelain/metal can be affected when the residual stress is released. Thus, the residual stresses in dental porcelain are significant factors effecting the strength and fit of porcelain/metal crowns.

Surface strengthening of glass or dental porcelain is achieved by the application of compressive stress to the surface. Tempering and ion exchange are well known as surface strengthening methods for porcelain. Tempering generates residual compressive stress by rapid cooling after heating. The operation causes compressive stress because the low thermal conductivity of ceramics results in a difference in temperature between the inside and the surface. The surface is rapidly cooled and solidifies first. The inside material then cools and contracts; compressing the surface. In ion
exchange, alkaline metallic ions in the surface of a glass are replaced by larger alkaline ions, and the difference in atomic radii generates compressive stress in the glass surface. In dental porcelain, sodium ions are replaced by potassium ions. Therefore, the surface residual compressive stress in dental porcelain increases its strength.

The most popular method in the field of engineering for estimating the residual stress of ceramics is X-ray diffraction (XRD). The residual stress in dental porcelain, however, is currently evaluated using the indentation–microfracture (IM) method. This method was originally devised for the estimation of fracture toughness of ceramics and then applied to the estimation of residual stress\(^5\). The residual stress generated in ceramics by tempering is also estimated with the IM method\(^4-14\), as is the compressive strength in porcelain treated by ion exchange\(^14-17\). The IM method is simple and convenient even though it is semi-empirical. However, the IM method is a destructive process and is thus not appropriate for the examination of finished materials. For this reason, residual stress, which is affected by the tempering method and thickness of the porcelain disk, is calculated in regions away from the edges by computer simulation\(^18\).

Laser–Raman spectroscopy has been applied to the estimation of residual stress in semiconductors\(^19-23\), microanalysis of stress in composite materials\(^23-25\), and so on. The Raman shift of a peak in the Raman spectrum is based on the following principle. When a phase in a material is irradiated with a laser beam, strong Raman scattering occurs due to the inherent vibration modes of the atomic bonds in the phase. The peak frequency of the Raman scattering is sensitive to the level of any externally applied stress or strain to the phase. The peak frequency shifts to a lower value under tension and to a higher value under compression\(^23-26\). One can therefore evaluate the levels of the stress or strain of a phase through the shift of the peak frequency. In addition, the full width at half maximum (FWHM) of the Raman peak changes with stress\(^27,28\). In spite of being a useful method for estimating residual stress, in the field of dentistry laser–Raman spectroscopy is only applied to the characterization of the adhesional structure between 4-META/MMA-TBB resin and dentine\(^29\) and enamel and hydroxyapatite\(^30\).

The purpose of this study was to attempt the estimation of residual stress in dental porcelain by examining the changes of the Raman spectrum. In this study, residual stress results from tempering and ion exchange procedures. Porcelain containing a small amount of leucite was employed because stress is generated in the feldsparic glass during heating and cooling by the mismatch in the coefficients of thermal conductivity between the glass matrix and leucite. Such stress may confound the estimation of residual stress due to tempering and ion exchange.

This study deals with shifts of Raman spectral peaks. Raman spectra are peak shifts themselves. Therefore, to avoid confusion, in this paper, the term “shift” refers to “Raman shift”, that is, a peak position expressed by wavenumber, while “peak shift” is the increase or decrease of a Raman peak’s position.
MATERIALS AND METHODS

Preparation of specimen
Commercial porcelain powder (VMK68 ENAMEL, A3, Lot No. 4100, VITA, Germany) was used as a starting material. The normal firing temperature and glass transition temperature of the porcelain were 930–980°C and 512°C, respectively. This porcelain was employed because it contains a small amount of leucite (22–23%)\(^{38}\). The porcelain powder was heated to 1200°C and the red-hot melted porcelain passed through ambient air as a homogenation heat treatment to remove leucite crystals. The bulk porcelain was then crushed into a powder. The powder was confirmed to be leucite-free using XRD (see Fig. 1-A). The powder was pressed in a stainless steel mold (10 mm in inside diameter) using a pressure of 9.8 MPa and powder compact was made. The powder compact was dry-fired on platinum foil up to 960°C under reduced pressure according to the manufacturer’s recommendation and cooled in a furnace under atmospheric pressure. The height and diameter of the compact were adjusted to 2 mm and 8 mm, respectively, by grinding and polishing. To generate compressive stress in the surface of the porcelain, two processes were used: tempering and ion exchange. In tempering, the porcelain disks were reheated at 660, 760, 860, or 960°C for 5 min each, then removed from the furnace and cooled with forced convection by the flow of compressed air at 0.8 MPa pressure through a nozzle 7.0 mm in diameter at 30 cm distant from the specimen. The cooling rate in the glass transition temperature region (ca. 500–600°C) was 70°C/s\(^{39}\). Two specimens were prepared by tempering at each temperature. The purpose of the treatment was not to generate one stress under a condition, but to generate various stresses under several conditions. For ion exchange, the porcelain disks were reheated once at 960°C for 5 min. The porcelain was coated with a commercial paste (CERAMICOAT, GC, Tokyo, Japan), composed mainly of potassium nitrate, and reheated at 450°C for 10, 15, and 20 min. Some of the sodium ions were replaced by potassium ions during heating. After heating, the specimens were cooled in ambient air and the paste was removed by washing in water. Two specimens were prepared for each heating time. Therefore, a total of six ion exchange residual stress specimens were generated. For control, two porcelain disks were reheated at 960°C for 5 min and slowly cooled in a furnace at a cooling rate of 0.1°C/s\(^{39}\). This manipulation produced porcelains with little residual stress as revealed with the IM method (see Results section later). A total of 16 residual stress specimens were prepared along with 2 control specimens (see Table 1). The finished surfaces of the specimens were shiny. One each of the tempered, ion-exchanged, and slow cooled (control) specimens were crushed to powder, and subjected to XRD. For comparison, single crystals of quartz and silica glass (fused quartz) were prepared.

Laser–Raman spectroscopy
Each of the specimens was analyzed by laser–Raman spectroscopy. Raman spectra of the porcelains, quartz, and silica glass were recorded in the Raman shift range of 20–2000 cm\(^{-1}\) by a Raman spectrometer (NR-1800, Jasco, Tokyo, Japan). A photo-
multiplier tube was used for the detection of light scattering. An argon laser with a wavelength of 415.4 nm and an energy of 100 mW was used as a light source. The laser beam in circle was focused on the specimen with a beam size approximately 100 \( \mu \text{m} \) in diameter. The size of the second phase (if present) at just a few mm is much smaller than that of a laser beam. An average of all phases resulted. The light scattered at a right angle to the incident beam was collimated and projected into the entrance slit of a triple monochromator. The laser beam was focused on the surface of the porcelains. Signals 30 nm below the surface were detected and the results were described as an average of the depth of the specimen sampled. The spectral slit width was around 0.1 cm\(^{-1}\), the resolutational power. Identical results were obtained at five different sites on the same specimen. The Raman spectrum was obtained from 20 scans. The Raman shift (wavenumber) of a peak was determined with a cursor on a computer. The surface temperature of specimens during laser–Raman spectroscopy was measured with a thermoelectric couple.

**Microfracture indentation**

After laser–Raman spectroscopy, the residual stress of each specimen were estimated with the IM method. The length of median cracks generated in porcelain specimens were measured with a Vickers hardness tester (MVK–E, Akashi, Tokyo, Japan). The residual stress in the porcelains was calculated using the length of the median crack, as described by Marshall and Lawn\(^6\).

**RESULTS**

Figure 1 shows the XRD patterns of the leucite–free porcelain and the porcelains after tempering, ion-exchange, and slow-cooling (control). No peak was observed before the treatments, so there was little crystalline leucite in the porcelain. However, the XRD showed small peaks originating from leucite crystal after the above treatments. The amount of leucite glass was estimated by comparison with XRD patterns from 100\% leucite and 40\% leucite-containing porcelain as about 6\%. During laser–Raman analysis, the increase in surface temperature of specimens was within 3 \(^\circ\text{C}\). The spectra of the porcelain, single crystals of quartz, and silica glass, are shown in Fig. 2. The largest peak was observed near 500 cm\(^{-1}\) in all materials. This peak was originated from Si–O bonding. The residual stress in the porcelains, as determined with the IM method is summarized in Table 1. The specimen with the lowest residual stress as measured by the IM method was given the value 0 MPa. The surface residual stress was compressive for all specimens. A range of residual stresses is evident. However, the differences in the stress generated by ion-exchange were small.

The peak near 500 cm\(^{-1}\) was decomposed to four peaks as shown in Fig. 3. The largest peak, Peak A originated from the sharpest and second largest peak in silica glass (Fig. 2). Peak B, which occurred at a higher energy site than peak A, originated from a peak near 500 cm\(^{-1}\) in silica glass (Fig. 2). The broad peak spreading to all wavenumbers, peak C, in Fig. 3 originated from the largest peak in silica glass
Fig. 1  X-ray diffraction patterns of porcelain before (A) and after tempering (B), ion exchange (C), and slow-cooling (D).

Fig. 2  Survey of Raman spectra obtained from the porcelain used in the study, quartz, and silica glass.

(Fig. 2). In addition, peak D originated from a peak near 600 cm$^{-1}$ in silica glass (Fig. 2). Therefore, all peaks originated from silica glass. The relation between residual stress and the Raman shift of peak A is shown in Fig. 4. The difference of the Raman shift increased proportionally with the increase in the residual compressive
ESTIMATION OF RESIDUAL STRESS IN PORCELAIN

Table 1 The residual stresses generated by tempering and ion exchange in porcelain as determined with the indentation microfracture method

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Condition</th>
<th>Residual stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow cooling</td>
<td></td>
<td>0.0</td>
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<tr>
<td></td>
<td></td>
<td>1.4</td>
</tr>
<tr>
<td>Tempering</td>
<td>660℃</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>760℃</td>
<td>14.8</td>
</tr>
<tr>
<td></td>
<td>860℃</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td>960℃</td>
<td>25.7</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>10 min</td>
<td>27.7</td>
</tr>
<tr>
<td></td>
<td>15 min</td>
<td>27.8</td>
</tr>
<tr>
<td></td>
<td>20 min</td>
<td>30.8</td>
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<tr>
<td></td>
<td></td>
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<tr>
<td></td>
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<td>53.3</td>
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<tr>
<td></td>
<td></td>
<td>63.7</td>
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<td></td>
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<td>57.1</td>
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<tr>
<td></td>
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<td>68.5</td>
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</tbody>
</table>

Fig. 3 Decomposition of the main peak near 500 cm⁻¹ originating from silica.

The residual stress was measured using the indentation microfracture method. The residual stresses generated by tempering and ion exchange in porcelain are shown in Table 1. The peak shifted according to the residual stress at a rate of 3.7 × 10⁻² cm⁻¹/MPa. The FWHM of peak A was also measured because the largest peak is the most accurate. The relation between residual stress and the FWHM is shown in Fig. 5. The FWHM was proportional to the residual compressive stress (R²=0.81). The FWHM changed according to the residual stress at a rate of −1.57 × 10⁻¹ cm⁻¹/MPa. In Fig. 6, the ratio of integrated intensity of peak A to that of peak B was calculated. The change in the ratio as a function of the residual stress is shown in Fig. 6. The ratio was also proportional to the compressive stress (R² =0.85).
DISCUSSION

A large amount of leucite in dental porcelain generates residual stress at the interface between leucite and the glass matrix and in the glass matrix because of the mismatch of thermal expansion. In this study, a tempering process was employed to generate the residual stress. A large amount of leucite complicates the generation and measurement of residual stress. Therefore, it is important to estimate the leucite in the...
porcelain after treatment. Leucite crystals disappeared during the treatment, as shown in Fig. 1 (A). However, about 6% leucite was generated in the porcelain after tempering, ion exchange, and slow cooling, as shown in Fig. 1 (B, C, and D). Such a small amount of leucite did not prevent the measurement of residual stress.

Heating of porcelain by a laser beam during spectral acquisition could release residual stress. However, the beam size in this study was relatively large (≈100 μm) and the surface temperature of the porcelain increased only 3°C. For release of the residual stress in dental porcelain, the temperature of porcelain has to increase above the glass transition temperature (512°C). Therefore, the residual stress in the porcelain was not released by such a slight increase of temperature.

The residual stresses showed slight differences even though the specimens were cooled from the same temperature. In other words, it is impossible to generate an identical stress even in specimens treated under the same conditions. In total, eight kinds of residual stresses were eventually prepared by the tempering.

The residual compressive stress in dental porcelain clearly appeared on the Raman spectrum as an increase in the Raman shift of the peak. The peak shifted according to the residual stress at a rate of $3.7 \times 10^{-2} \text{ cm}^{-1}/\text{MPa}$. If the stress in porcelain was tensile, the peak should shift to the smaller wavenumber side. In the case of the residual tensile stress in fibres in composites, the peaks shifted at a rate of $-3.8 \times 10^{-3} \text{ cm}^{-1}/\text{MPa}$. The absolute value of this rate is one tenth of that obtained in this study. Therefore, the detection of the residual stress in porcelain is easier than that in a fibre in a composite material, and more accurate. Laser–Raman spectroscopy may be suitable for the estimation of residual stress in dental porcelain. However, it was revealed that the FWHM of a peak in the Raman spectrum changed according to the residual stress$^{31,20}$. Also in this study, the FWHM of peak A, the largest peak obtained from the porcelain, decreased with the increase of the residual stress at a rate of $-1.57 \times 10^{-1} \text{ cm}^{-1}/\text{MPa}$. We could not determine whether this rate is larger than that in other materials. The FWHM of the smaller peak is unlikely to give a good correlation because the change in the FWHM is too small. In any case, we can use the FWHM for the estimation of the variation of residual stress. In addition, the ratio of the integrated intensities of the two peaks changed according to the magnitude of residual stress. Each peak on a Raman spectrum originates from a phonon. Therefore, the integrated intensity of a peak changes according to the conditions which affect the lattice vibration of the crystal in the material like temperature, stress and so on$^{31–30}$. These induce a change in the ratio of the integrated intensities of different peaks. We can estimate the residual stress of a material with laser–Raman spectroscopy by using the shift, FWHM, and the ratio of integrated intensity of a peak. There may be other factors with which to estimate the residual stress by laser–Raman spectroscopy. When the change of one of these parameters of a peak can be detected on the Raman spectrum, the residual stress in the material should be determined using laser–Raman spectroscopy. Therefore, laser–Raman spectroscopy is a useful method for the estimation of residual stress in dental porcelain.
The correlations between various changes in the Raman spectrum and residual stress obtained by this study results in a standard line for the determination of residual stress in the this porcelain using laser-Raman spectroscopy. Although a different standard line has to be made for every material, the same line can be applied to the estimation of the same types of material. The stress could be estimated in a phase of only a few μm because dimensional resolution as small as 1 μm can be obtained in micro-analysis with an optical microscope. In addition, the stress can be estimated in situ in air and even in a liquid. The most important advantage in the estimation by laser-Raman spectroscopy is that the specimen is not destroyed. These advantages are especially useful for dental materials. Thus, laser-Raman spectroscopy is useful for the evaluation and development of dental porcelain.

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REFERENCES