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An analysis of the *in vivo* deterioration of Co–Cr–Mo implants through wear and corrosion

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Abstract: The degradation of Co–Cr–Mo ASTM F75-92 hip implants after a harvesting period of 8½ months in sheep was investigated. Hip prostheses and tissue samples were obtained from a medical study involving total hip arthroplasty of the cemented type in 12 sheep. Upon euthanasia, the explants were retrieved for analyses of the surfaces and evidence of degradation, while tissue samples from the interface regions were harvested for chemical analysis and evidence of Co, Cr, and Mo contents. Clear evidence of wear and corrosion was detected. Results also indicated that the modes of metal transport through the poly(methyl methacrylate) bone cement play an important role as the surface degradation mechanisms of the metal. The results are being discussed in terms of electrochemical and triboelectrochemical behaviour of the Co–Cr–Mo alloy.

Keywords: hip prosthesis, wear, corrosion, Co–Cr–Mo alloy

1 INTRODUCTION

Co–Cr–Mo alloy is regarded as a highly biocompatible material and has been employed in the fabrication of hip prostheses since the 1940s. Its biocompatibility is closely linked to the high corrosion resistance due to the spontaneous formation of a passive oxide film, mainly composed of Cr₂O₃, the integrity of which has been strongly correlated to the chemical and mechanical stability of implants [1–3].

Nonetheless, the implantation of each spontaneously passive metallic device is associated with the release of metal on a small scale owing to the uniform passive dissolution resulting from the slow diffusion of metal ions through the passive film, and on a larger scale owing to breakdown of passivity as a consequence of chemical (pitting and crevice

corrosion or transpassive dissolution) [4–11] or mechanical (fretting corrosion) events [12, 13]. Mechanical breakdown of passivity takes place for example when rubbing occurs between the passive metal and a counter-body. Under these circumstances, local abrasion of the passive film leads to wear-accelerated corrosion because of the rapid dissolution of the depassivated metal surface, followed by repassivation. Wear-accelerated corrosion phenomena have been investigated and recently reviewed [14], in particular by combining electrochemical and wear test techniques. In addition, models relating wear-accelerated corrosion to passivation kinetics [15] or to mechanical, material, and operating conditions [16] have been developed. In the case of implanted prostheses, small-amplitude sliding (or fretting) is known to occur between the metal implant and a counter-body such as bone or bone cement, leading to the release in the body of solid particles as well as of dissolved metal ions [17].

The release of metal has been known to lead to local and remote consequences such as metabolic,

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bacteriological, and immunological effects [18–25]. Wear particles may originate from wear of the prosthesis components such as metal from the femoral stem, poly(methyl methacrylate) (PMMA) from the bone cement, or polyethylene from the acetabular cup. Evidence of Co–Cr wear particles in synovial fluid, in acetabular cups, within the bone, and within the interfacial membrane have been widely reported from a number of *in vivo* investigations [26–33].

Total hip arthroplasty is a successful surgical operation, which has gained acceptance worldwide in the last few decades. Despite improvements regarding the technique, the implant design, and the biological aspects of the procedure, every year up to 20 per cent of human patients require revision surgery owing to complications, the major cause of implant failure being aseptic loosening [34]. The latter has been associated with the formation of a synovial-like tissue at the interface between the bone and the implant, or between the bone and the cement mantle for cemented hip prostheses, in response to the interaction of mechanical, electrochemical, and biological processes [35–37]. Micromotion and wear particles are thought to be involved in eliciting host-specific responses that activate cell mechanisms such as the production of cytokines, the release of local inflammatory mediators, and matrix metalloproteinases, which in turn have been reported to play a role in osteolysis typical of aseptically loosened prostheses [38–42]. However, it is still discussed in the literature whether micromotion or wear particle formation is the initial trigger for the process of aseptic loosening [43, 44]. It has been suggested that micromotion due to an incomplete cement mantle and/or mechanical malpositioning of the prosthesis may be the initial trigger that induces inflammation, leading to the formation of an interface membrane [45]. The latter in turn may release substances that may further accelerate bone resorption in the adjacent bone tissue. An increase in implant instability may then be the cause for the establishment of a vicious circle that will add to excessive wear of the prosthesis components [46]. Debonding and failure of the prosthetic–PMMA interface has also been implicated as a primary cause of loosening in cemented femoral components [47, 48]. Debonding has, in fact, been shown to result in substantial increases in stress levels in the PMMA bone cement mantle, leading to extensive cracking of the PMMA and the premature failure of the cemented systems. Saline solutions tend to enhance cracking between the interface [48].

In this study, an animal model for interface tissue formation in cemented Co–Cr–Mo hip replacements was exploited to investigate the processes occurring

at the implant–biological interface [46, 49]. The major aim of this work was to increase the understanding of the degradation processes that take place at the implant surface from the material's surface point of view, i.e. considering possible corrosion and tribocorrosion events taking place.

2 EXPERIMENTAL DETAILS

2.1 Clinical study

In the current paper, 12 female Swiss Alp adult sheep with an average mass of 60.8 kg were employed [46]. The sheep were submitted to a standard protocol of total hip replacement [50] using a cemented modular system consisting of ASTM F75-92 Co–Cr–Mo prostheses (BioMedtrix, size 9 femoral and 27 mm polyethylene acetabular cup, New Jersey, USA) as described elsewhere [46, 50]. According to the manufacturer, the composition of the Co–28Cr–6Mo alloy was as follows: C, 0.26 wt %; Mn, 0.54 wt %; Si, 0.81 wt %; Cr, 29.38 wt %; Ni, 0.60 wt %; Mo, 5.98 wt %; Fe, 0.61 wt %; Co, balance. The prostheses were vacuum solutioned at 2225 °F for 4 h and the Rockwell C hardness was 25–35 HRC. No coatings were applied on the prostheses.

The sheep were divided into two groups. In short, in one group the prostheses were fixed with PMMA-retrograde injection in order to achieve a complete mantle (Surgical Simplex P, Howmedica International Ltd, Limerick, Ireland), while in the other group a primary cement mantle defect was produced using a small osteotome. The stability of the implants was assessed manually by the surgeon at the end of each implantation. The prostheses were found to be well fixed and stable. The animals were sacrificed 8½ months after surgery, during which time the sheep were confined to small stalls in groups of two sheep according to guidelines recommended by the Swiss Society for Animal Welfare and Protection [51]. Clinical assessment during the 8½ months did not reveal clinical lameness in the sheep. Radiographically, severe cracks in the PMMA cement mantle were observed in most sheep of the group with a primary cement mantle defect. These were predominantly localized in the region of the tip of the femoral implant.

2.2 Sample retrieval

The femurs of the operated limbs were collected immediately after euthanasia. Transverse 3 mm bone sections of the femurs were made using an oscillating saw (Exakt System, Hamburg Germany). The first cut

in the femur was placed immediately below the tip of the implant, in order to facilitate the retrograde removal of the femoral metal component within the cement mantle without destroying the structure of the bones and interface membranes. During the prostheses extraction procedure, a subjective clinical evaluation of the stability of the shaft of the implant within the femur showed differences between individual implants. The degree of fixation of the metallic shafts within the bone was subjectively (qualitatively) categorized as *well-fixed*, *fixed*, and *loose*. This classification reflected the degree of mobility of the prostheses within the cement mantle and the ease with which the latter could be removed at the time of euthanasia. The ranking of the prostheses is presented in Table 1. The prostheses were subsequently stored for surface analysis.

Sections of the femoral stem were cut according to five different regions delineated with the aid of a standardized template. Macroscopic analysis of the transverse bone sections revealed an interface tissue with scar-like dark-red colouration between the PMMA mantle and the bone. The latter was considerably more prominent in sheep with clinically more unstable implants. In the clinically stable implants, an immediate contact between bone and cement was present without interposition of an interface tissue. Furthermore, areas with small air bubbles, cement shrinkage, or cement cracks presented growth of interface tissue also into the cement mantle, although only localized to the immediate neighbourhood of the small cement mantle defects. An example of distinct cases with a *well-fixed* and a *loose* implant is illustrated in the transverse bone sections shown in Fig. 1. Capsular and synovial tissue of the pelvic (hip) joint and interface membrane was collected for evidence of corrosion and wear products.

Table 1 Ranking of prostheses according to the degree of fixation within the bone

Sheep number	Clinical evaluation of prosthesis
502	Fixed
505	Fixed
511	Fixed
513	Well-fixed
514	Loose
515	Loose
517	Fixed
518	Fixed
520	Fixed
521	Loose
523	Fixed
524	Fixed

Fig. 1 Transverse sections from (a) a fixed implant with only small bubbles (arrows) at the cement (C)–bone (B) interface and (b) from a very loose implant, where the interface membrane (IMF) is extremely thick and cement cracks (arrow) are visible. The interface membrane was removed from the transverse section for inductively coupled plasma mass spectrometry analysis

2.3 Chemical analysis of interfacial and joint capsule tissue

Quantitative determination of Co, Cr, and Mo in tissue taken from the interfacial and joint capsule region was carried out by inductively coupled plasma mass spectrometry (PE/SCIEX Elan 6100 DRC mass spectrometer). Tissue samples of each type were collected on the day of euthanasia and immediately placed in liquid nitrogen, prior to storing at -80°C . For the analysis, the samples were dried to a constant weight in an oven at 60°C , after which they were digested in a microwave oven (MLS Ethos, MLS-Mikrowellen-Laborsysteme) with 65 per cent HNO_3 and 30 per cent H_2O_2 . The resulting samples were subsequently analysed for Co, Cr, and Mo. Joint tissue from the leg of a non-operated sheep served as a control to provide background concentrations of the three metals (blank). The latter was collected and analysed according to the same procedure. The metal concentrations are given in parts per billion and are to be regarded as absolute values. The weight of samples was taken into consideration.

2.4 Surface characterization of the explants

The surfaces of the explants were investigated microscopically using optical stereomicroscopy, scanning electron microscopy (SEM) (Jeol 6300F scanning electron microscope equipped with energy-dispersive X-ray analyser for chemical analysis) and non-contact laser profilometry (UBM Telefokus). SEM investigations were carried out on an as-received

virgin prosthesis and on explant 514 only, the latter having been classified as clinically unstable. Prior to SEM and laser profilometry measurements, the samples were cleaned in an ultrasonic acetone bath for 15 min followed by an ethanol bath for a further 5 min. Quantitative measurements of surface topography were carried out using non-contact laser profilometry (UBM Telefokus). A laser probe of 1 μm diameter was scanned over an area of 1 mm $\times$ 1 mm at 2 μm steps and the corresponding height profile was simultaneously measured with a vertical resolution of 0.01 μm . The UBM linear regression routine software was employed to compensate for the tilt angle between beam and surface. The acquired data was plotted in a three-dimensional grey level profile using NIH 1.64 software. The root mean square (r.m.s.) roughness R_q was determined on selected profile lines as a function of distance using the software developed by Chauvy *et al.* [52] for variable-length-scale analysis. The latter enabled the evaluation of the effect of scale on the surface topography. In accordance with this analysis, the distance over which the profile is measured is divided into a finite number of intervals of identical length. After levelling via a least-squares fit, the R_q value is calculated over each interval and an average value determined. Subsequently, the interval distances are increasingly lengthened and for each length the R_q computation is repeated. The smallest and largest interval distances were 20 μm and 1 mm respectively. The calculated average R_q values were then plotted as a function of interval length on a logarithmic scale.

2.5 Chemical surface analysis

Auger electron spectroscopy (AES) analysis was carried out in a Perkin–Elmer 660 scanning Auger spectrometer using a 10 keV (50 nA) electron beam (LaB₆ source). Depth profile acquisition was performed by scanning a 2 keV Ar⁺ beam over an area of 1.5 mm $\times$ 1.5 mm. The sputter rate of Ta₂O₅ standards measured under these conditions (5 nm/min) was used to convert the sputter time into the approximate sputter depth. Quantification was carried out using elemental sensitivity factors taken from the 660 AES operator's reference manual, version 5.0, P/N 622879. To check for reproducibility, two depth profiles were measured for each of the analysed prostheses. Depth profiles were recorded on the smooth part of the implant (zone A) at distances of approximately 5 and 8 mm from the tip of the stem. The size of the analysed spot was given by the diameter of the electron beam (approximately 200 nm under the present settings).

3 RESULTS AND DISCUSSION

3.1 Metal release in tissue

Tissue samples from the PMMA–cortex interface and from the joint capsule regions retrieved from the experimental sheep after euthanasia were analysed for evidence of Co, Cr, and Mo, as a result of wear and/or corrosion reactions at the surface of the metal implant. In Fig. 2 the results of the chemical analyses of tissue samples from the interfacial region are shown, plotted as a function of the ranking of the implant stability within the cement mantle at the time of retrieval. The data are plotted in terms of absolute concentrations of the metal (in parts per billion) and represent the total amount of metal release within the samples, since the digestion procedure adopted ensured the destruction of cells and the dissolution of any insoluble metal oxide particles present. The tissue samples collected did not stem from specific regions along the femoral length but rather represented an average over the whole distance. It is important to note that the reason for which tissue samples from only eight sheep were analysed is that the quantity of interfacial tissue that could be collected in sheep with fixed prostheses was often too little for measurements to be conducted.

It is clear from Fig. 2 that in all cases a release of metal from the prosthesis has taken place. In fact, in all the experimental sheep analysed, the metal concentrations exceeded those measured in the blank tissue, in which the concentrations were found to be 15.8 ppb Co, 327 ppb Cr, and 136 ppb Mo (values hardly visible on the scale of the plot). In addition, the concentrations of all three metal elements

Fig. 2 Plot of the absolute concentrations of Co, Cr, and Mo measured in interfacial membrane samples versus clinical stability of the state of the implant within the bone at the time of retrieval. The sheep numbers are given on top of the bars

measured in the tissue very strongly increase with increasing instability of the implant.

Of particular note are the relatively constant concentration ratios of the three metal elements. In all samples analysed, in fact, the concentration of Co always largely exceeded that of Cr and Mo, with the latter occupying the last place. This is illustrated in Table 2, in which the absolute concentrations are divided by the blank values of the respective metals, so that the data reported represent the degree of metal release from the metallic prosthesis to the tissue. From Table 2 it can be noted that increased levels of Co range from a factor of 9 in the case of a very stable implant to up to about 1000 in cases with fixed implants to about 50 000 in the cases of clinically very loose implants. In contrast, maximum increased levels of Cr and Mo were found to lie in the region of about 1000 for Cr and 470 for Mo.

Overall, the concentration proportion between the elements appears to tend to a ratio of 1 Mo:2 Cr:100 Co, in particular in samples containing higher total metal release. This ratio does not reflect the composition of the alloy (61.82 wt % Co, 29.38 wt % Cr, and 5.98 wt % Mo, i.e. a weight ratio of 10:5:1 for the respective elements) or that of the passive film (high enrichment with chromium oxides [1–3, 53]. Hence, the results suggest that a selective dissolution of Co takes place. From the literature it is well known that Co is mainly passive under alkaline conditions. Experiments by the present authors have illustrated [54] that, in physiological saline solutions with a neutral pH value, Co actively dissolves whereas Cr shows stable passivity. Hence, the strong selective accumulation of Co in the tissue could result from cyclic mechanical depassivation and subsequent repassivation events. Mechanical depassivation (due to micromotion) exposes a bare metal surface to the body environment. In the subsequent repassivation step, Co can be expected to dissolve (as it does not

show stable passivity in neutral chloride), whereas oxidized Cr remains on the surface forming the passive film. In this way, continuous activation–repassivation cycles would lead to strongly increased levels of Co ion release.

Interestingly, selective dissolution of Co from the Co–28Cr–6Mo has also been observed in *in vitro* experiments under special electrochemical conditions [54]. Under cyclic polarization between cathodic and anodic potentials, which lead to electrochemical activation and repassivation of the sample surface, non-stoichiometric metal release with an increased Co concentration was observed. This is in contrast with constant polarization under oxidizing conditions leading to passivity breakdown by oxidation of the Cr₂O₃ passive film into soluble Cr(VI) species, in which case almost stoichiometric dissolution of all the alloying elements was observed. These results, in connection with the present data of the *in vivo* study, hence suggest that, generally, activation–repassivation cycles of the Co–Cr–Mo alloy lead to selective dissolution of Co, the activation being either electrochemical or mechanical.

Generally, Co and Mo ions are known to have considerably higher solubility constants in the neutral pH regions than do Cr³⁺ ions [55]. A more quantitative forecast of the degree of solubility of the different ions would require access to thermodynamic data in the form of potential–pH stability diagrams. However, such data are not available owing to the complexity of the biological environment, for which local acidity and temperature changes and the presence of complexing agents would need to be taken into account.

Further important points to consider are the forms of mass transport of metal from the metal implant–cement interface across the cement mantle to the interfacial tissue, and of mass transport of metal from the tissue to other parts of the body. The

Table 2 Concentrations of metal measured in interfacial tissue samples. The absolute concentrations have been divided by the respective concentrations of the different metals measured in normal joint tissue (blank). The numbers in italics in parentheses represent the ratio of the metal components in the tissue

Sheep number	Concentration in membrane (concentration in blank)						Clinical observation
	Co		Cr		Mo		
513	8.9	(3)	3.8	(1.2)	3.1	(1)	Well-fixed
524	137	(27)	3.8	(1)	4.9	(1)	Fixed
502	2 746	(63)	63	(1.5)	43	(1)	Fixed
517	1 407	(88)	32	(2)	16	(1)	Fixed
523	5 241	(37)	140	(2.4)	58	(1)	Fixed
521	7 492	(100)	156	(2)	74	(1)	Loose
514	51 952	(110)	1014	(2)	470	(1)	Loose
515	46 999	(111)	903	(2)	422	(1)	Loose

concentrations measured in the tissue will reflect not only the nature of the corrosion reactions at the surface of the implant, but also the nature and rate of mass transport of the species to the tissue and away from the tissue. In fact, mass transport can take up different forms and, according to the element and speciation in the tissue, species can be eliminated from the local tissue and find their way to the blood stream and in urine [21, 23, 56–58]. It is interesting to note that Co ions have been reported to be eliminated rapidly from local tissue to urine, while Cr ions are stored and eliminated much more slowly [58]. Nonetheless, high concentrations of Co were found in the tissue, which further confirms the hypothesis that Co is selectively dissolved. The comparatively low values of Cr found in the tissue, on the other hand, may be explained by the low solubility of Cr^{3+} . Cr_2O_3 wear particles might predominantly remain close to the surface of the implant, their transport away from the implant surface being hindered. Therefore the Cr measured in the tissue could be regarded as the portion of Cr_2O_3 particles transported through to the tissue as well as dissolved Cr ions.

Corrosion products and wear particles have been evaluated also in implants retrieved from animal models and from human surgeries either at post-mortem or at the time of revision surgery [25, 27, 28]. In the latter cases, the corrosion products were present at the junction of the modular head and neck and as particles within the periprosthetic tissues as early as 8 months post-operatively [25]. However, direct comparison of the concentrations found is not feasible, owing to the large differences in experimental conditions of the different reported data. Nonetheless, in the reported studies, no correlation between quantification of metal particulates and clinical stability of the implants could be established [27].

The analysis of tissue samples retrieved from the interface between the joint capsule and the polyethylene acetabular cup yielded much lower metal concentrations (Fig. 3) in comparison with values measured in interface membrane samples. The highest concentrations were found to lie in the range of 11 000 ppb Co, 4000 ppb Cr, and 2000 ppb Mo. In Fig. 3 the relative concentrations, obtained by dividing the absolute values by the concentrations in the blank tissue, are shown. The relative concentration ratios for the three metal elements are also quite different in this tissue. In joint capsule tissue, the concentration of Mo appears to be higher than that of Cr and the concentration ratio of Co to Mo appears to reflect that of the alloy composition 1 Mo:10 Co, with an average of 16 (for $n = 10$). In contrast, the

Fig. 3 Plot of the absolute concentrations of Co, Cr, and Mo measured in joint capsule membrane samples versus clinical stability of the state of the implant within the bone at the time of retrieval. The sheep numbers are given on top of the bars

ratio of the concentrations of Cr to Co is approximately 1:50 as found in interface membrane samples, with the exception of samples of sheep with prostheses defined as very well fixed.

The metal concentration in the joint capsule tissue is smaller than the values found in the interface membrane. A correlation between metal release and clinical evaluation of the stability of the prosthesis (as observed in Fig. 2) is not evident in Fig. 3. For example, values for the alloy components found in sheep 502 and 523, defined as having fixed prostheses, are more elevated than those in sheep 521, 514, and 515 categorized as having loose prostheses. These findings indicate that the stability of the prosthesis is related to the metal released from the shaft rather than from the prosthesis head. However, the load, movement, and materials within the acetabular cup are quite different from those occurring along the stem of the prosthesis and a direct comparison is not straightforward. In this paper, the main focus was placed on processes and phenomena occurring along the stem of the implant, and further investigations in the joint capsule area were beyond the scope of this work.

3.2 Surface damage of implants

The hip prostheses retrieved from the 8.5 months *in vivo* study were analysed for evidence of wear and degradation during the time of implantation. In Fig. 4, a photograph of the Co–Cr–Mo hip prosthesis employed in the study is shown. Two distinct zones, A (smooth) and B (rough), as shown in Fig. 4, were considered for surface characterization. Zone B

Fig. 4 Photograph of explant 514 showing the two zones (A and B) considered for surface analysis

was systematically investigated on all explants. Zone A could not be analysed on all samples because several *fixed* implants required cutting of the stem during the extraction procedure. Optical microscopy was used to identify surface modifications resulting from wear, such as scratches or presence of debris, and from corrosion events, such as pits or etching. Although isolated residues of cement or organic tissues were found on several explants, surface damage could be observed on explant 514 only. On the latter, in fact, several bright spots resulting from mechanically flattened asperities were observed in zone A. Under the optical microscope, these features appeared as darkened areas, which are clearly visible in Fig. 5. SEM images of details of these damaged areas on implant 514 are shown in Fig. 6 together with an image from an as-received sterilized virgin (non-implanted) hip prosthesis. The image quality of implant 514 is poorer than that of the virgin prosthesis. This is possibly related to a change in the surface composition during clinical use. In Fig. 6(c), the flattening of asperities is clearly shown. The extent of polishing taken place is normally observed on metals after having undergone mild wear, often involving tribochemical mechanisms [59]. It is therefore plausible that, during clinical use, repeated sliding conditions were locally established between

Fig. 5 Optical microscopy image of damaged areas on explant 514. The damaged areas (indicated by arrows) appear dark in the photograph although they have a shiny appearance to the eye

Fig. 6 SEM images taken in zone A: (a) virgin prosthesis showing the typical morphology before clinical use; (b) typical morphology on explant 514; (c) flattened region situated within the damaged areas shown in Fig. 5

the prosthesis and the PMMA cement mantle, the effects of which could be exacerbated by the presence of debris on the prosthesis surface, leading to the removal of metallic particles and/or of the passive oxide film covering the metal. The tribological nature of the observed surface deterioration is confirmed by the presence of cracks and detached particles observed by SEM and by the large amounts of debris found around prosthesis 514 during extraction from the bone.

The dark contrast in the surface surrounding the flat area in Fig. 6(c) is due to surface contamination

from carbon, as confirmed by energy-dispersive X-ray analysis. It is as yet unclear whether this contamination is related to residues of PMMA bone cement or of organic tissues. The morphology of the surface of implant 514 surrounding the bright spots (see Fig. 6(b)) differs from that of the virgin prosthesis shown in Fig. 6(a). This indicates that some friction and wear occurred in zone A during clinical use.

The topography of zone B is rougher than that of zone A and is characterized by the presence of relatively large grooves, typically of the order of 0.1–0.2 mm, uniformly dispersed at a distance of 0.2–0.3 mm. These features are likely to be due to the specific surface preparation (sand blasting) employed by the manufacturer. No apparent surface damage could be observed in zone B under optical microscopy in all the explanted prostheses. However, some prostheses were found to be smoother in appearance than others and than the virgin prosthesis. SEM investigations carried out on zone B of explant 514 showed two distinct features, which are clearly illustrated in Fig. 7. In the profile depressions, the morphology (Fig. 7(b)) is similar to that observed on the virgin prosthesis (Fig. 7(a)). On many asperities, however, important plastic deformation appears to have occurred, which can typically be related to abrasion, typified by grooves and waves in Fig. 7(c). The origin of this plastic deformation is not clear. It can result from single or multiple scratching of the surface by a relatively hard counter-body under loads exceeding the yield strength of the alloy.

In order to obtain a quantitative assessment of the extent of plastic deformation in zone B, three-dimensional optical profilometry images were recorded systematically on three selected locations of each explanted prosthesis. Typical results are shown as grey-level contrast plots in Fig. 8, in which an as-received virgin prosthesis is compared with explant 514. The two surface structures appear quite similar except on a horizontal scale of 10–20 μm , where the virgin surface exhibits sharper features. Although minor differences in surface structure could be noted among the explanted prostheses, all indiscriminately showed coarsening compared with the virgin prosthesis.

The r.m.s. roughness R_q was determined on selected profile lines as a function of distance for each of the three analysed locations. The results of the variable-length-scale analysis of the roughness are plotted in Fig. 9 as a function of interval distance for one of the selected locations. Overall, no major differences among the explants investigated and the as-received virgin prosthesis are observed. How-

Fig. 7 SEM images taken in zone B: (a) virgin prosthesis showing the typical morphology before clinical use; (b) typical morphology in surface depressions observed on explant 514; (c) typical abraded appearance of asperities observed on explant 514. Arrow 1 indicates a scratch while arrow 2 indicates a wave formed by material pushed away from the scratch

ever, an influence of clinical use on surface structure is clearly noted at small interval distances. In fact, all explants exhibit systematic lower R_q values over distances below approximately 100 μm compared with a non-implanted as-received prosthesis in all selected locations. This corresponds to the typical dimensions of the flattened areas noted on explant 514 (see Fig. 7(c)).

At interval lengths above 100 μm a large scattering in the measured roughness is observed. It is essential to note, however, that the roughness values measured on this scale are largely controlled by the

Fig. 8 Three-dimensional grey-level plots of surface profiles measured using non-contact laser profilometry in zone B: (a) virgin prosthesis; (b) explant 514. The size of the plotted area is 1 mm × 1 mm, and the point density is 500 points/mm

number of grooves present in the analysed locations. Since the distances between the grooves and their sizes are of the same order of magnitude as the length of the analysed area, significant statistical scattering in R_q may occur. This is confirmed by the fact that good reproducibility of R_q is observed on single prostheses independent of location at interval lengths below 100 μm , but not above.

No evident correlation could be found between the roughness below 100 μm and the clinical behaviour or the metal concentration measured in the interfacial membranes (see Table 1 and Table 2).

3.3 Surface chemistry

Measured AES depth profiles are shown in Fig. 10. C was detected only at the outermost surface and its signal disappeared after less than 3 nm sputtering. Adsorption of organic molecules from the air typically causes this kind of surface contamination by C. Characteristic peaks of Co, Cr, O, and Mo could be identified in the spectrum. The Mo signals were

Fig. 9 Plots of r.m.s. roughness R_q versus the interval length on a double-logarithmic scale. Roughness profiles were measured on the different explants and on an as-received virgin prosthesis on the same location of zone B (point density, 500 points/mm)

extremely weak and were not plotted in Fig. 1 for clarity.

The Auger profiles show that on all implants a Cr-rich oxide film covered the Co–Cr–Mo alloy. The film thickness, as determined by taking the depth at which the O signal was at 50 per cent of the maximum amplitude, varied among the analysed specimens. The oxide on the virgin surface was thicker than 160 nm, while much smaller values ranging between 10 and 15 nm were measured on the explants. The difference in surface compositions confirms that materials deterioration occurred during clinical use.

Figure 11 shows the evolution of the atomic concentration ratio of Cr to Cr + Co as a function of the sputter depth. Enrichment in Cr is observed in the outermost surface layer corresponding to the oxide film. This is consistent with previous surface analytical investigation showing that the passive film formed on Co–Cr–Mo alloys consists essentially of chromium(III) oxide [54].

Below the oxide film, the concentration ratio rapidly attains the value corresponding to the alloy composition. The observed evolution is in agreement with the previously described depassivation–repassivation mechanism. The removal of the

Fig. 10 Auger depth profiles measure on: (a) the virgin implant, (b) stable implant 502, and (c) unstable implant 514. For clarity the signals of C (outermost surface contamination only) and Mo (very weak) are omitted (a.u., arbitrary units)

chromium oxide film exposes to the solution the bare metal surface that subsequently oxidizes; oxidized Co dissolves in the solution while oxidized Cr forms the oxide film. This repeated process results in a metal release into the body corresponding to the stoichiometry of the alloy but with Co released as dissolved ions while Cr is released as solid oxide particles. Because of the greater mobility of dissolved ions, the relative concentration of Co is thus expected to increase with increasing distance from the implant. This mechanism may explain the higher Co concentration found at the cement–bone interface evidenced by the tissue analysis. Quantification of the spatial distribution of metal concentration in the cement surrounding the prostheses would be needed to confirm this mechanism.

Fig. 11 Evolution of the atomic concentration ratio of Cr to Cr + Co as a function of depth for the virgin implant, stable implant 502, and unstable implant 514

3.4 Correlation between different experimental findings

To illustrate the correlation between the different experimental findings, the case of sheep 514 is discussed in more detail. This implant was very loose at post-mortem and could be moved easily within the bone. The unstable character of the implant was confirmed by significant interface membrane formation and evidence of cement fracture. In addition, most of the cement–implant interface was covered over a large fraction by grey–black particles, which suggested major implant damage by wear and/or corrosion during the implantation time. Damage was confirmed by the disappearance of the initial thick oxide film observed on the virgin prosthesis prior to surgery from the AES profiles (Fig. 10) recorded on the explants. The chemical analysis (see Table 2) showed that the levels of Co, Cr, and Mo were elevated by factors of 51 952, 1014, and 470 respectively compared with levels found in blank tissue. Surface analyses investigations revealed the presence of several bright spots resulting from mechanically flattened asperities in zone A of the prosthesis (Fig. 5) while, in zone B, SEM investigations revealed important plastic deformation on many asperities (Fig. 7), likely to have originated from abrasion.

From the results presented, it is evident that a good degree of correlation exists between the clinical evaluation of the implant stability or fixation and the chemical analysis of the interface tissue. On the other hand, measurements of the surface roughness and composition along the stem show that a certain degree of wear occurs in all implanted prostheses, irrelevant of the degree of fixation of the implant within the PMMA mantle.

Although a direct correlation of the surface roughness with degree of implant fixation was not possible,

it is important to note that the data cannot be conclusive, since the measurements were undertaken at specific sites of the surface, thus not necessarily reflecting possible more dramatic local roughness changes along the shaft area. Nonetheless, the data clearly demonstrate that fretting wear does take place, even in implants that are very well fixed within the cement mantle. This may also indicate that the quantity of metal found in the tissue will also reflect the compactness of the cement mantle, which represents a mass transport barrier. It cannot be excluded that the presence of cracks and air bubbles in the cement mantle may enhance the transport of species away from the implant interface.

4 CONCLUSION

The collected explant surface and retrieved tissue chemical analysis data clearly indicate that generation of metal particles takes place by a degradation mechanism involving a mixture of wear and tribo-corrosion in all implanted hip prostheses. Concomitantly, elemental chemical analysis in the interface tissue between cortex and PMMA bone cement revealed the presence of the alloying elements, the concentrations of which correlated well with the subjective clinical classification of the stability and fixation of the hip prosthesis within the bone at post-mortem. A strong selective enrichment of Co in the tissue was observed, although AES surface analysis revealed that no selective metal release from the alloy occurred. The selective enrichment of Co in the tissue could stem from continuous activation–repassivation cycles, whereby, in the reoxidation process of the mechanically activated surface, Cr remains on the surface, forming a non-soluble chromium oxide passive film, and Co is dissolved in the surroundings. No evident correlation could be found between the surface morphology and roughness data and either the degree of fixation of the implants or the tissue chemical analysis classifications. This would therefore suggest that the modes of mass transport between the implant surface and the tissue play an important role as the surface degradation mechanisms of the metal. The mode and degree of mass transport might depend on the presence of cracks or defects in the bone cement as well as on the local physiological constitution.

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