HRTEM observation of bonding interface between Ce-TZP/ Al_2O_3 nanocomposite and porcelain

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The surface of a ceria-stabilized tetragonal zirconia polycrystal (Ce-TZP/ Al_2O_3) nanocomposite was sandblasted by alumina particles and veneered with feldspathic porcelain *via* a conventional condensation method. The part of each specimen containing the interface layer was sliced to ultrathin sections with an argon ion slicer, and these sliced sections were observed using high-resolution transmission electron microscopy (HRTEM). For both interfaces, Ce-TZP/porcelain and Al_2O_3 /porcelain, no transition layers due to abrupt changes in atomic distributions were observed. Besides, the porcelain layers of both interfaces consisted of homogeneous amorphous phases. These results suggested that both Ce-TZP and Al_2O_3 could be directly bonded to porcelain by Van der Waals forces arising from the close contact between them.

Keywords: High-resolution transmission electron microscopy (HRTEM), Zirconia, Alumina, Porcelain, Interface

INTRODUCTION

Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) possess the requisite properties for use in dental restorations such as crowns, bridges, implant fixtures, abutments, and orthodontic brackets¹⁻³. An intragranular type of Ce-TZP/ Al_2O_3 nanocomposite was developed in which extremely fine Al_2O_3 and Ce-TZP particles are located within submicron-sized Ce-TZP and Al_2O_3 grains respectively⁴. The toughness, strength, and hardness of this nanocomposite are two to three times those of conventional Y-TZP⁵. Ban *et al.* have shown its general superiority as a dental restorative material over myriad commercial dental ceramics⁶⁻⁹.

For use in crowns and bridges, the surface of zirconia is generally veneered with feldspathic porcelain to compensate for its insufficient translucency. Moreover, porcelain-fused-to-metal has been a popular esthetic restorative option. On porcelain adherence to metals, it is established through a reaction layer that forms between the veneered porcelain and metal substrate because of chemical bonding between them¹⁰⁻¹³. In contrast, adhesion mechanism between zirconia and porcelain is yet to be ascertained. Suggestions have been many and varied, such as adhesion by micromechanical interlocking due to intervention of a reaction layer and/or fine unevenness of an interface produced by sandblasting. However, efforts to confirm the existence of a reaction layer between zirconia and porcelain through field emission scanning electron microscopy (FESEM)¹⁴⁻¹⁶ and wavelength-dispersive X-ray spectroscopy (WDS)¹⁶ have been unsuccessful.

As part of a case study on Ce-TZP/ Al_2O_3

nanocomposites, the aim of this research was to clarify the conditions necessary for the formation of a bonding interface between zirconia and porcelain, on an atomic scale, through high-resolution transmission electron microscopy (HRTEM).

MATERIALS AND METHODS

A presintered Ce-TZP/ Al_2O_3 nanocomposite blank (P-NANOZR, Panasonic Healthcare, Ehime, Japan) was cut to obtain disk-shaped specimens. These specimens were sintered at 1450°C for 2 h to obtain sintered disks of 12 mm diameter and 1 mm thickness. Surfaces of these disks were sandblasted (Hi Blaster Ovaljet, Shofu, Kyoto, Japan) using 70- μm alumina particles. Feldspathic porcelain (Vintage ZR, Shofu, Kyoto, Japan) (8.2 wt% Na_2O , 3.9 wt% CaO , 17.1 wt% Al_2O_3 , 61.2 wt% SiO_2 , 9.5 wt% K_2O)¹⁷ veneers of about 1 mm thickness were obtained by a conventional condensation method. Opaque porcelain was heated to an initial temperature of 450°C, dried for 8 min, heated again to 940°C at a heating rate of 40°C/min, and held at this temperature for 1 min. Finally, a dentin porcelain was heated to an initial temperature of 650°C, dried for 6 min, heated again to 920°C at a heating rate of 40°C/min, and held at this temperature for 1 min.

Specimens for HRTEM (JEM-2100F, JEOL, Tokyo, Japan) observation were prepared by slicing the part of porcelain-veneered disks containing the interface layer to ultrathin sections with an argon ion slicer (EM-0900IS, JEOL, Tokyo, Japan). Accelerating voltage for HRTEM operation was 200 kV and magnification was $\times 100,000$ – $1,000,000$. WDS (JXA-8530FA, JEOL, Tokyo, Japan) observations were also carried out under the following operating conditions: 10 kV accelerating

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voltage; 5.0×10^{-8} A filament current; 20 ms counting time; measurement area of 350×262 pixels, and pixel size of 0.0343×0.0343 μm . Specimens for WDS observation were sectioned using a cross-section polisher (SM-09010, JEOL, Tokyo, Japan).

RESULTS

Figure 1 shows the element distribution maps, obtained by WDS, for zirconium (Zr), silicon (Si), aluminum (Al), oxygen (O), and cerium (Ce), alongside a secondary electron image (SL) of the interface between Ce-TZP/ Al_2O_3 and veneered porcelain. The Ce-TZP/ Al_2O_3 nanocomposite was composed of a matrix of 10 mol% ceria-stabilized tetragonal zirconia polycrystals (Ce-TZP) and a secondary dispersion of 30 vol% Al_2O_3 . Dark grains of about 0.4 μm in size, which were located in the lower half area of SL, were identified to be Al_2O_3 grains. This was confirmed by the element distribution map of aluminum. Opaque porcelain was composed of a matrix

of feldspathic glass and a dispersion of zircon (ZrSiO_4) particles¹⁷. Zircon particles were located in the black regions in aluminum distribution map, green regions in zirconium map, and green regions in the silicon map.

HRTEM was carried out to identify two different interfaces: one between Ce-TZP grains and veneered porcelain (Ce-TZP/porcelain), and the other between Al_2O_3 grains and veneered porcelain (Al_2O_3 /porcelain). HRTEM images of Ce-TZP/porcelain and Al_2O_3 /porcelain interfaces are shown in Figs. 2 and 3 respectively. Al_2O_3 and Ce-TZP grains were discriminated in terms of crystal lattice spacing in higher-magnification images and area percentage in lower-magnification images.

In the case of Ce-TZP/porcelain interface, the reaction layer which was to be formed by the diffusion of compositional elements was hardly observed. On the side of the interface where Ce-TZP grains were (Fig. 2d), regular arrays at 0.30 nm intervals were observed. These arrays were probably related to the lattice spacing of (101) tetragonal ZrO_2 planes. On the porcelain side of

Fig. 1 Element distribution maps of zirconium (Zr), silicon (Si), aluminium (Al), oxygen (O), and cerium (Ce), alongside a secondary electron image (SL) of the interface between Ce-TZP/ Al_2O_3 and veneered porcelain.

Fig. 2 HRTEM images of the interface between Ce-TZP grains and veneered porcelain. Magnification increases from (a) to (d), and each white rectangles indicates the part of image to be subsequently magnified.

Fig. 3 HRTEM images of the interface between alumina grains and veneered porcelain. Magnification increases from (a) to (d), and each white rectangles indicates the part of image to be subsequently magnified.

the interface, no such arrays were detected, indicating an amorphous phase. In the case of Al_2O_3 /porcelain interface, similar observations were made. Regular arrays at 0.25 nm intervals were also observed on the Al_2O_3 grains' side (Fig. 3d). and these arrays were probably related to the lattice spacing of (104) Al_2O_3 planes. However, the Al_2O_3 /porcelain interface had an inarticulate architecture with a fine uneven structure.

DISCUSSION

The existence of a reaction layer at the bonding interface between Ce-TZP/ Al_2O_3 and porcelain could not be ruled out as conclusively as in previous reports which observed TZP/porcelain interface using micro X-ray diffraction (μXRD)^{18,19}, energy-dispersive X-ray spectroscopy (EDS)^{20,21}, and WDS^{15,22}. Due to insufficient resolution in these studies, the interfacial transition layer could only be declared as non-existent with a caveat.

HRTEM observation in the present study revealed that no interfacial transition layers, due to abrupt changes in atomic distributions, were observed for both Ce-TZP/porcelain and Al_2O_3 /porcelain interfaces. In addition, the porcelain layers of both interfaces consisted of homogeneous amorphous phases. These results suggested that no strong chemical bonds, such as ionic and/or covalent bonds, existed at the Ce-TZP/porcelain and Al_2O_3 /porcelain interfaces, and that both Ce-TZP and Al_2O_3 might be directly bonded to porcelain by Van der Waals forces.

When compared with metal-ceramic systems, porcelain-zirconia systems appear to be more problematic as it is not easy to characterize ceramic-ceramic compatibility. Like metal-ceramic systems, porcelain chipping is also a frequently reported failure of porcelain-zirconia systems^{23,24}. However, it is not likely to be due to a simple thermal expansion coefficient mismatch between the bulk materials²⁵. The thermal conductivities of zirconia and porcelain are quite low at 2.5 W/(m.K)²⁶ and 1.0 W/(m.K)²⁷ respectively. One cause could be the occurrence of final sintering around the interface between zirconia and porcelain, which is due to heat conduction from each side of the materials exposed in the porcelain furnace. On the other hand, first sintering may occur around the interface between metal and porcelain due to the relatively high thermal conductivity of metals. For example, the thermal conductivity of Au-Ag-Pd alloy is 125.5 W/(m.K)²⁷. Pores may then remain in the porcelain around the interface between zirconia and porcelain.

Our previous studies have demonstrated that the bonding strength between porcelain and zirconia was independent of the surface roughness of zirconia¹⁴, but was strongly affected by the firing temperature¹⁵. FE-SEM revealed that the number and size of pores decreased with the firing temperature. Similarly, another study reported that the porosity of dental porcelain was affected by the sintering temperature²⁸. In the present study, no phase transformation was

observed in zirconia, alumina, and porcelain. It has been reported that veneer sintering did not change the lattice structure of zirconia, which remained to be a tetragonal structure²⁹. These results could be explained by the existence of Van der Waals forces arising from the close contact between zirconia and porcelain, which are also affected by porosity.

Bonding between solid objects depends on mechanical bonding (anchor effect), physical interaction, and chemical interaction. Van der Waals forces are a kind of physical interaction and seem to be the principal mechanism of adhesion in most cases. When two solid objects approximate in atomic level are allowed to be in complete contact without a gap, they adhere strongly even without any adhesive. The electrons are in motion around the nucleus, even in the lowest electronic state. At any time, a non-vanishing electric dipole moment may come into existence from this motion. This dipole moment creates Van der Waals forces which are inversely proportional to the sixth power of the interatomic distance³⁰. Although the present study was undertaken to gain more insight into the interface between Ce-TZP/ Al_2O_3 and porcelain, this concept might also be applicable to the interface between Y-TZP and porcelain.

CONCLUSION

The interface between Ce-TZP/ Al_2O_3 and veneered porcelain was characterized by HRTEM. No transition layers, due to abrupt changes in elemental distributions around Ce-TZP and Al_2O_3 grains, existed at both Ce-TZP/porcelain and Al_2O_3 /porcelain interfaces. Within the limitations of this study, it was established that arising from the close contact between Ce-TZP/ Al_2O_3 and porcelain, Van der Waals forces were their principal mechanism of adhesion.

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