Bonding between Bioactive Glasses, Glass-Ceramics or Ceramics in a Simulated Body Fluid

Tadashi KOKUBO, Tetsuya HAYASHI, Sumio SAKKA,
Toshiaki KITSUGI* and Takashi YAMAMURO*

Institute for Chemical Research, Kyoto University
Gokasho, Uji-shi 611
*Faculty of Medicine, Kyoto University

Two rectangular bars of glass-ceramic A-W, its parent glass G, Bioglass Bg or hydroxyapatite ceramic HAp were respectively bound and soaked in an acellular simulated body fluid for various periods up to 6 months. Tight chemical bond was formed between the two bars after a certain period of time for all these bioactive materials. The ability of forming such bond increased in the order HAp<G<A-W<Bg. The bond was achieved by an apatite phase newly formed at the interfaces of the specimens in the simulated body fluid. In the present arrangement of the specimens, bonding took place in the peripheries within the interface, indicating that under area for bonding and accordingly stronger bonding can be expected if the arrangement is designed so that the fluid might circulate into the central part of the interface. The present results indicate a possibility that when artificial bone made of those bioactive materials is accidentally broken in a body, the separate pieces can be recombined like the natural bone.

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Key words: Glass-ceramic A-W, Bioglass, Hydroxyapatite, Apatite, Bioactive, Bone, Mutual bond

1. Introduction

It has already been reported by the present authors that glass-ceramic A-W containing apatite and wollastonite can form tight chemical bond with living bone in a body5,4) keeping a fairly high mechanical strength for a long time even under load bearing conditions in a body.3,4,5) Animal and clinical experiments for application of this glass-ceramic as artificial bone and tooth root are now being conducted.4) It has also been found that pieces of glass-ceramic A-W can form mutual bond between themselves in a body, indicating that when an artificial bone made of this glass-ceramic is separated into pieces by accidental breakage, they can possibly be recombined with each other in a living body as a natural bone heals.

The present work has been undertaken to examine whether the mutual bond between artificial bones is also formed in an acellular simulated body fluid and how such bond is formed. Other bioactive glass and ceramic than glass-ceramic A-W, which form tight chemical bond with living bone, have also been examined in order to discuss the mechanism of the mutual bond formation.

2. Experimental

2.1 Test of mutual bond

Four kinds of samples given in Table 1 were used for the experiments. A-W is a glass-ceramic in the system MgO-CaO-SiO2-P2O5, which contains 35 wt % oxy-fluoroapatite (Ca10(PO4)6(O,F)x) and 40 wt % β-wollastonite (CaO·SiO2) as crystalline phases, G is a parent glass of glass-ceramic A-W. A-W was prepared by sintering

Table 1. Nominal composition and phase of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (wt%)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-W</td>
<td>4.6 44.7 34.0 16.2 0.5</td>
<td>a, w, g</td>
</tr>
<tr>
<td>G</td>
<td>4.6 44.7 34.0 16.2 0.5</td>
<td>g</td>
</tr>
<tr>
<td>Bg</td>
<td>24.5 45.0 6.0</td>
<td>g</td>
</tr>
<tr>
<td>HAp</td>
<td>Ca10(PO4)6(O,F)x</td>
<td>a*</td>
</tr>
</tbody>
</table>

a: oxy-fluoroapatite
w: β-wollastonite
g: glassy phase
a*: hydroxyapatite
and crystallizing a powder compact of glass G, Details of the fabrication method of these samples were described elsewhere. Bg is a glass in the system Na₂O-CaO-SiO₂-P₂O₅ having the same composition as Bioglass 4555 reported by Hench. It was prepared by melting a powder mixture of reagent grade chemicals at 1400°C. HAp is a dense hydroxyapatite ceramic which was prepared by sintering a powder compact of a nominal composition of Ca₁₀(PO₄)₆(OH)₂ at 1200°C and supplied by Mitsubishi Mining and Cement Company. It had a relative density of 98.5%. All these samples had already been confirmed to form tight chemical bond with living bone.

Rectangular bars 4×4×26 mm were cut from a block of bioactive materials and the surfaces were finished with # 2000 alumina powders. Two bars of the same materials were bound in parallel by a Nylon string as shown in Fig. 1 and the couple was soaked in a simulated body fluid of 90 ml at 36.5°C. The fluid was prepared by dissolving given amounts of reagent grade chemicals of NaCl, NaHCO₃, KCl, K₂HPO₄·3H₂O, MgCl₂·6H₂O and CaCl₂ into pure water. The ion concentration of the fluid were almost equal to those of the human blood plasma, as shown in Table 2. The fluid was buffered at a pH of 7.25 with 50 mM trishydroxymethane ((CH₂OH)₃CNH₂) and 45 mM hydrochloric acid (HCl). Neither living cell nor organic substances were added.

After soaking for various periods, the couples of specimens were taken out from the fluid and examined whether one bar of a couple can be detached from the other by applying tensile, shearing and torsional forces by hands, as shown in Fig. 1.

2.2 Analysis of microstructure of bonding

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Ion concentration (mM) of the simulated body fluid and human blood plasma.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na⁺</td>
</tr>
<tr>
<td>Simulated fluid</td>
<td>142.0</td>
</tr>
<tr>
<td>Human plasma</td>
<td>142.0</td>
</tr>
</tbody>
</table>

Specimens mutually bonded were detached and their interfaces were observed under a metallurgical microscope (Olympus, Model N) and a scanning electron microscope (Hitachi, Ltd., Model S-450). The same interfaces were analyzed with a micro-beam X-ray diffractometer (Rigaku Denki, Model PSPC/MDG). X-ray irradiation area was 100 μm in diameter. Specimens mutually bonded were transversely cut and the cross-sections were analyzed with an electron microprobe X-ray analyzer (Hitachi, Ltd., Model X-650).

3. Results and discussion

3.1 Mutual bond

Results of the test on mutual bonding of the samples are given in Table 3.

Glass-ceramic A-W formed such strong mutual bond in one month that one bar of a couple could not be detached from the other by both the tensile and shearing forces. Detaching was hardly made by the torsional force, too. The same result was obtained for the specimens soaked up to at least 6 months. Glass G gave the same results. Glass Bg gave the same result for soaking of one month, but for longer soaking periods, the bonding was stronger to such an extent that any forces of tensile, shearing and torsional one can not detach one bar from the other until the couple is finally broken transversely. Hydroxyapatite ceramic HAp did not form a mutual bond in one month and

Fig. 1. Methods for soaking specimens in a simulated body fluid (left) and for testing their mutual bonding (right).
Table 3. Results of test of mutual bonding.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Soaking Time (month)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>A-W</td>
<td>T</td>
</tr>
<tr>
<td></td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>G</td>
<td>T</td>
</tr>
<tr>
<td></td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Bg</td>
<td>T</td>
</tr>
<tr>
<td></td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>HAp</td>
<td>T</td>
</tr>
<tr>
<td></td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

T: Tensile force. S: Shearing force. D: Torsional force
0: Not detached. x: Detached

took 3 months to form a mutual bond to such an extent that the tensile and shearing forces can not detach but the torsional force easily do. For longer soaking periods, the same results were obtained up to 6 months.

These results show that all the examined bioactive glasses, glass-ceramic and ceramic which form a tight chemical bond with living bone in a body can form also a mutual bond between themselves sooner or later even in the simulated body fluid containing no living cell. The ability to form the mutual bond, however, largely depends upon the kind of the samples, i.e., it increases in the order of HAp<G=A-W<Bg. These indicate that the mutual bonding of glass-ceramic A-W in a body which was previously reported is attributed to a physicochemical reaction between the glass-ceramic and the body fluid rather than to a biological reaction in which living cell plays an important role.

3.2 Microstructure of bonding region

Figure 2 (a) shows a metallurgical micrograph of an interface of glass-ceramics A-W which were mutually bonded by 3 months soaking and detached by the torsional force. Figure 2 (b) is a scanning electronmicrograph of a part near the periphery of the interface. It can be seen from these photographs that a narrow ridge about 1 mm wide and 5-6 μm high is formed on the interface at a short distance toward the inside from the periphery, as schematically shown on Fig.2 (c). This indicates that the mutual bond in glass-ceramic A-W had been achieved by only this narrow ridge, as shown in Fig.2 (d).

Figures 3 (a), (b) and (c) show scanning electronmicrographs taken under a high power magnification for a portion inside, just on and outside the ridge, respectively. Figure 4 shows those for a portion just on the ridge. It can be seen from these photographs that a portion inside the

Fig. 2. Metallurgical (a) and scanning electron (b) micrographs of an interface of glass-ceramics A-W mutually bonded by 3 months soaking. (c) and (d) are schematic representation of the structure of the interface and the cross-section of the bonded specimens.
ridge was only slightly corroded by the fluid whereas portions just on and outside the ridge so actively reacted with the fluid to form a lot of fragmental particles. This indicates that the mutual bond of the specimens at the ridge had been achieved by coagulation or recrystallization of these fragmental particles.

Figure 5 shows micro-beam X-ray diffraction patterns of a portion just on and inside the ridge on the interface of glass-ceramics A-W mutually bonded for 4 months soaking. It can be seen from Fig. 5 that both the wollastonite and apatite constituting the glass-ceramic are detected inside the ridge whereas almost only apatite is detected just on the ridge. Then, the fragmental particles observed just on and outside the ridge are identified as apatite phase. It was reported in the previous paper[1] that glass-ceramic A-W forms a thin layer about 5 μm thick of carbonate-containing hydroxyapatite of small crystallites with a lattice distortion on it in 7 days when exposed to the simulated body fluid. The apatite phase detected on and outside the ridge would be the same type of the apatite. It had been already confirmed that such type of apatite plays an important role in forming a chemical bond between the glass-ceramic and living bone in a body.[1,12] The results described above indicate that such apatite phase plays an important role also in forming mutual bond between the glass-ceramics in a body.

Figure 6 shows a scanning electronmicrograph of a part near the periphery of a transverse cross-section of glass-ceramics A-W mutually bonded for 2 months soaking, and a result of electronmicroprobe X-ray analysis of the same section. It can be confirmed from Fig. 6 that a couple of the specimens are bonded only near the periphery and that the bonding phase is rich in Ca and P but deficient in Si and Mg.

The reason why the formation of apatite was limited to the area near the periphery of the interface of the glass-ceramics might be interpreted in terms of circulation of the fluid. The apatite starts to form from the periphery of the interface, and hence circulation of the fluid...
Further into the central part is blocked by the apatites. As a result, the bonding area is limited to a narrow region on the interface in the present arrangement of the specimens. If the specimens are arranged so that the fluid can circulate into the central part of the interface, stronger mutual bond can be expected.

Similar interface structures were observed also for other samples. Figure 7 shows micro-beam X-ray diffraction patterns of a portion just on and inside the ridge on the interface of glass G mutually bonded by 4 months soaking.

Fig. 5. Micro-beam X-ray diffraction pattern of a portion just on and inside the ridge on the interface of glass-ceramics A-W mutually bonded by 4 months soaking. a: apatite, w: wollastonite

Fig. 6. SEM picture (a) and a result of electronmicroprobe X-ray analysis (b) of a transverse cross-section of glass-ceramics A-W mutually bonded by 3 months soaking.
inside the ridge on the interface of glasses G mutually bonded by 4 months soaking. The apatite phase is formed only near the periphery of the interface and that a couple of the specimens are bonded by the apatite phase, in this case too. Figure 8 shows micro-beam X-ray diffraction patterns of a portion just on and inside of the ridge on the interface of glasses Bg mutually bonded by 3 months soaking. In this case, the apatite phase is formed not only just on the ridge but also inside it. Figure 9 shows a scanning electronmicrograph of a transverse cross-section of a couple of glasses.

Fig. 8. Micro-beam X-ray diffraction pattern of a portion just on and inside the ridge on the interface of glass Bg mutually bonded by 3 months soaking.

Fig. 9. SEM picture (a) and a result of electronmicroprobe X-ray analysis (b) of a transverse cross-section of glass Bg mutually bonded by 1 month soaking.
Brg mutually bonded by 1 month soaking and a result of electronmicroprobe X-ray analysis of the same section. In this case, glasses are bonded not only near the periphery but also at the central part of the interface by the Ca- and P-rich phase. This might be the reason why glass Brg showed the strongest mutual bond among the samples examined in the present study.

Figure 10 shows micro-beam X-ray diffraction patterns of a portion just on and inside the ridge on the interface of hydroxyapatite ceramics HAp mutually bonded by 4 months soaking. It can be seen from Fig. 10 that the portion just on the ridge gives a little broader peaks although all peaks from both the portion are ascribed to apatite. The broader peaks are characteristic of the apatite phase newly formed in the fluid. This indicates that the mutual bond in the specimens is achieved by the apatite phase formed near the periphery. The reason why the hydroxyapatite ceramic HAp showed the lowest ability of forming the mutual bond among the examined samples might be attributed to its low activity in forming the apatite phase in the fluid.

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References