Analysis of Retrieved Hydroxyapatite-Coated Hip Prostheses

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Hydroxyapatite (HAp) coatings are used extensively on orthopaedic devices to improve the adhesion of bone to the prosthesis. This approach increases the integrity and longevity of the implanted prosthesis. Four HAp-coated hip components recovered from patients during revision surgery were investigated for bone attachment and coating modification after storage in ethanol or formaldehyde. Orthopedic components displayed preferable bone attachment on microtextured areas and little bone on smoother areas. The coating microstructure differed between three coatings that remained on the prosthesis surface, ranging from completely crystalline coatings made by vacuum plasma spraying to less crystalline coatings manufactured by air plasma spraying. Coating failure for the lower crystallinity coatings was observed by a crack at the interface that was possibly caused by the dissolution of an amorphous phase. While higher crystallinity coatings degraded by coating delamination, the lower crystallinity coating produced loose particulate on the outer coating surface. Coating morphology as observed by scanning electron microscopy (SEM) displayed lamellae fracture, chemical dissolution, osteoclastic resorption, and precipitation in agreement with previously identified in-vitro events. The coating longevity appeared to be extended in those areas subject to lower levels of stress and more bone coverage.

1. Introduction

Hydroxyapatite (HAp) is routinely coated onto smooth, ribbed, threaded, and macrotextured hip prostheses to promote fixation to bone. The osteoconductivity of HAp facilitates bone contact by directing bone growth towards the implant both to the coating[1,2] and neighboring uncoated areas,[3] thus allowing gaps of several millimetres to be closed between the osseous cavity and the implant.[4] The combination of mechanical fixation with flutes, ribs, or steps together with bone bonding through a HAp coating offers a useful combination of two different complementary fixation mechanisms. Mechanical fixation becomes effective immediately after prosthesis insertion; however, bonding of the HAp coating to bone is established over a week or more, depending upon the nature of the coating, to further strengthen the fixation between the bone and implanted prosthesis. Where a porous surface (sintered mesh, sphere, or plasma sprayed titanium) is used, the osteoconductivity of hydroxyapatite coatings can guide bone growth into the pore space to enhance the mechanical bonding at a later stage.[5] The bonding of such surface-modified prostheses is incremental, improving over a period of time.

Prosthesis coverage with a coating can include a partially to fully coated HAp layer. Initially femoral stems were fully coated to maximize the fixation and reduce the possibility of interface motion that could otherwise lead to eventual implant loosening. Radiographic evaluation of fully bonded stems, however, indicated more extensive bone loss[6] confirmed by finite element analysis.[7] It was also found that the stress transfer to the surrounding bone could be relocated from the distal two thirds to the proximal third by coating the upper section of the stem (proximal area) instead of the entire length.[8-10] Proximal load transfer allows bones to be stressed at normal physiological levels to maintain periprosthetic bone mass.[11] While many femoral stems today are partially coated, some prosthesis designs include full coating coverage.

Coating placement on the acetabular shell is equally important. A fully coated acetabular shell compared with an uncoated shell provides five times less inclination,[12] less migration,[13] and very good initial stability[14] with more bonding to the rim than the dome.[15] The primary fixation provided by a threaded socket for mechanical interlock coupled with a HAp coating produces better results than smooth HAp press fit sockets.[16] A HAp coating on the dome may assist in stabilization where a central gap exists between the dome of the shell and the acetabular bone.[17]

While HAp coatings have been recognized to provide many benefits, the sensitivity of HAp to loads and dissolution is not widely known. Insertion procedure, type of bone adjacent to the coating, and extent of bending of the coated implant all influence coating integrity. The distal (lower for stems) location of the femoral stem has a lower stiffness and could transfer higher loading conditions to the coating in those areas. This has implications for the longevity of the coating in the distal location on the prosthetic stem. A coating on the upper proximal third is subjected to less bending and is in contact with cancellous bone, which has a different load transfer compared with cortical bone.

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The coating may further experience loading upon prosthesis insertion as it is subjected to loading forces. Abrasion studies with a bone analogue have shown that coating roughness is a key parameter that dictates the modification of the coating surface and particle release upon insertion.[18] Loading of the coating during insertion and use of the prosthesis are important factors that influence the coating integrity, degradation, and resulting prosthesis integration.

Prosthesis performance has usually been monitored by incidence of pain for the patient,[19] subsidence of the implant,[20-22] or by information on bone density surrounding the implanted device recorded by radiography[23-25] or x-ray absorptiometry.[26-28] Radiography may be effective in assessing bone density around implants and interfacial bonding by the presence/absence of radiolucent lines[29]; however, the direct assessment of the HAp coating is not possible with these techniques. Detachment of the coating from the implant, particle release may not result in radiographically detectable changes in bone density around the implant.[30]

Assessment of the coating condition and type of bone in contact with the coating is usually determined from revision surgeries or with postmortem retrievals.[31-34] The report of the coating condition has usually been limited to the coating thickness, coating adherence, and presence/absence of loose particles in the surrounding bone.[35] These features are important signs for the overall implant performance but do not address the cause of coating failure. Established microstructure/property relationships can provide insight into the performance of the coating on a particular implant surface, bone environment, and loading condition. This paper will analyze the microstructure of several retrieved HAp coated orthopedic devices in cross-section and from the surface to illustrate the importance of the coating microstructure on the functionality and performance of the coating.

2. Materials and Methods

2.1 Description of Retrieved Prostheses

Four retrieved hip prostheses components collected at The Prince of Wales Hospital or The Royal Perth Hospital of different designs were further investigated for coating condition. Coated prostheses were stored in ethanol solution or in formaldehyde. All implants were grit blasted and coated by plasma spraying. The ABG femoral stem consisted of a vacuum plasma sprayed coating over a layer of pure titanium. Coating placement varied depending upon the device. The S-Rom sleeve and the acetabular shell were totally coated, but only the proximal location of the ABG femoral stem and the McMinn shell were coated.

The retrieved prostheses are described separately and a picture of the remaining coated area is shown in Fig. 1.

1) A HAp coating S-Rom sleeve (Johnson and Johnson, New Brunswick, NJ) implanted into a 61-year-old male suffering from rheumatoid arthritis was removed after a year due to a dislocated hip.
2) A McMinn acetabular component (Corin Medical Ltd, Cirencester, UK) removed from the right hip of a 45-year-old male recipient after infection. The patient received the implant in Great Britain, December of 1992 in a revision surgery. The in situ time was 1.5 years.
3) A retrieved ABG femoral stem (manufactured by Howmedica in 1994) (Mahwah, NJ) was implanted into the hip of a 72-year-old male recipient with osteoarthritis in July 1996. It was removed after the patient fell and caused a femoral fracture. The in situ time was 1.5 months.
4) The Omnifit acetabular shell has a knurled rim to promote stabilization. An Omnifit HAp coated acetabular shell (Osteonics, Mahwah, NJ) was implanted into an 80-year-old male suffering from osteoarthritis in November 1991 and was removed after two years due to joint instability and poor positioning.

2.2 Microstructural Analysis

Prostheses exhibiting traces of HAp, as determined from viewing under a stereo microscope, were sectioned with a diamond blade. Ethanol was chosen as a lubricant to prevent any further dissolution/degradation of the implant. After sectioning, the coating was washed in ethanol to remove any loose debris. The samples were then dried in an oven set at 100 °C for 10 h and cooled to room temperature before mounting in a slow curing epoxy resin. The coating cross sections were prepared manually by grinding on 600, 800, and 1000 grit silicon carbide grade papers. Polishing was conducted on a rayon cloth with 3 and 1 μm diamond paste and a kerosene lubricant. Final polishing with 0.3 and 0.05 μm alumina on a short napped surface preferentially removed the amorphous phase to distinguish the crystalline and amorphous areas in the coating microstructure.

X-ray diffraction (XRD) was performed to identify the chemical phases on the McMinn acetabular component with a Siemens (Karlsruhe, Germany) D-5000 x-ray diffractometer. Cu K_α radiation diffracted from the sample passed through a 1 mm antiscatter slit and a 0.02 mm divergence slit. The diffracted signal was collected over a two-theta range of 20-60° at a scan rate of 0.5° per minute and 30 kV and 30 mA.

Cross sections and coating surfaces were sputter coated with a 25 nm film of carbon. A JEOL 6300F (Tokyo, Japan) with a field emission gun was used for viewing the surface and cross section at an accelerating voltage of 8 kV.

3. Results and Discussion

3.1 Bone Attachment and Coating Fragmentation

Bone bonding to the prosthesis can be inferred from observation of the prosthesis surface. Inspection of the retrieved prostheses is then assumed to provide some indication of the bonding before extraction. Bone was found attached to three of the prostheses, the quantity being site specific (Fig. 1). Bone was preferentially located on the threaded areas of the S-Rom sleeve, within fenestrations of the ABG femoral stem or on the knurled rim of the Omnifit acetabular shell.

Inspection of the Omnifit shell with a stereomicroscope presented no visible trace of a coating. It appeared that the coating was uniformly removed from the entire surface of the shell.

The S-Rom sleeve was well integrated with the bone, displaying bone bonding to specific areas of the sleeve. Bone attachment penetrated to the bottom of the spaced grooves. The raised profile of the bone on the S-Rom sleeve suggests that abrasion against the sleeve during extraction was unlikely.
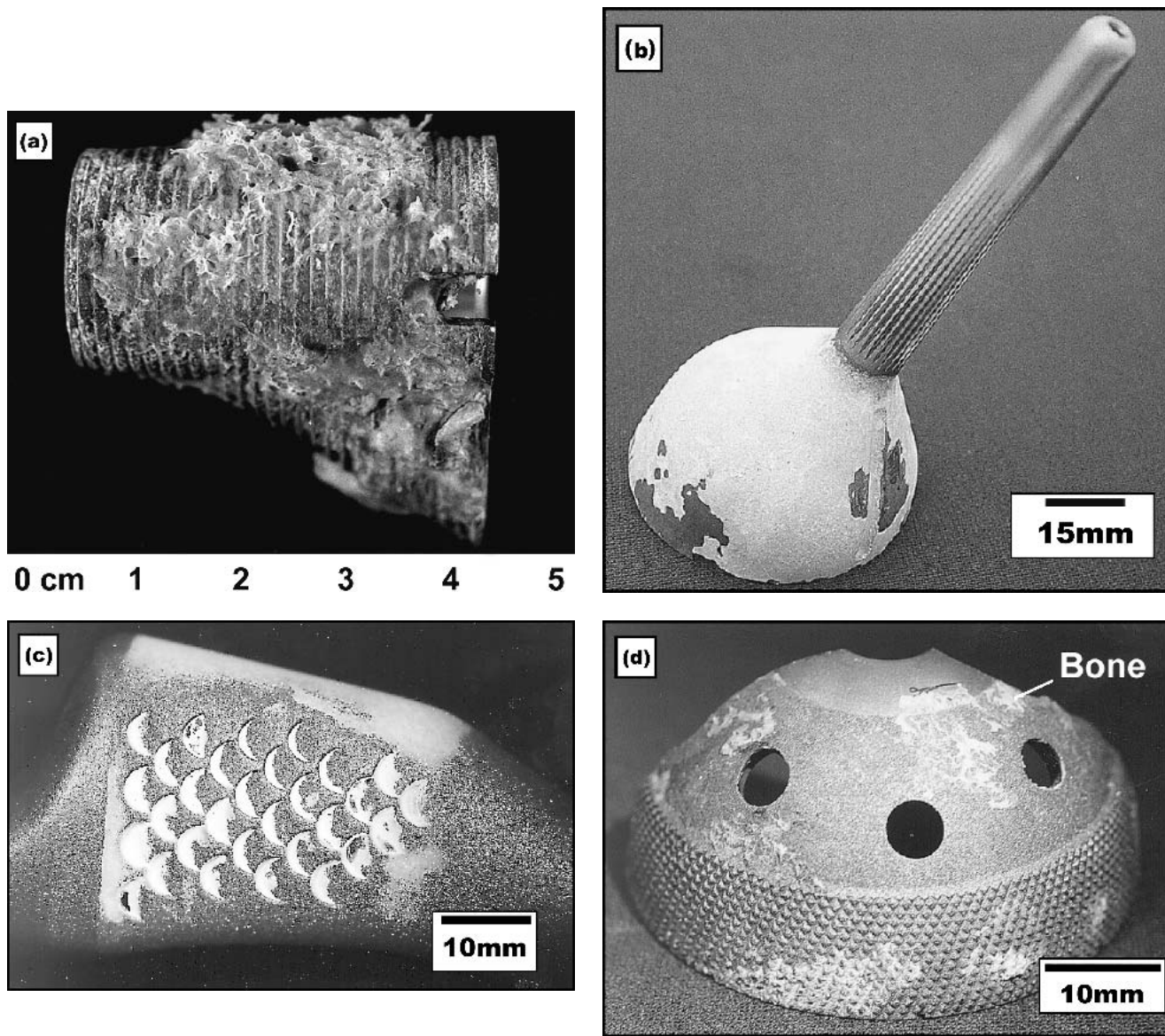
Fig. 1 Retrieved HAp coated orthopaedic components showing remnant coating and areas with attached bone on **(a)** an S-Rom sleeve, **(b)** a McMinn shell, **(c)** an ABG femoral stem, and **(d)** an Omnifit acetabular shell. The S-Rom sleeve slides onto the cylindrical stem and sits in the upper component of the prosthesis.

The coating from the S-Rom sleeve was removed from the top surface of the ribbing. The coating is very loose on the tip of each rib, and in some places has been totally removed. The thread tip also corresponds to the highest stress location. The root of each rib appeared to contain relatively dense coating fragments (Fig. 2).

Removal of bone from the implant with a probing tool revealed a denser coating underneath. This implies that the coating covered by bone was less likely to undergo continued dissolution. Examination of a similar dense area in cross section with the scanning electron microscope showed coating delamination from the substrate. The coating appeared to contain cracks and loose material within the coating (Fig. 3a). This fragmented coating remains stable and relies on mechanical fixation between the bone and the surface with the spaced grooves. It is
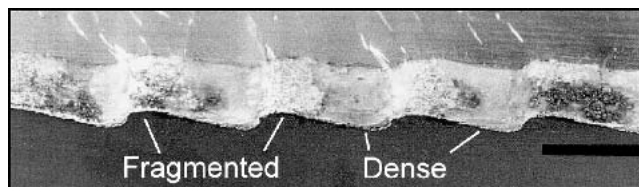

Fig. 2 Angles section of an S-Rom sleeve showing coating present at the root of the threads

believed that bone coverage and location of the coating at the bottom of each rib increases coating longevity.

Bone debris attached to the ABG stem is darker in color than the coating that is white. Bone appears to be detected
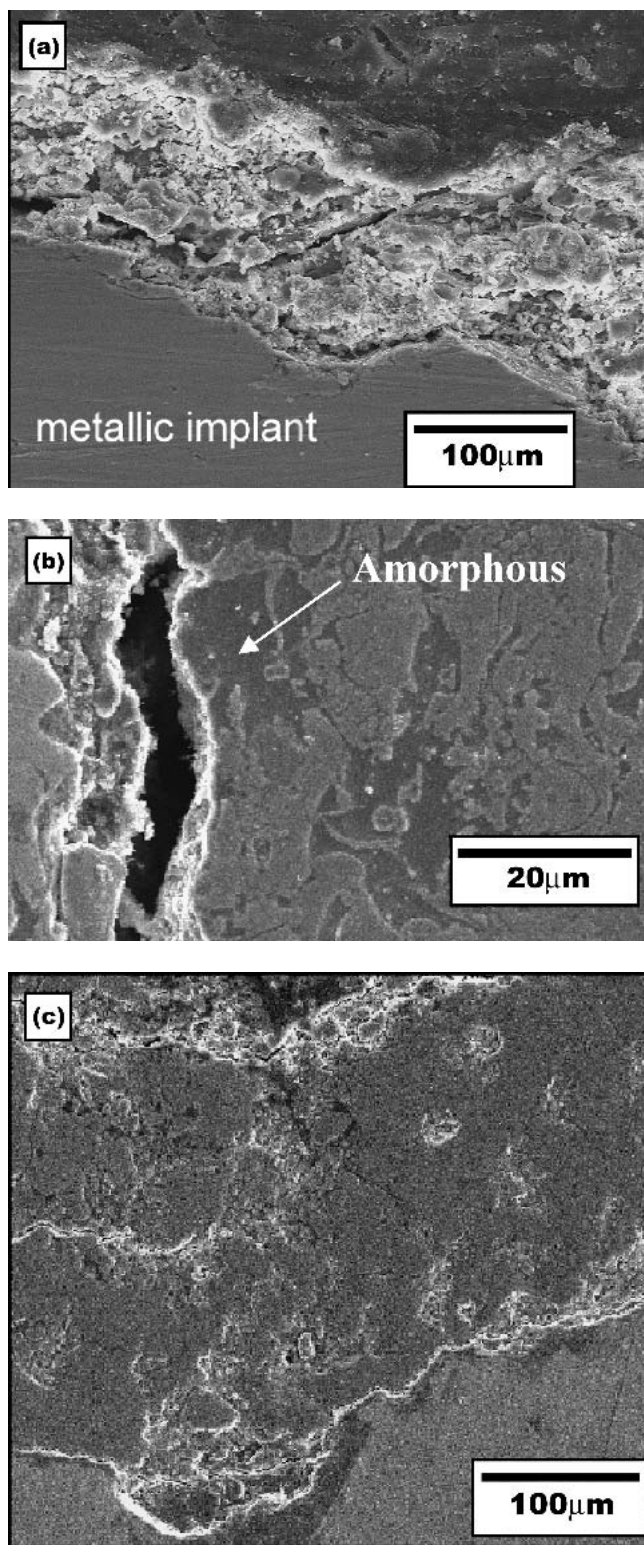
Fig. 3 Cross section of the HAp coating from the **(a)** McMinn shell, **(b)** S-Rom sleeve, and **(c)** the ABG stem

within the fenestrations of the orthopaedic stem. Similarly, for the acetabular shell, bone has bonded mainly to a larger portion of the knurled section than the flat grit blasted area.

Coating dissolution and degradation occurred quite globally on the ABG femoral stem with the majority of the coating dissolved in less than two months. The coating was removed to a greater extent from the smooth area except on the curved surface. XRD indicated a very high crystallinity in the remaining coating.

The medial scales, which increase in depth with the height, were occupied by a HAp coating. Coating removal from the scales appeared to begin at the bottom of each scale and progress towards the deeper section of the scale, which is a site of lower stress. Examination of the coating cross section within the scales indicated good bonding to the substrate after a quick inspection (Fig. 3c). A more detailed examination revealed a hairline crack at the interface. It is not known whether this occurred during residence within the body, sectioning, or polishing. The coating appeared dense with no trace of an amorphous phase. While such a coating would represent failure within tensile loading, the mechanical lodgement of this coating segment and the shear loads along the prosthesis surface would prevent coating removal within the clinical setting. The mechanical surface features assist the longevity of the coating and removes the likeliness of prosthetic failure linked to coating delamination.

Loss of the HAp coating has been reported as bone remodels in response to changing loads[32] or continual loading.[36] This produces a decrease in coating thickness over a larger area than the more localized loss associated with areas facing medullary cavities[37] or remodeling canals.[15] Less coating resorption will then be expected to occur in areas covered by bone,[38,39] as observed on the S-Rom sleeve when the bone was manually removed. The blood flow in cancellous bone is higher than in cortical bone,[40,41] so the type of bone attached to the implant will further influence the rate of coating loss.

The stress on the coating can emphasize loss of the coating thickness and can be manifested in three forms. The stress can arise from (a) plasma spraying induced residual stress, (b) implant loading stresses, and (c) stress in the surrounding bone, which through bone remodeling produces osteoclastic resorption. The global coating loss on the ABG femoral stem could not be related to any specific mechanism; however, the coating remaining in the scales suggests that implant loading stresses may have placed the coating into compression and shear and decreased the coating resorption.

Other studies have shown that more coating resorption occurs in locations subject to higher loading.[42] The same observation has been made for coated dental implants.[43,44] The stress on the coating is believed to vary over the device and depends upon the geometry and mechanical fixation features included in the design. Where the prosthesis geometry does not have flutes and threads for mechanical fixation, the loading on the coating will be more severe and thus subject the coating to greater dissolution. In situations where a mechanical bond is established between the bone and the prosthesis, the stress levels on the overall surface of the prosthesis will be lower; however, higher loads are expected in those areas providing the mechanical bonding and thus subject to greater resorption.

3.2 Influence of Coating Microstructure

Further insight into the integration of a coated prosthesis can be gained by knowledge of prosthesis alignment, patient's age,
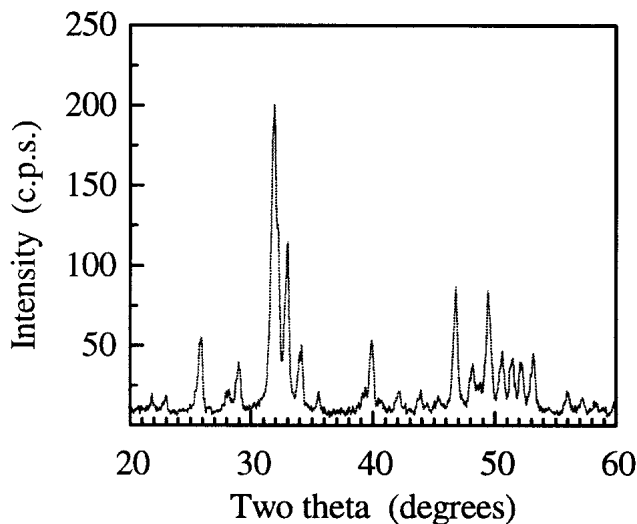
Intensity (c.p.s.)

250

200

150

100

50

20   30   40   50   60

Two theta (degrees)

Fig. 4   XRD of the remaining coating from the McMinn shell

patient's activity, and coating microstructural features. This section will initially describe the coating microstructure on each of the three prostheses and then use this information in discussing the degradation of the coatings based solely upon the microstructure. Although only material characteristics will be discussed, one must not separate the contribution of the other factors.

The microstructure of the coatings on three of the retrieved prostheses displayed different features. The 150 μm thick coating on the McMinn prosthesis appeared very dense. Crystalline areas, observed from the lighter raised areas in the polished coating, are enclosed with the amorphous areas (Fig. 3b). The amorphous content appeared greater within the first 50 μm of the coating adjacent to the substrate and decreased to a very low value in the outer section of the coating. This type of microstructure suggests two aspects of coating manufacture. First, the presence of enclosed amorphous areas suggests that the heat was sufficiently great to produce crystallization, such that amorphous areas are no longer interconnected. Secondly, an increase in the crystallinity with the thickness is indicative of a rise in coating temperature during the coating process. It is expected that the increase in coating temperature during spraying a thicker coating, such as the one located on the McMinn implant, would be sufficient to cause partial crystallization of the first deposited layers. XRD of the outer layer revealed a high crystallinity coating in agreement with the observations from the coating cross section (Fig. 4).

The coating on the McMinn prosthesis exhibited the least degradation, leaving a coating on most of the shell. Closer examination of the coated region in a polished cross section with a scanning electron microscope revealed a clear separation of the coating from the prosthesis. The coating remained attached by mechanical interlocking to the roughened prosthesis surface (Fig. 3b). The dense arrangement of the crystalline and amorphous phases suggests slow resorption; however, the presence of the amorphous phase at the interface indicates that access of physiological fluids to the amorphous region could initiate failure. It is quite possible that the cracked area could have been

occupied by an amorphous phase since molten HAp tends to form the amorphous phase quite easily on metallic substrates not subjected to preheating.[45] Dissolution of the amorphous phase adjacent to the substrate may be responsible for failure of the McMinn prostheses as reported in other studies[46] in which delamination of large coating fragments were attributed as the main cause for the loss in integration. Delamination could have occurred from the residual stress retained within the coating that shifts the failure location from within the coating to the interface for thicker coatings.[47]

The fragmented cross section of the coating on the S-Rom sleeve indicates that the amorphous phase was the likely bonding phase for the crystalline islands within the coating (Fig. 3a). The amorphous phase forms preferentially from the outer layers of deposited molten particles and hence leads to a microstructure of crystalline sections surrounded by the amorphous phase. An amorphous layer can be assumed at the interface where such a microstructure is observed. Fragmentation of the coating occurs by dissolution of the amorphous phase, thus providing a loose assembly of particles and a weakly bonded layer to the underlying metallic alloy prosthesis.

All HAp-coated implants followed the predictable stages of coating modification by partial or entire coating resorption. Dissolution of the coating is not detrimental since bone normally undergoes remodeling where it is resorbed and then restructured.[48] From the amorphous and crystalline phases typically found within the plasma sprayed coatings, the amorphous phase dissolves at a faster rate but also leads to more rapid bone remodeling by precipitation on the coating[49,50] and by mineralization in the surrounding bone.[51] Calcium release from the coating produces a higher calcium content in bone directly in contact with the implant[31,52] and a greater appositional bone index and higher bone volume.[53,54]

Degradation products must be small in size to dissolve. Small loose particles from the implant can then usually be removed by phagocytosis.[55] Particulate material produced by coating dissolution may be released at a later stage and could be incorporated in the mineralizing bone.[32] The size of the coating constituents released is important in dictating the cellular response. Larger coating fragments or large particles will cause macrophages to dissolve the particle by lowering the pH on a local scale.[56] If the fragment is too large, the body's defense may lower the pH on a larger scale, which will lead to accelerated coating dissolution and may sacrifice any established bone-coating bond.[57] Given unimpeded transport, there is a possibility that large particulate material could move to the lubricating joints,[58] produce third body wear,[59] and sacrifice the motion of the joint.[60] The peri-implant particle migration can be prevented[61] and is dependent upon the fixation and concentration of evolved particles.

Early in vitro studies on hydroxyapatite particulate have not positively identified bone growth.[62] A recent in vitro investigation found that the increase in expression of cytokines and proteases associated with HAp particulate enhances bone resorption.[63] Implanted coatings differ from these studies in that an amorphous phase is present, the particulates are possibly more soluble, and both the concentration and particle size changes during coating resorption.[64] Once a particle is released from the coating, more amorphous calcium phosphate is exposed, which provides a short burst of dissolved calcium and
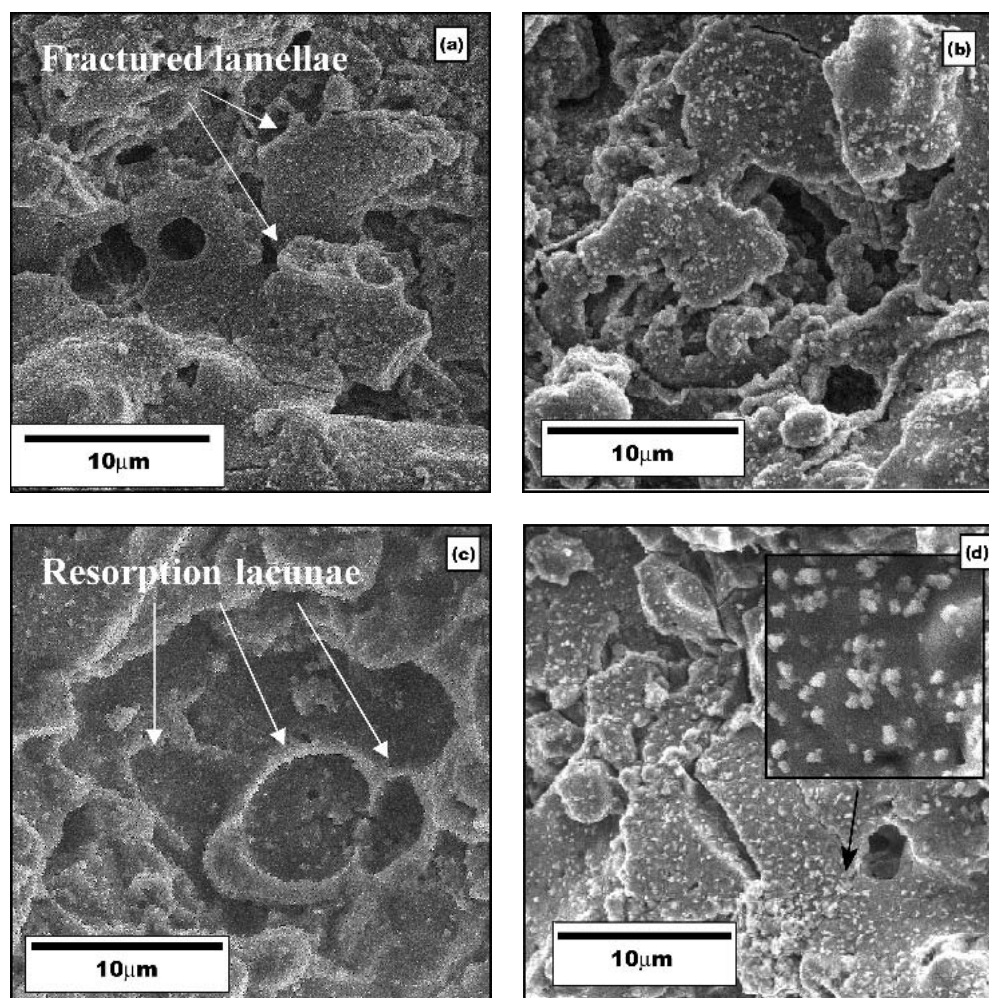
Fig. 5 Topography of the coating remaining on the McMinn shell showing **(a)** fractured lamellae, **(b)** rounding of lamellae from dissolution, **(c)** resorption lacunae from osteoclasts, and **(d)** precipitated carbonated apatite

phosphate. The combined effect of released particles and dissolved amorphous phase may be interpreted in the following way. While particulate may lead to loosening, the underlying exposed amorphous calcium phosphate stimulates bone growth. If it can be assumed that the interface is already established and there is no micromotion between the prosthesis and bone, the overall result is that released particulate leads to bone resorption, but the amorphous calcium phosphate promotes bone growth. The two factors are believed to counteract one another. More focused in vitro studies on this topic will reveal the governing factor.

Several issues are very important in controlling the degradation. First, the degradation must occur from the outer coating surface so that the implant remains integrated. Dissolution of the coating at the coating-substrate interface will decrease the implant fixation. The bone may be attached to the coating, but if the coating-substrate interface is weakened, the implant may become loose, leading to pain and prosthesis loosening.

The third type of coating microstructure appears very dense and contains a high crystallinity HAp (Fig. 3c). This coating is subjected to more heating during the deposition and also during the layering process. Vacuum plasma spraying processing produces a more uniform microstructure within the coating, which is predominantly HAp with a larger grain size than atmospherically deposited layers. The large average grain size of 1-2 μm for the vacuum plasma sprayed coating, comparable to sintered apatites, is a factor of ten larger than in conventional air plasma sprayed coating.

3.2 Remodeling of the Coating

The coating surface morphology on the McMinn shell was examined and several degradation signs could be observed. The surface became very tortuous as a result of implantation. Remnant lamellae could be identified and it was apparent that the coating had degraded by lamellae fracture (Fig. 5a) and dissolution (Fig. 5b). These features have been recorded as normal signs for coating degradation.[65] In addition, circular resorption lacunae that represent markings of osteoclastic resorption,[66] could be observed (Fig. 5c). The coating was thus subjected to lamellae fracture, dissolution, and cellular resorption.

It has been established that coating loss by dissolution occurs

to a greater extent than loss due to cellular resorption.[67] Coating resorption saturates the surrounding fluid with calcium and phosphate ions. A coating with a higher tendency of dissolution will create a higher concentration of dissolved species in a shorter time. Osteoclasts participate in modifying the surface as part of the bone remodeling.[37,55,68,69] Osteoclast activity is based on dissolution where an acidic environment of pH 4.8[70] is established under the osteoclasts to produce resorption in a specific coating area. The extent of osteoclastic resorption is mediated by the intrinsic solubility of HAp and amorphous phase that supplies the necessary calcium for bone growth.[71]

Lamellae fracture can occur from (a) release of shrinkage stresses in each lamella or (b) loading of lamellae that have lost the underlying support as a result of the dissolution process. Upon immersion in solution, the residual stresses within surface lamellae are released to provide a cracked appearance. Although cracking does occur, it is presently thought that this mechanism does not contribute significantly to the weight loss from the surface of the coating.

Well-distributed submicron white deposits covered the surface of the lamellae on the McMinn prosthesis (Fig. 5d). These deposits represent a carbonated apatite precipitate, as a result of the dissolved calcium and phosphate species from the coating combined with dissolved carbonate in the surrounding physiological fluid. The sparsely separated deposits could suggest
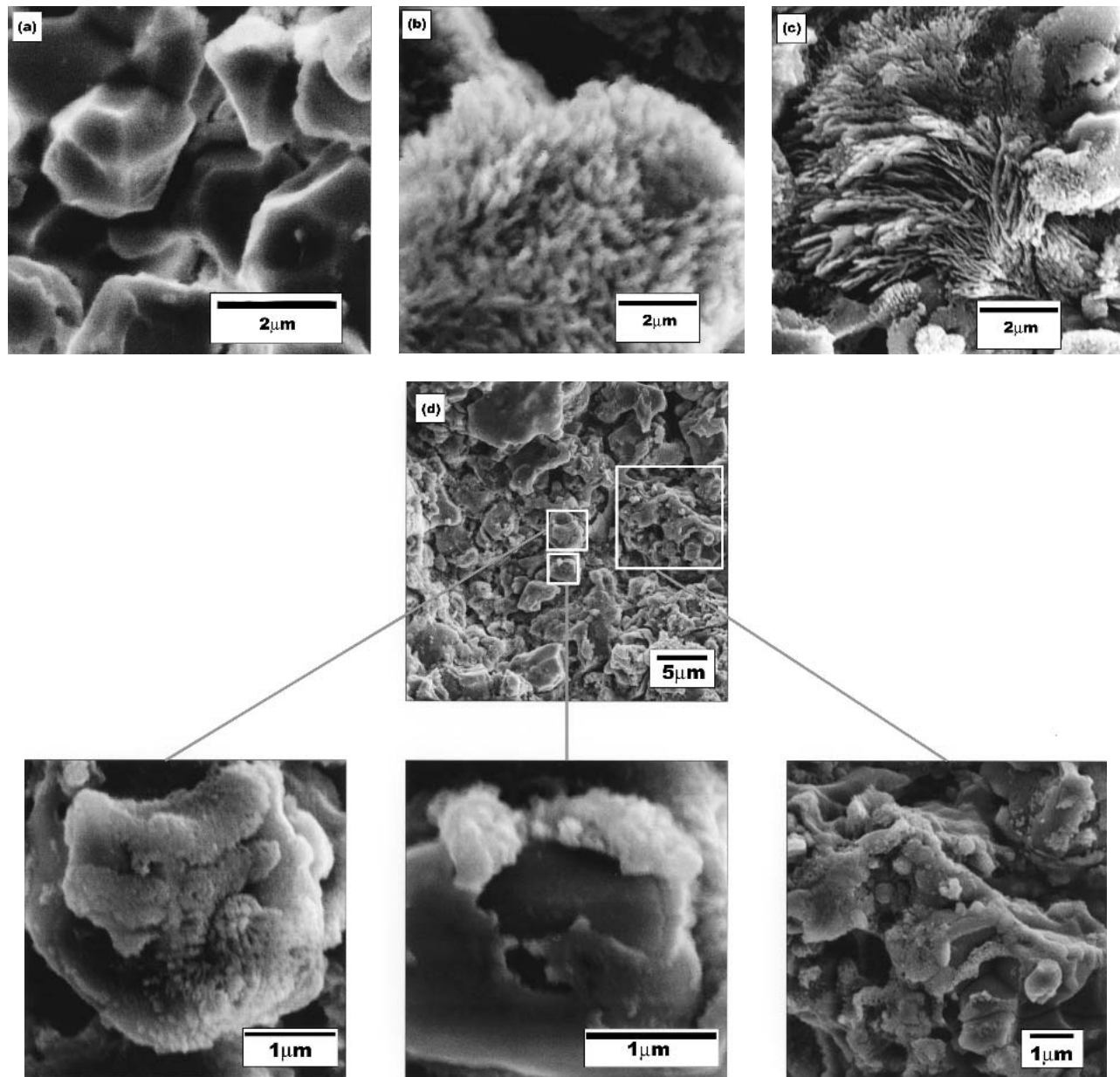

Fig. 6 Topography of the remaining coating on the ABG femoral stem showing **(a)** crystalline facets of the crystalline HAp, **(b)** acicular precipitate, **(c)** plate-like precipitate, and **(d)** precipitation on the resorbed coating surface

that a particular crystallographic orientation is favored for nucleation and growth. The size of these deposits is about 10 times larger than the crystallites within the coating, about 50-100 nm in diameter.

The coating on the ABG femoral stem also exhibited the presence of a dense precipitated layer, which covered most of the coating surface. It was difficult to view at lower magnifications and appeared out of focus (Fig. 6d); however, at higher magnifications a fine structured continuous blanket over selected areas could be identified as acicular precipitate where growth occurred directly from the surface (Fig. 6b) or plate-like precipitate where growth occurred partially along the surface (Fig. 6c). The availability of a range of crystal faces in the coating for precipitation without a precipitate in seen in Fig. 6(a).

Precipitation is effective after a high level of dissolved calcium and phosphate has been established[72-74] and produces cluster-like deposits, which upon closer examination resemble the plate-like or needle like crystals from simulated body fluid experiments.[75] The first phase of precipitation can take place on preferred crystal faces starting as a cluster like precipitate, which then transforms into a continuous blanket of vertically oriented needles over particular microstructural details. This type of precipitation correlates with results of coatings immersed in simulated body fluid[50] and coatings implanted into sheep.[76] The needle-like crystals seem to grow on particular crystallographic grain faces, which suggests that precipitation is favored by a specific underlying crystal orientation. When the dissolution/reprecipitation phenomena has produced a stable carbonated layer, cell proliferation can commence to produce bone growth.[77] Electron microscopy studies of the bone/implant interface have shown direct bone growth from such aligned mineral crystals.[78]

Positive results of HAp coated compared with cemented, and press fit ridged stems[79] advocate the continual use of HAp coatings for improved bone bonding given good coating design and coating application. The high survival rate, 97% for the ABG femoral hip prosthesis after 7 years, offers a good resulting hip fixation as the coating slowly resorbs.[80] The removal mechanism of these coatings is dictated by the coating microstructure. Coating microstructure can be illustrated in polished coating microstructures[81,82] and the effect ascertained in dissolution experiments[83] and in vivo animal studies.[84]

4. Conclusions

Examination of four retrieved HAp coated orthopaedic prostheses has indicated bone attachment, along with coating removal, from a range of areas on the prosthesis surface. Coating removal occurred by dissolution but provided the higher bone-remodeling rate accompanied by the release of calcium and phosphate. Coatings dissolved faster on elevated areas or those subjected to a higher level of loading. Coatings located in less-loaded areas provided a higher longevity. Analysis of the coating surface indicated dissolution, osteoclastic resorption, and carbonate apatite precipitation identical to observations from previous in vitro studies. The microstructural investigation was able to display coating resorption and reveal the degradation mechanism of different HAp coatings.

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