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Properties of two biological glasses used as metallic prosthesis coatings and after an implantation in body

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Introduction

Biomaterials and their associated medical devices are an important future technology, both in terms of their health care capabilities and the opportunities they present for wealth creation. Biomaterials development is essentially a multidisciplinary activity.

In orthopaedic or dental surgery, most prostheses are made with metal or metallic alloys. A successful long-term implant requires biocompatibility, toughness, strength, corrosion resistance, wear resistance and fracture resistance [1]. Three groups of metal prevail for clinical application[2]: stainless steels, cobalt-based alloys and titanium or titanium alloys.

Nevertheless, metal, in contact with body fluids, forms corrosion products which cause different tissue reactions according to the metal. A metallic contamination surrounding tissues may play a major role in aseptic loosening of the implant. A way to prevent this problem of corrosion is to use a biomaterial coating. A layer thickness of few tens of micrometers allows to isolate the implant from the corrosive environment during some months, to confer the layer biocompatibility on the prosthesis and to keep the mechanical properties of the supporting metal. Such as hydroxyapatites ceramics, biological glasses are good candidates for coating metallic prostheses. In contact with cell tissue, they show in vivo and in vitro biocompatibility, no inflammatory and no toxic processes. They can be bioactive or bioinert according to their composition in oxides. The bioactive fixation is defined as an interfacial bond between implant and tissues by means of formation of a biologically active hydroxyapatite layer on the implant surface [3].

We have studied two different glasses marked off BVA and BVH. Both glasses are used as coating of titanium alloy prostheses (Ti6Al4V). Several methods have been performed in these studies such as nuclear and physico-chemical techniques. The implant with its coating is in contact either with trabecular bone or with lacuna site.

Materials

Glasses are manufactured [4] by melting the components and heating them between 1300 °C and 1600 °C. They are cast, crushed and transformed into powder of grain suitable to the spraying process. They are deposited on sand blasted Ti6Al4V cylinders, 18 mm in length and 4 mm in diameter. The compositions are shown on table 1.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Na₂O</th>
<th>CaO</th>
<th>P₂O₅</th>
<th>K₂O</th>
<th>Al₂O₃</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>BVA</td>
<td>47 %</td>
<td>19 %</td>
<td>20 %</td>
<td>7 %</td>
<td>5 %</td>
<td>1 %</td>
<td>1 %</td>
</tr>
<tr>
<td>BVH</td>
<td>71 %</td>
<td>14 %</td>
<td>9 %</td>
<td>–</td>
<td>1 %</td>
<td>2 %</td>
<td>3 %</td>
</tr>
</tbody>
</table>

Table 1: Composition (% wt) of biological glasses: BVA & BVH.
The coating consists of small granules linked together in an heterogeneous and non continuous form which provides a favorable surface for the attachment of bone tissue. The thickness ranges from 30 to 100 \( \mu m \).

The rods are implanted into lateral femoral epiphysis of sheep by manual pressure. The animals are sacrificed at 3, 6 and 12 months after implantation. The samples are embedded in PMMA resin and cut in transversal sections of 400 \( \mu m \) thickness.

**Methods**

Scanning Electron Microscopy (SEM), Scanning Transmission Electron Microscopy (STEM) and Energy Dispersive X-ray Spectroscopy (EDXS) are used firstly for a qualitative and quantitative analysis of the coatings according to the implantation duration. For STEM and EDXS, some samples are cut into ultra-thin sections of about 100 nm with a diamond ultra-microtome. Bone tissues and coating are also studied simultaneously by Particle Induced X-ray Emission (PIXE) and Rutherford Backscattering Spectrometry (RBS) with nuclear micro-probe (protons of energy 3 MeV, intensity 600 pA and 5 \( \mu m \) beam diameter). PIXE is performed to identify trace elements and to cartography their repartition and RBS to determine organic matrix composition and to measure the electric charge received by the sample during irradiation. This experimental setup has been published elsewhere [5][6].

**Results and discussion**

With BVA and when the coating is in contact with trabecular bone, there is gel formation relatively dense and homogeneous. When the coating is in contact with lacuna site, this gel has different densities and is heterogeneous. The BVA glass proved to be bioactive: it is transformed into a silicon gel with incorporation of protein and trace elements: Zn and Sr. This gel disappears gradually and is replaced by neoformed bone at 6 months after implantation. These transformations lead to a better osseointegration of the coated implant than uncoated prostheses [7]. Bony contact perimeter is increased, then BVA glass permits to limit micro-motion of the implant.

The BVH glass is bioinert: there is no gel formation. Its composition is constant versus time. However, the formation of a 2 \( \mu m \) thickness interface, induced by plasma spray coating process, weakens the inter-granular connections. This fact results in the fragmentation of the coating and the migration of glass particles through the lacunar network of surrounding bone. Its expected function is to protect metallic prosthesis against corrosion: BVH coating is used like a cement.

In table 2, we present mean titanium concentration values measured in surrounding bone of the implant for each kind of coating and for the three implantation durations. In the case of uncoated implants, we found that after a period of establishment, the titanium contamination in bony tissue is constant (about 1200 ppm). This result is consistent with the observation of Agins [8]. We consider that the two glasses protect efficiently the implanted metallic prostheses against the corrosion since we do not detect titanium in bone directly in contact with glass (table 2). In the same time, coating glasses can be contaminated themselves by metallic elements coming from the metallic prosthesis. In both glass coating, we have detected titanium contamination. But, as mentioned above, BVA glass completely disappears between 3 and 6 months after implantation and BVH glass is gradually detached from the prosthesis. Then a large part of prosthesis surface becomes uncoated and the corrosion begins. And after 12 months of implantation, the titanium amounts in bony tissue directly in contact with metal of uncoated and initially
Table 2: Titanium concentration in ppm (LOD = Limit Of Detection).

<table>
<thead>
<tr>
<th></th>
<th>3 months</th>
<th>6 months</th>
<th>12 months</th>
</tr>
</thead>
<tbody>
<tr>
<td>bone directly in contact</td>
<td>−</td>
<td>285 ± 14</td>
<td>888 ± 86</td>
</tr>
<tr>
<td>with prosthesis initially</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>coated with BVA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bone directly in contact</td>
<td>−</td>
<td>387 ± 246</td>
<td>1307 ± 167</td>
</tr>
<tr>
<td>with prosthesis initially</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>coated with BVH</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
</tr>
<tr>
<td>bone directly in contact</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>with the glass (BVA or BVH)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bone directly in contact</td>
<td>651 ± 26</td>
<td>1221 ± 99</td>
<td>1134 ± 67</td>
</tr>
<tr>
<td>with prosthesis initially</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>uncoated</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

coated prosthesis are similar. The protective effect of glasses is thus effective as a long time as glasses remain in place. If we look to the contamination away from the edge of the implant, we observe that it is concentrated in the first 100 μm and that it decreases fastly after some hundred micrometers (fig. 1).

Figure 1: Profile of titanium contamination of bony tissue surrounding an uncoated implant after 12 months of implantation.

**Conclusion**

The two glasses have different behaviour during the first months after their implantation in the body. However, they prevent metallic contamination of surrounding tissues. One year after implantation, BVA is resorbed and BVH is destroyed into debris and the contamination from metallic prosthesis began.
It is shown that the bioactive glass BVA coating enhances the osseointegration of a metallic implant: this is an advantage in the first months after surgery. On the other hand, the plasma spraying at high temperature can induce surface modification and we look after an alternative technique.

References


