Hydroxyapatite coating on zirconia using glass coating technique

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The aim of this study was to develop a novel hydroxyapatite (HA) coating method on zirconia using glass coating technique. A borosilicate glass, the mixture of the glass and HA (30, 50, 70, and 90 mass%), and the 100% HA were coated on two kinds of zirconia discs and fired at 900–950°C. After the final coating, the surface of the sample was etched for 3 min in an acid-mixture of 3% HF and 5% HNO3 to remove the surface layer covered with glass and to obtain the biocompatible surface layer with HA. The shear bonding strength of the glass to zirconia fired at 950 and 1050°C were determined. There were no significant difference in the bonding strengths between the kind of zirconia (p > 0.05). Whereas, the bonding strengths fired at 1050°C were significantly higher than those at 950°C (p < 0.05). These results suggest that the HA containing glass-coated zirconia, namely functionally gradient structure, could be systematically produced using the glass coating technique and the acid etching.

Key-words: Zirconia, Hydroxyapatite, Biocompatibility, Implant, Functionally gradient material

1. Introduction

Ceramics are attractive dental materials, because of their superior aesthetics, inertness, and biocompatibility. However, ceramics are generally brittle and subject to premature failure, especially in repeated contact loading and moist environments. The origin of the interest in using zirconia as a ceramic biomaterial was its good chemical and dimensional stability, its mechanical strength and toughness, and coupled with a Young’s modulus in the same order of magnitude of stainless steel alloys.1,2 It was introduced into medicine and dentistry as an ideal replacement for metal. Zirconia are frequently used in the high load-bearing sites such as orthopedic and dental implants, but they are bioinert, and do not naturally form a direct bond with bone and thus do not provide osseointegration. HA is a major inorganic component of mammalian bones and has been shown to have a high biocompatibility in vitro. One of the authors participated to the development of the HA coating on titanium using a glass coating technique.3-7 The aim of this study was to develop a novel HA coating method on zirconia using the glass coating technique.

2. Experimental procedure

Ceria stabilized tetragonal zirconia polycrystals (TZP)/Al2O3 nanocomposite (Matsushita Electric Works, referred to CZT), a conventional yttria stabilized TZP (Tosoh, referred to 3Y-TZP) were used in this study. These powders were pressed to a cylindrical rod, 25 mm in diameter and 60 mm in thickness, using a cold isostatic pressing method. After peeling of the rod surface, the rod of CZT and 3Y-TZP were fired at 1450°C for 2 h and at 1350°C for 6 h, respectively. After cooling, disk specimens, 14 and 7 mm in diameter and 2 mm in thickness, were prepared by cutting and grinding with a 400-grid diamond wheel. These discs were ground by diamond paper (#220, #400, and #600) and sandblasted by 70-μm Al2O3 powder for 10 s under air-pressure of 0.4 MPa perpendicular to the surface from 10 mm apart.8 After sandblasting, CZA and 3Y-TZP discs were heated for 5 min at 1000°C in air. These discs were ultrasonically cleaned for 10 min in acetone, ethyl-alcohol, and distilled water. The experimental glass was fired on the discs at 950°C in air. The glass frit used to form the HA-containing glass (HA-G) layer on zirconia is almino-borosiliclate glass which composition of the glass frit was originally designed for the coating on titanium.9 Table 1 shows the composition of the almino-borosilicate glass. After preparation of the mixture of the glass and HA (30, 50, 70, and 90 mass%), theses mixtures and 100 mass% HA were painted on zirconia. These laminated layers were fired at 900°C in air. After final firing, these specimens were ultrasonically cleaned for 5 min in distilled water. Furthermore, the surface of the specimens was etched in mixtuer solution of 3%HF and 5%HNO3 to remove the surface layer covered with thin glass and obtain the bioactive surface layer with exposed HA particles. Figure 1 shows schematic drawing of a cross section of HA-G zirconia composite (HA-G-Zr). The thickness of the
coating layer was about 100 μm. These samples were characterized by X-ray diffractometry (XRD) (RINT-2500, Rigaku, Tokyo). Surface morphology was observed by scanning electron microscopy (SEM) (JSM-5510LV, JEOL, Tokyo). The element maps around the interface between the glass and CZA were generated using an energy dispersive X-ray spectrooscope (EDS) (JED-2201, JEOL, Tokyo). To determine shear bonding strength of the glass to zirconia, the pure glass was painted on one side both zirconia discs, 14 and 7 mm in diameter, and fired at 950 and 1050°C for 5 min, and subsequently a stack of two discs were fired at 950 and 1050°C for 5 min, respectively.

3. Result and discussion

Figure 2 shows XRD patterns of HA-G coated CZA and 3Y-TZP. After final procedure (etched in the mixture solution of 3%HF and 5%HNO3), diffraction peaks due to HA were only observed and there were no peaks of CaF2. Furthermore, no diffraction peaks due to zirconia as substrate were observed, because the diffracted X-ray of zirconia was completely absorbed by the thick layer of HA-G, about 100 μm. Figure 3 shows SEM photograph of the surface of pure glass, 30, 50, 70, 90, and 100 mass% HA-G layers. The area of exposed HA particles increased with the HA content in the mixture of glass and HA. A great number of fine HA particles stacked together in the glass were exposed to form uneven and roughened surface by the etching, wherein microcracks and many voids are present. Figure 4 shows EDS image (SEI and element map of Zr, Si, and Al) of a cross section of the interface between the glass and CZA. Zr was only observed on the CZA region and showed relatively clear boundary. Si was observed on the glass region and gradually decreased to the inside to CZA. Although Al was originally contained in both the glass and CZA, the content of Al in the outermost layer of CZA was smaller than the other area. It suggests that the reaction layer, about 2–3 μm, was formed by the reaction between SiO2 of glass and Al2O3 of CZA, and between SiO2 of glass and ZrO2 of CZA. Figure 5 shows the shear bonding strengths of the glass to CZA and 3Y-TZP fired at 950 and 1050°C for 5 min. There were no significant difference in the shear bonding strengths between CZA and 3Y-TZP (p >
While the bonding strengths fired at 1050°C were significantly higher than those at 950°C ($p < 0.05$). It implies that the glass bonds to zirconia with chemical bonding. These results suggest that the HA containing glass-coated zirconia, namely functionally gradient structure, could be systematically produced using the glass coating technique and the acid etching. It can be expected that this coating result in biocompatible surface on zirconia applicable to medical and dental implants. Further investigation on biocompatibility test is now on going.

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