Hydroxyapatite coating by dipping method, and bone bonding strength

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Hydroxyapatite (HA) was coated onto titanium rods by a dip coating method using HA sol. The HA sols were prepared by dispersing HA crystals less than 100 nm length in distilled water or physiological salt solution using an ultrasonic homogenizer. The surface of the HA coating was homogeneous as determined by scanning electron microscopy (SEM). After implantation of uncoated and HA dip coated titanium rods in dog femurs, new bone formation was observed only around the coated material. The bone bonding strength to HA coated rods was 1.0, 1.5, 2.0 and 2.5 Mpa after 1,2,3 and 4 weeks implantation, respectively, as determined by pull-out testing. These values were over twice that of the uncoated titanium rods at 1–4 weeks after implantation. The dip coated titanium exhibited superior biocompatibility to the uncoated implant and may be of great value for bone repacement applications.

1. Introduction

There are a number of techniques for coating HA on metals, including plasma spraying, flame spraying, ion sputtering, chemical vapour deposition and thermal decomposition techniques. Among these techniques, the plasma spraying technique is presently being used worldwide (1–8). However, these are all high-temperature techniques. Therefore, it is very difficult to coat HA onto metals homogeneously with a thickness of less than 10 μm, without either decomposition or reaction with the metal substrate. In this study, HA was coated on titanium metal by dipping it into HA microcrystal suspension, i.e. HA-sol as developed by Aoki *et al.* (9, 10). The HA-coated titanium rods were implanted into dog femurs, and the biocompatibility and bone bonding strength were evaluated.

2. Materials and methods

2.1. Materials

HA crystals (Fig. 1) were prepared by the neutralization reaction of calcium hydroxide suspension and phosphoric acid solution using an ultrasonic homogenizer (Fig. 2). The HA crystals were dispersed into distilled water or physiological salt solution in order to prepare HA sols. Pure titanium rods were dipped once and seven times into HA sols of concentrations between 1.5 and 10 wt %. The coating layer was characterized by X-ray diffraction (XRD) and infrared spectroscopy (IRS). The thickness of HA coating was measured and the surface was examined by scanning electron microscopy (SEM).

2.2. Animal testing

The experimental animal used was one male beagle dog, over 1 years of age and with a weight of 12 kg. Anesthesia was induced with an intravenous injection of GOI and with nitrous oxide inhalation according to accepted standards. Twelve HA-coated titanium rods were implanted into femurs of dog. The bone tissue reaction of the materials was examined histologically and the bone bonding strength was measured by pull-out testing at a speed of 0.5 mm/min after implantation for 1 to 4 weeks.

3. Results

3.1. Dip coating method

The hydroxyapatite crystals were less than 100 nm in length and had a plate-like morphology. The concentration of HA sol ranged from 1.5 to 10 wt %. The coating thickness ranged from 10 μm to 200 μm and depended on the dipping time and the concentration of the HA sol. The coating thickness increased notably with the number of dips and in sols of concentration of 7 wt % or more. Titanium pretreated by sandblasting provided a much better coating substrate than the smooth untreated surface (Fig. 3). Thin coatings less than 50 μm in thickness were obtained in dilute HA

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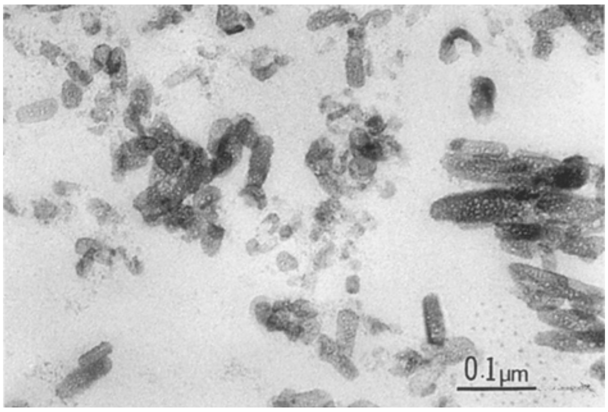

Figure 1 Transmission electron micrograph of HA crystals.

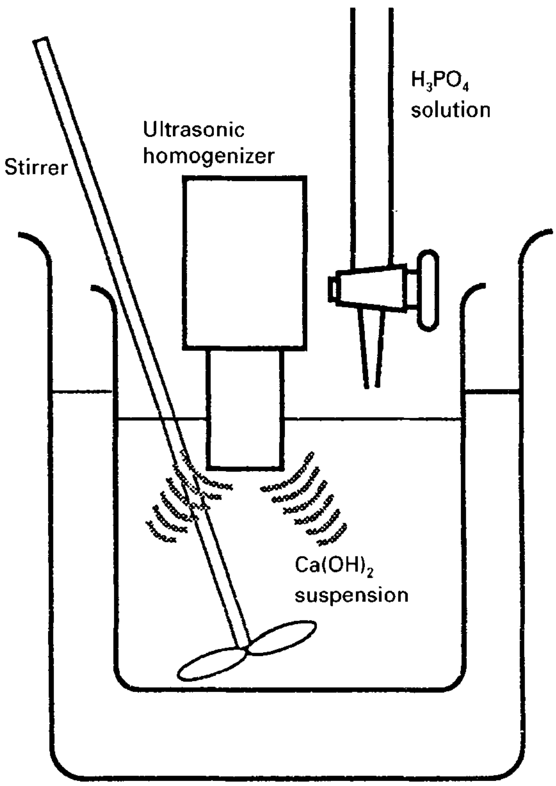

Figure 2 Schema of preparation of HA crystals by ultrasonic irradiation.

sol less than 5.34 wt %. The HA was deposited homogeneously.

3.2. Histology

Fig. 4a is a micrograph illustrating new bone growth in close contact with an HA dip coated implant after 2 weeks *in vivo*. Fig. 4b shows the histology of the control titanium implant. Fibrous connective tissue was observed after 2 weeks.

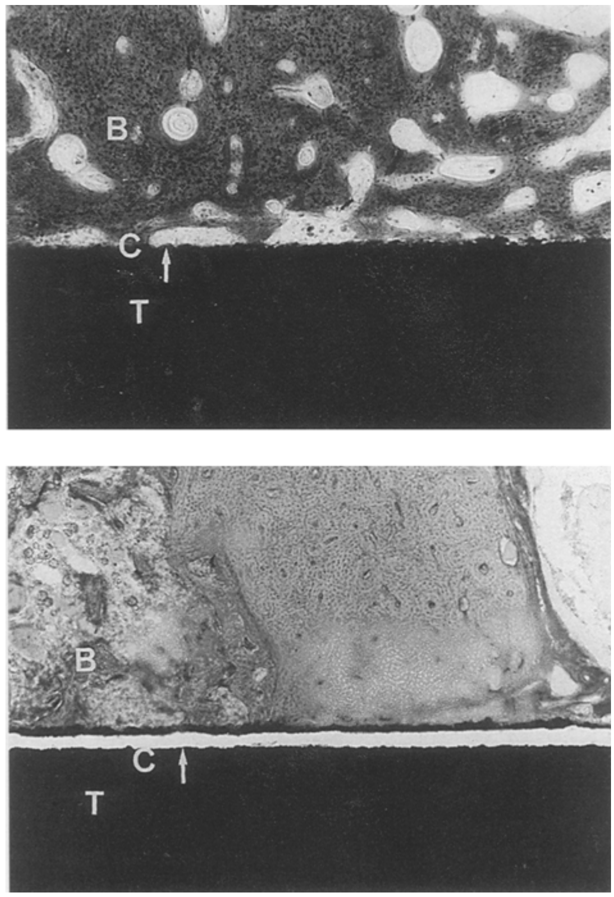

Figure 4 Undecalcified histological section of femora 4 weeks after implantation (H. E. stain, 200) T: titanum, C: coated layer, B: bone. (a) HA-sol coated implant; (b) titanium control implant.

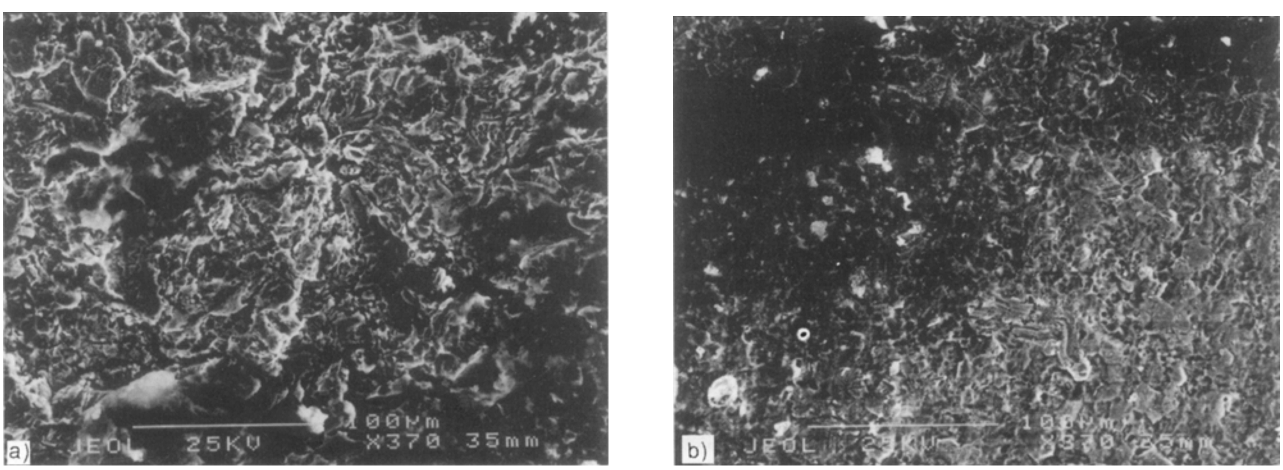

Figure 3 SEM micrographs of HA coating layer after dipping titanium with (a) smooth surface and (b) sandblasted surface once in 5.34 wt% HA sol.

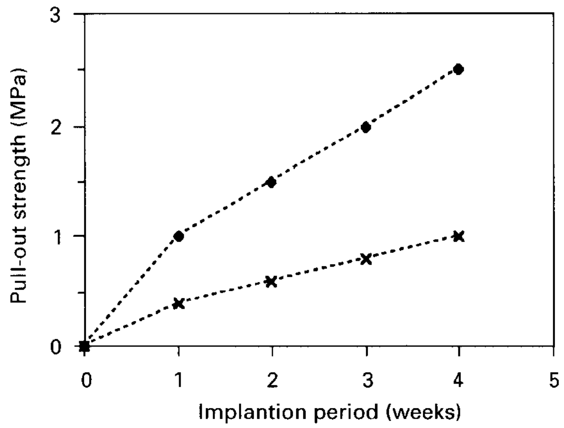

Figure 5 Changes in pull-out strength of uncoated (×) and HA-coated (◆) titanium implants as a function of implantation period.

3.3. Bone bonding strength
Fig. 5 shows the changes in bone bonding strength of HA dip coated on titanium. The bonding strength of HA coating was over twice that of titanium rods at 2–4 weeks after implantation.

4. Discussion
The dip coating method coated HA homogeneously on titanium with a 10–200 μm thickness at room temperature and therefore no reaction occurred between HA crystals and titanium metal. The coating layer was composed of nanoscale HA crystals and the bonding strength between HA and titanium was very weak. The microcrystals quickly induce new bone formation by bonding with some bone formation components in blood and then they will be absorbed into cells for a short time. Therefore, HA coated by the dip coating method is only useful for quick bone formation, as the HA coating layer will disappear relatively quickly.

5. Conclusions
HA-sol was prepared by dispersing HA microcrystals into distilled water or physiological salt solution using an ultrasonic homogenizer. HA coating of titanium was prepared by dipping titanium into HA sol at room temperature. The coating thickness was very thin, ranging from 10 μm to 200 μm.

Bonding strength between hydroxyapatite and titanium was very weak, however, bonding strength between bone and HA-coated titanium was stronger, over twice that of uncoated titanium. The dip coated HA was quickly absorbed into cells. It was concluded that the dipping method is an effective technique for preparing HA coated titanium materials with complicated shapes. The material had good biocompatibility and may be effective for use as prostheses.

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