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Review

Special modes of corrosion under physiological and simulated physiological conditions

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Abstract

The aim of this article is to review those aspects of corrosion behaviour that are most relevant to the clinical application of implant alloys. The special modes of corrosion encountered by implant alloys are presented. The resistance of the different materials against the most typical corrosion modes (pitting corrosion, crevice corrosion and fretting corrosion) is compared, together with observations of metal ion release from different biomaterials. A short section is dedicated to possible galvanic effects in cases when different types of materials are combined in a biomedical device. The different topics covered are introduced from the viewpoint of materials science, and then placed into the context of medicine and clinical experience.

Keywords: Biomaterials; Corrosion; Alloys; Physiological solution; Arthroplasty

Contents

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1. Introduction

The performance of a biomaterial is determined by its chemical, physical and biological properties [1]. The key to understanding host response and, to a lesser degree, material response is knowledge of the participation of the material in the physiology of the host [2–4]. The majority of biomaterials present in clinical use are interactive materials, i.e. implantable materials designed to elicit specific, beneficial responses, such as ingrowth and adhesion. This article deals with metallic implant materials. One of the most important issues in the use of metallic biomaterials is their corrosion behaviour [5–8]. The corrosion behaviour of an implant is influenced by a wide variety of factors, including the material itself (e.g. the chemical composition, microstructure, surface condition), the surroundings (e.g. pH, temperature, O_2 content), as well as the construction (e.g. presence of crevices). Changes in these variables can have a further influence on the mode and rate of metal ion release. The tissue reaction to released metal species can vary considerably, from a mild response to severe disturbance of the local homeostasis within the host tissue adjacent to the metal implant [1]. Increased metal release eventually may lead to severe complications and failure of an implant system. Therefore, mechanistic information on the mode of metal release is required to predict behaviour in the biological environment.

2. Passivity and breakdown of passivity

The metallic materials which are typically used in biomedical applications, such as surgical stainless steel, and Co–Cr- and Ti-based alloys, are self-protected by the spontaneous formation of a thin oxide film. The passive layer formed on Ti-based alloys is mostly composed of TiO_2, whereas the passive films formed on surgical stainless-steel- and Co-based alloys are strongly enriched in Cr_2O_3 oxide [9–13]. Although the thickness of these passive films is typically only a few nanometres, they act as a highly protective barrier between the metal surface and the aggressive biological environment. Consequently, the passive film kinetically retards the rate of dissolution by many orders of magnitude. The protectiveness of the passive film is determined by the rate of ion transfer through the film, as well as the stability of the film against dissolution (Fig. 1). A variety of factors can influence ion transport through the film, such as the film's chemical composition, structure, thickness and presence of defects. Principally, the nature and stability of a passive film on a particular metal or alloy

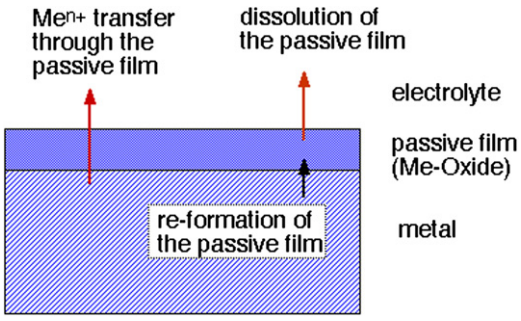

Fig. 1. Schematic illustration of a passive surface.

depend on the environmental conditions, such as the composition of the electrolyte, the redox conditions, the exposure time and temperature.

Depending on the type of oxide formed, the passive film may or may not remain stable and hence sustain passivity upon exposure to the biological environment, as will be discussed in this paper. Under certain conditions, localized breakdown of passivity takes place, leading to fast dissolution at the site of breakdown. Localized corrosion typically starts at sites characterized by inhomogeneities either in the material, or in the surrounding environment. Even though most of the surface is still covered by the intact passive film, the corrosion rate at locally activated sites can reach very high values. Localized corrosion may thus lead to unexpected deterioration of the whole system with disastrous consequences, although the total mass loss is actually small. Therefore, localized corrosion processes are more dangerous in nature and far less easy to predict than uniform corrosion.

3. The human body as a corrosive environment

The corrosive environment of body fluids can generally be simulated by a 0.9% NaCl solution containing small amounts of other inorganic salts at a temperature of 37 °C. Table 1 shows the chemical composition of human blood

Table 1
A typical chemical composition of normal human blood plasma

Ion	Concentration (mmol l^{-1})
Na^+	142.0
K^+	5.0
Mg^{2+}	1.5
Ca^{2+}	2.5
Cl^-	103.0
HCO_3^-	27.0
HPO_4^{2-}	1.0
SO_4^{2-}	0.5

plasma [14]. The chemical environment of blood plasma is highly aggressive for many metals and alloys, due especially to the presence of a high concentration of chloride ions and their ability to induce localized corrosion. Other ions may also contribute to the corrosion process, either as accelerators or inhibitors. For instance, layers of Ca-phosphates precipitate on Ti and Ti-based alloys in simulated body fluids, as well as in vivo, but the effect of such deposit layers on the corrosion process has scarcely been considered.

The body temperature of 37 °C can accelerate electrochemical reactions and even change the mechanism of corrosion from that occurring at room temperature. Studies conducted at room temperature may lead to an underestimation of the risk of corrosion and direct extrapolation to body temperature is not straightforward. For example, the above-mentioned precipitation of Ca-phosphates is much more likely to occur at 37 °C than at room temperature.

In addition to inorganic species, body fluids contain different types of biomolecules and cells, which may attach to the biomaterial surface and affect the surface reactions. Proteins are a primary constituent of the synovial fluid in total joints with other organic components such as hyaluronic acid and lubricin. The formation of a protein-containing biofilm on the metal surface has been shown to enhance the corrosion process of the base alloy [15]. Although the biofilms also lubricate the surface, the total material degradation was increased due to increased corrosion [15]. However, it has not yet been clarified unambiguously whether biomolecules accelerate or inhibit electrochemical reactions [15–20]. Most probably the effect is specific for a particular metal/biomolecule combination. Cr and Co have similar protein-binding affinity and bind to protein in proportion to the added concentration ratio. However, Ni shows significant competition for Cr and Co binding moieties [19]. The concentration of released Fe, Cr and Ni ions from stainless steel immersed in Hank's physiological solution increased in the presence of various proteins in the following order: fibrinogen < globulin < transferin < albumin [16]. The enhancement of dissolution rate in the presence of proteins can be explained by the formation of complexes between metal ions and proteins [7,8]. These complexes can be transported away from the immediate vicinity. To retain the equilibrium the dissolution rate of a base metal increases and, consequently, suppresses the formation of the passive layer [16,17].

On the other hand, the proteins were reported to increase the corrosion resistance of the Ti-based alloy. Proteins, namely albumin, have been reported to interact with the repassivation process of the surface of Ti-alloys due to the change in the charge owing to their zwitterion character [20]. As the pH increases, the corrosion resistance of Ti-based alloys improves, which has been ascribed to the adsorption of metal/protein/hydroxide complex at the metal surface which consequently restricts the dissolution of metal. Contu et al. observed higher polarization resistance in serum solution than in sodium sulphate [21]. This observation was ascribed to the adsorbed layer of organic molecules that hindered the oxygen evolution reaction and the charge transfer responsible for the passive film dissolution. The most relevant experiments in terms of physiological applications were performed by Hsu et al. [22]. The corrosion resistance of Ti–6Al–4V alloy in joint fluid was found to be significantly lower than in serum or urine.

Another significant factor determining the corrosion behaviour of metals is the pH of the environment. Typically, changes in the pH value in the body fluids are relatively small since the fluids are buffered. On implantation, the pH of the tissue surrounding the implant may decrease to values around 5, and then recover to 7.4 within weeks [23]. Local variations in pH value have been measured in periprosthetic tissue of revised hip implants [24,25]. Recurrence of pain in patients with cemented Müller straight femoral stems of Ti forged alloy was ascribed to the high acidity initiating crevice corrosion [24]. pH values were measured intraoperatively on explanted prostheses using a sting pH electrode [25]. Whereas the pH at the control point was 7.4 ± 0.06, the pH values at the pathological interface tissues in aseptic and septic loosening varied between 4.38 and 7.7, i.e. the H^+ concentration varies over 1000-fold. [25]. In addition, hydrodynamic conditions (e.g. blood flow) around the implant surface influence mass transfer, and consequently the corrosion reactions.

From the corrosion point of view, the prevailing redox conditions are important. The oxygen content in the surroundings can vary depending on the specific application. In the case of alloys, the passivity of which is based on the presence of Cr_2O_3-rich passive film on the surface, highly oxidizing conditions can lead to dissolution of the passive film by formation of soluble Cr(VI) species. Besides dissolved molecular oxygen O_2, more active oxygen species such as H_2O_2 can be formed in biological reactions. The stability of the passive film is dependent on the availability of oxygen. The adsorption of proteins and cells onto the surface of materials could limit the diffusion of oxygen to certain regions of the surface, causing preferential corrosion of the oxygen-deficient regions and leading to the breakdown of the passive layer [1].

In addition to consideration of the chemistry surrounding an implant, the design of the implant and its surface treatment, particularly at the bone implant interface, affect the degradation mechanism of an implant. For instance, using a good cementation technique for a hip implant diminishes micromotions and fretting corrosion [26,27]. Patients with failures of the bone–implant interface have been reported to have higher metal levels in blood and urine compared to patients with well-fixed implants [28].

4. Relevant implant alloys

4.1. Stainless steels

In medicine, the stainless steel which is typically used (AISI 316L, ASTM F-55 and F-138) contains 17–20%

Cr, 13–15% nickel, 2–3% molybdenum and small amounts of other elements [29]. The notation "L" indicates that the steel has a low carbon content (<0.03%) and is therefore not susceptible to intergranular corrosion due to precipitation of Cr-carbides at the grain boundaries. Cr is the element mainly responsible for the high passivation ability of these alloys. An increase in Cr content, as well as in Mo content, strongly increases the resistance against localized breakdown of passivity. Stainless steel implants are used as temporary implants to help bone healing, as well as fixed implants such as for artificial joints. Typical temporary applications are plates, medullary nails, screws, pins, sutures and steel threads and networks used in fixing fractures. Use of steel in joint replacements has decreased since Co- and Ti-based materials became available. However, steel joints are still very popular and have an appreciable market share. The possible conversion of cutaneous metal sensitivity to Ni or Cr in patients receiving stainless-steel-based implants has also restricted its use although there is no evidence to support this danger [30]. Normally the body contains approximately 3–4 g iron. Clinical experience and accumulated knowledge suggest that the human body tolerates leachables from steel relatively well. Nevertheless, efforts have been taken to develop new, Ni-free stainless steels.

4.2. Cobalt-based alloys

As in stainless steels, alloying Co with Cr greatly enhances corrosion resistance [31–33]. Since the passivation of pure Co takes place only in alkaline solutions, Cr is the key alloying element in Co alloys with regard to corrosion resistance in oxidizing media. Mo has been found to be beneficial, especially under active corrosion conditions such as in hydrochloric acid. Co-based alloys used in total joint replacement surgery are cast Co–Cr–Mo alloy (Co–28Cr–6Mo, ASTM F-75) and wrought Co–Cr–Ni alloys (Co–Cr–W–Ni, ASTM F-90 and Co–Ni–Cr–Mo, ASTM F-562). The microstructure of the alloys and the resulting properties depend strongly on the production route (e.g. casting or forging), degree of cold-working, and heat treatment. The wrought Co–Ni–Cr–Mo alloys appear to have slightly better corrosion behaviour than the as-cast Co–Cr–Mo alloy [31]. Contemporary Co–Cr alloys are superior to stainless steel, both in fatigue and wear resistance, and are therefore preferred in total joint replacements, in both supportive and articulating locations. However, fatigue fracture still remains a possible complication [34], and corrosion issues after porosity initiation may occur.

4.3. Titanium-based alloys

Titanium (cp-Ti, ASTM F-67) and its alloys typically used in biomedical applications (Ti–6Al–4V, ASTM F-136-02a and Ti–6Al–7Nb, ASTM F-1295-05) can be considered as the most corrosion-resistant of the alloys described here. This is based on the very high stability of the TiO_2 passive film that forms spontaneously on the alloy surface [35]. TiO_2 is thermodynamically stable in the pH range between 2 and 12, and only complexing species, such as HF or H_2O_2, lead to substantial dissolution [35]. The effect of H_2O_2 (which may be generated in biological reactions) on the nature of the passive films formed on Ti in physiological solutions has been explored by Pan et al. [36,37]. Ti-based implant alloys also show stable passivity in neutral halide solutions. However, upon acidification, the Al-containing alloys (Ti–6Al–4V, Ti–6Al–7Nb) are significantly more prone to accelerated dissolution than cp-Ti [38].

The wear resistance of Ti and its alloys is relatively low and these materials should not be used where contact wear can occur. Metallosis, i.e. black coloration of the tissue induced by the release of wear metal particles, is often a consequence of wear due to metal-to-metal contact brought about by the changed geometry of the system [39,40], or modular interface corrosion between Co–Cr heads and Ti alloy stems [41].

5. Special modes of corrosion of implant alloys

5.1. Pitting corrosion

Pitting corrosion is a type of localized corrosion caused by local dissolution of the passive film and the formation of cavities surrounded by an intact passivated surface [42]. Pitting usually occurs in halide containing solutions, of which, for most metals, chloride ion is the most aggressive. Surgical stainless steel shows higher susceptibility than Co- and Ti-based alloys to pitting and crevice corrosion in halide solutions. Corrosion damage is frequently observed at screw holes after removal of temporary stainless steel plates (Fig. 2). The resistance to pitting corrosion is dependent on Cr and Mo content, as well as on the content of MnS inclusions, where pit initiation takes place preferentially. The pitting potential of surgical-grade stainless steel measured in vitro is situated in a range which may be relevant to the prevailing redox conditions in the body. More-

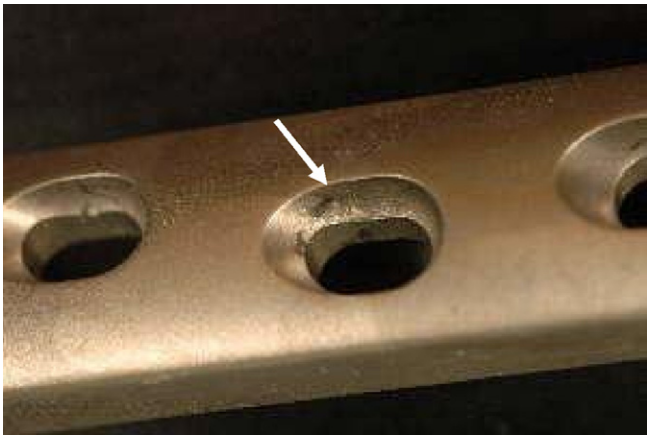

Fig. 2. A stainless steel plate, popular in the fixation of hip fractures, removed after two years: corrosion can be observed at a screw hole.

over, relatively small variations in the steel composition (e.g. purity grade) or surface condition (e.g. roughness) may significantly influence the pitting behaviour.

Pitting corrosion of Co–28Cr–6Mo alloy is seldom observed, since it typically fails by transpassive dissolution. In contrast, pitting corrosion of surgical stainless steel is possible since the pitting potential is lower than the Cr(III) oxidation potential. In vitro study showed that transpassive dissolution of Co–Cr–Mo alloy leads to activation of the surface due to oxidation of the insoluble Cr(III) oxide layer to soluble Cr(VI) species [43]. Consequently, the metal ion release drastically increases. In the case of a passive film on stainless steel, secondary passivation by Fe oxides prevents the complete activation of the surface due to oxidation of Cr(III) to Cr(VI) species. For Co-based alloys, however, secondary passivation is not possible, since Co oxides are not stable under these conditions. Therefore, transpassive dissolution under moderately strong oxidizing conditions may be relevant for the performance of Co-based implants since it may induce the release of the toxic and carcinogenic Cr(VI) species.

Ti and Ti-based alloys show very high pitting potentials in chloride-containing solutions (around 10 V). Therefore, stable pitting corrosion is not a relevant failure mode for these materials in biomedical applications, since the relevant potential region in the body is clearly <1 V. Nevertheless, metastable pitting corrosion has been observed for cp-Ti and for the Ti–6Al–4V implant alloy in simulated physiological solutions [44]. Metastable pitting corrosion, which can be observed in an electrochemical experiment in the form of current transients, takes place in the potential region of stable passivity (i.e. below the pitting potential). In this case, local passivity breakdown events take place (pit nucleation/initiation), but little or no pit propagation takes place as for stable pitting corrosion. Instead, the small pits do not remain active and relatively fast repassivation takes place. Even though metastable pitting does not lead to a complete deterioration of the system, it nevertheless indicates that the metal is not completely stable in its environment. Moreover, it contributes to metal ion release into the surroundings. Metastable pitting corrosion has been quite widely studied for stainless steels, but much less for biomedical implant materials. For Ti, metastable pitting has been reported to take place in bromide solutions [45], and also in physiological media [44,46–48]. Metastable pitting activity was higher for the Ti–Al–V alloy than for pure Ti. In contrast to the metastable pitting of stainless steels, in which case the number of pit initiation events typically decreases as a function of time, the metastable pitting activity of Ti-based alloys remained high over the duration of the experiment. This behaviour may have some relevance to the mode of metal ion release from Ti-based implants.

5.2. Crevice corrosion

Crevice corrosion is a type of localized corrosion closely related to pitting corrosion. It occurs preferentially in regions on the metal surface where mass transfer is limited, e.g. in narrow crevices or under deposits. At these occluded areas the concentration of aggressive chloride ions, decrease in pH value and depletion of oxygen can rapidly lead to activation of the surface.

Stainless steel is the most susceptible of the three alloy groups discussed to crevice-induced localized corrosion. Pitting and crevice corrosion of Co–Cr alloys has not been studied as thoroughly as for stainless steels. Due to the very high Cr-content in the passive film of Co–Cr–Mo alloys, the material can be expected to be quite resistant against activation on local acidification. Our own unpublished work indicates that Co-wrought 28Cr–6Mo alloy shows practically no change of the dissolution rate upon acidification of a simple saline solution (0.14 M NaCl) at 37 °C from pH 7.4 to 4 or even 2, which confirms the stability at low pH.

Traditionally, it is claimed that crevice corrosion of Ti in chloride-containing solutions only takes place at elevated temperatures. A critical temperature of about 70–80 °C in chloride solutions has often been reported [49,50]. However, this process could also take place in crevices, where the pH value becomes reduced due to the hydrolysis of dissolved and trapped metal cations. Therefore, it has been recommended that cementation should not be used for Ti-based implants, to avoid the risk of locally increased dissolution rates in the crevice formed between the implant surface and the bone cement [24]. In vivo localized attack in the crevice region of a cemented Ti–6Al–4V stem is illustrated in Fig. 3.

5.3. Tribocorrosion/fretting corrosion

Tribocorrosion is defined as the conjoint action of mechanical wear and corrosive attack on a material surface. A special mode of tribocorrosion highly relevant to the field of biomedical implants such as hip, knee and shoulder replacements is fretting corrosion. Fretting cor-

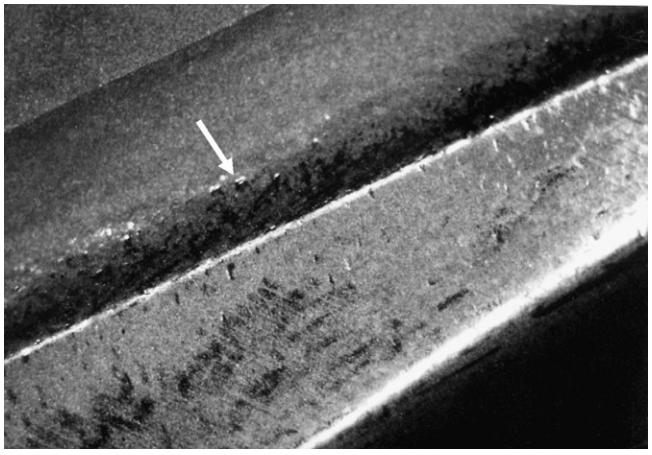

Fig. 3. Localized corrosion on a cemented Ti–6Al–4V stem region due to crevice attack (magnification 70×).

rosion is a form of damage which occurs at the interface of two closely fitting surfaces when they are subjected to slight oscillatory slip and joint corrosion action. The damage is mostly restricted to the local site and the generated debris (mostly oxide) is usually accumulated locally, leading to an increase in stress. An increase in hardness generally leads to a reduction in fretting wear. Fretting corrosion can drastically alter the corrosion behaviour by mechanically destroying the passive film. Consequently, the ability of the material to repassivate, i.e. to rebuild the passive layer, becomes crucial. Fretting corrosion, alone or in combination with crevice corrosion, has been identified as one of the most important factors in implant corrosion [51–53]. Fretting scars observed on explanted implant made of Ti-based alloy are presented in Fig. 4.

It was reported that a decrease in pH had a negative effect on the fretting corrosion behaviour of stainless steel, but showed no effect for Ti or the Co–Cr alloy [54]. In another study, the stainless steel AISI 316L was found to exhibit better fretting corrosion behaviour than the titanium alloy Ti–6Al–4V [55]. The fretting corrosion of the latter depended critically on the prevailing electrochemical potential [56]. The two-phase α/β alloys Ti–Al–V and Ti–Al–Nb have been shown to possess a better combination of corrosion and wear resistance than cp-Ti, whereas pure Ti shows better corrosion behaviour [57].

The repassivation behaviour is of utmost importance for metal ion release during cyclic activation/repassivation events, such as those that take place under fretting conditions. For stainless steels, repassivation of bare metal surfaces has often been studied for other applications. For other metallic biomaterials, only a few studies on repassivation behaviour have been reported [58,59]. The repassivation rate of Ti was reported to be slower in a simulated physiological solution than in a simple NaCl solution [59]. Such findings demonstrate that the risk of metal ion release should be studied under as realistic conditions as possible.

5.4. Observations on metal ion release

The biological risks of metal ions include wear debris, colloidal organometallic complexes, free metal ions, and inorganic metal salts or oxide formation [60]. Metal ion release from implants has been reported in vitro as well as in vivo. Since the release of alloying elements can lead to toxic, allergic and idiosyncratic symptoms, the issue of metal release deserves special attention. Metal release can be measured locally, in periprosthetic tissue, or more relevantly, in body fluids, i.e. blood, serum or urine, which show systemic impact of metal release. The comparison of literature data is often not straightforward, since mass transport and metabolism play a role on the accumulation in the tissue vs. transfer into the blood or urine [60]. It was reported that the relative metal ion concentration in blood of patients with Co–Cr–Mo implants differs from that in their urine, i.e. 33% of Co, 51% of Cr and 16% of Mo in blood compared to 76% of Co and 24% of Cr in urine [60]. The difference can be explained by considering the fact that Cr is taken up by red blood cells, whereas Co is transported from tissues to the blood and is eliminated in the urine.

Mechanisms of metal ion release from metal implants have been recently summarized [61,62]. The aspect of preferential dissolution of certain alloying elements is emphasized. In the case of stainless steel, Fe was the major element released; Ni and Cr were detected in lesser but similar amounts that did not correspond to the alloy composition. Preferential release of Co was observed from Co–Cr–Mo alloy. For the Ti-based (Ti–Al–V, Ti–Al–Nb, Ti–15Zr–4Nb–4Ta) alloys, mostly Ti was released, but also significant amounts of Al and a small amount of V (for the Ti–Al–V alloy) could be detected. The amounts of Ti and Al release were similar for the two Ti–Al–(V,Nb) alloys. However, the quantity of Ti released from the Ti–Zr–Nb–Ta alloy was much smaller than the quantity released from the Ti–Al–(V,Nb) alloys. This may reflect the very stable passivity of the alloy containing only valve metals as alloying elements.

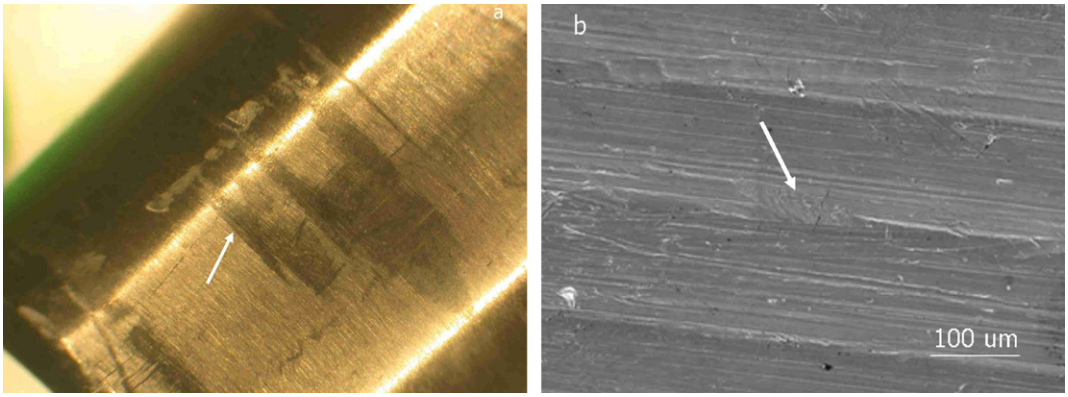

Fig. 4. (a) Optical micrograph of fretting scars on the taper neck of a Ti–6Al–4V cemented stem and a Ti–6Al–4V head after 17 years in vivo, magnification 7×. (b) SEM image of fretting scars on the taper neck of a Ti–6Al–4V stem and AISI 316L stainless steel head after 14 years in vivo, showing fretting scars perpendicular to the machine lines.

A shift in pH value affects the metal ion release [61,62]. The amount of Co released from Co–Cr–Mo alloy was not affected by pH shift in the acid direction. However, for stainless steel AISI 316L and for different Ti-based materials, acidification induces an increased metal ion release, especially below pH $\approx$ 4. The in vivo results were qualitatively in good agreement with the in vitro experiments; among different simulated physiological solutions, lactic acid appears to be the most suitable accelerated immersion test solution [61]. Since the experiments were carried out either by simply soaking the materials in the different solutions or by implantation in rat tibia, the effects of a conjoint action of wear and corrosion could not be evaluated [63]. Nevertheless, the data is valuable is assessing the chemical stability of the different materials.

Cr ions exist in two oxidation states: Cr^{3+} and Cr^{6+}. The Cr^{6+} ion is more harmful since it is carcinogenic. The release of hexavalent Cr from stainless steels and from Co–Cr alloys has been studied in vivo and in vitro [64]. Significantly higher amounts of released Cr were detected in vitro in the plasma following accelerated corrosion studies under anodic polarization for the F75 Co–Cr–Mo alloy than for stainless steel 316L. However, direct comparison of the Cr release from the two alloys is difficult due to different conditions of pre-passivation of the two alloys. Since the oxidation state of released ion depends on the redox potential of the environment, the question remains as to whether the redox conditions in the body are oxidizing enough to lead to transpassive dissolution.

Despite the high corrosion resistance of Co–Cr alloys, increased metal ion concentrations have been frequently observed in blood, urine, body tissues or organs of patients with implants. The potential effects and consequences of the release of alloying elements Co, Cr, and in some cases Ni, vary from cellular reaction to DNA damage [65]. In many cases the metal ion release may be due to combined mechanical and chemical effects: micromotions between the implant surface and bone cement mechanically activate the implant surface and, in the subsequent repassivation step, metal ion release takes place. Such continuous activation/repassivation cycles can lead to significant amounts of metal dissolution, as demonstrated in the laboratory [43].

Metal ion release has recently been debated in the clinical arena related to metal-on-metal articulation. Modern metal-on-metal designs manufactured from polished Co–Cr–Mo alloy show decreased wear compared to traditional metal-on-polyethylene designs but lead to the increased metal ion levels in blood in urine, even in patients with well-functioning implants [66,67]. Although, so far, elevated serum metal levels have not been linked to adverse health reactions, the long-term effects are not yet known. However, end-stage chronic renal diseases are regarded as a contraindication for the use of metal-on-metal articulation [66]. Malfunctioning devices may put the patient at considerable risk [68] and require prompt detection and revision.

5.5. Galvanic and modularity effects

Galvanic corrosion occurs when dissimilar metals are in direct electrical contact in corrosive solutions or atmospheres. Enhanced corrosion of the less noble metal takes place, whereas the corrosion rate of the more noble metal is reduced or even completely suppressed. However, once the metal or alloy is covered by a protective passive layer, the corrosion potential is typically that of a more noble metal than that of the bare metal surface. Therefore, judging solely by the standard potential values, one would overestimate the danger of galvanic corrosion. Since passive films act as very efficient barriers to corrosion, the danger of galvanic corrosion is lower for passive materials than for the coupling of actively corroding metals. Relative movement between the implant and the tissue, e.g. at a bearing surface or on a cyclically loaded implant, will cause mixing at the interface and will modify the composition of the electrolyte and may modify the surface of the alloy [1,53]. The charge imbalance thus created will result in sustained corrosion.

Due to the stable passivity of the alloys used, it has also been argued that galvanic corrosion poses no risk in a biomedical device [69]. This argument is valid for combinations of Ti and Co alloys. The values of corrosion potential, E_{corr}, after a 32-day exposure in Ringer's solution at pH 6.2 show stable passive behaviour with the following values: AISI 316L stainless steel −0.03 V, Co–28Cr–6Mo alloy −0.05 V and Ti–6Al–4V −0.15 V vs. saturated calomel electrode (SCE) [70]. Clinically, however, modular interfaces where Co–Cr and Ti alloys contact are a frequent origin of clinically significant corrosion-related problems [71,72]. Modularity may cause corrosion damage even when combining the same materials with different surface finishes. Fig. 5 shows damage on a rough taper neck made of Co–Cr alloy articulating inside a Co–Cr head. Improved tolerances of the mating surfaces in the Morse taper junction [26] or even coating the Co–Cr female

Fig. 5. Morse taper neck of a femoral Co–Cr stem corroded against a Co–Cr head in a non-cemented, modular early design. See the roughness of the Morse taper.

junction in the femoral head [73] may solve the problem of malfunctioning modular components. Generally, modular junctions are still considered a weak link of joint replacement and a possible source of complications.

Surgical steel should not be used in contact with Co-based implants, because the relatively poor corrosion resistance of steel can lead to rapid galvanic corrosion, if the stainless steel suffers pitting corrosion. However, if the conditions are not aggressive enough to trigger pitting or crevice corrosion of the stainless steel, and both materials remain in the stable passive state, coupling of the two materials will not lead to any significant change of the corrosion behaviour of the materials [74]. This situation was reported for spinal implants where galvanic corrosion between a Ti alloy and stainless steel was insignificant [75].

6. Concluding remarks

This paper described the behaviour of specific implant alloys in physiological and simulated physiological conditions. Even though generally recognized as a key issue in the success of a metallic implant, many questions still remain for a complete elucidation of the complex corrosion mechanisms at play. One drawback of in vivo studies is that it is more or less impossible to study the effect of single-parameter variations, and hence to identify the most critical factors leading to failure. Moreover, the understanding of the implant behaviour requires the analysis of failed implants. On the other hand, in vitro experiments inherently lack the direct correlation to the real case, as a reasonable simulation of the in vivo case is difficult. Therefore, to truly understand the corrosion mechanisms at the implant/biology interface, and to fill the gap between in vitro and in vivo studies, joint efforts between medicine, biology, materials science and engineering should be aimed at.

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