Corrosion fatigue of biomedical metallic alloys: Mechanisms and mitigation

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ABSTRACT

Cyclic stresses are often related to the premature mechanical failure of metallic biomaterials. The complex interaction between fatigue and corrosion in the physiological environment has been subject of many investigations. In this context, microstructure, heat treatments, plastic deformation, surface finishing and coatings have decisive influence on the mechanisms of fatigue crack nucleation and growth. Furthermore, wear is frequently present and contributes to the process. However, despite all the effort at elucidating the mechanisms that govern corrosion fatigue of biomedical alloys, failures continue to occur. This work reviews the literature on corrosion-fatigue-related phenomena of Ti alloys, surgical stainless steels, Co–Cr–Mo and Mg alloys. The aim was to discuss the correlation between structural and surface aspects of these materials and the onset of fatigue in the highly saline environment of the human body. By understanding such correlation, mitigation of corrosion fatigue failure may be achieved in a reliable scientific-based manner. Different mitigation methods are also reviewed and discussed throughout the text. It is intended that the information condensed in this article should be a valuable tool in the development of increasingly successful designs against the corrosion fatigue of metallic implants.

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1. Introduction

The selection of a metallic biomaterial to be employed as a load-bearing orthopedic device should be based on a reliable analysis of relevant materials properties. Fatigue resistance is perhaps the most important issue to be addressed in this case. Several reports indicate that fatigue-related mechanisms are responsible for the most part of mechanical failures of implantable medical metallic components [1–4]. Chao and López [5] reported that nearly 90% of the surface fracture of cementless hip prosthesis manufactured with Ti–6Al–4V alloy was due to fatigue mechanisms. In addition to oscillating mechanical loads, implants are exposed to the physiological fluid that consists of a saline solution [6] including Na+, Mg2+, Cl−, SO4 2− and HCO3−. Metallic implants owe their corrosion resistance to the formation of a stable, compact and continuous oxide surface film called passive film that prevents the underlying bare metal surface from coming into contact with these aggressive ions [7]. However, the passive film may be locally dissolved, especially by chloride ions, generating pits that rapidly propagate, leading to pitting corrosion. Nucleation of fatigue cracks has been related to the presence of pits on the surface of metallic materials [8]. Under fatigue conditions, the aqueous environment can accelerate the initiation of a surface flaw and propagate it to a critical size, leading to fracture. This process is known as corrosion fatigue, denoting the failure of a material under the simultaneous action of cyclic loads and chemical attack [9]. The reduction in fatigue life of metallic implants under corrosion fatigue has been well documented [10–12].

Teoh [13] emphasizes the importance of knowing the surface substructure of biomaterials in order to understand the mechanisms of fatigue failure. The substructure is composed of three distinct layers – a molecular absorbed layer, the passive oxide film and the deformed layer – as shown in Fig. 1. Cyclic loadings lead to the generation of wear debris (contact body). The molecular absorbed layer consists of growing tissue (cells) in contact with the physiological environment and the passive layer on the surface of the metallic implant. The deformed layer arises from the cyclic loadings that cause localized plastic deformation, forming the damage zone in the microstructure of the metallic implant. Many questions arise from this picture: how does the intrinsic microstructure of the alloy influence the ability of the material to withstand cyclic loadings without fatigue failure? How does the stability of the passive film in contact with the physiological environment affect corrosion fatigue mechanisms? Does wear participate in the overall fatigue resistance of the material? How does one evaluate these phenomena? How does one maximize the performance of the medical device against corrosion fatigue? Answering these questions correctly may be the difference between a successful implant life and a premature catastrophic failure. If one thinks that all these phenomena are self-related and thus have...
a simultaneous action within the human body, the complexity of this task appears to be extreme. A sound knowledge of materials science concepts owing to processing, heat treatment, microstructure of specific metallic alloys, corrosion, wear, fatigue and surface modification methods is needed to achieve a reliable finished product. These issues are explored in this work, with particular emphasis on the more common biomedical metallic materials, i.e. titanium and titanium alloys, austenitic stainless steels, Co–Cr–Mo and biodegradable magnesium alloys.

2. Corrosion fatigue of metallic implants

2.1. Fatigue: basic concepts

The fatigue of metals has been extensively studied [14–17]. The fluctuating stresses typical of fatigue may lead to the initiation and growth of a crack that, upon reaching a critical size, leads to fracture [18]. Fatigue crack initiation is frequently reported to occur at stress concentration sites and manufacturing defects of the metallic component, such as holes, fillets, welds, notches, pits and surface imperfections from machining operations [19–21]. If such design or manufacturing factors are absent, fatigue cracks may initiate in microstructural defects, such as grain boundaries and non-metallic inclusions [22–24].

The role of the microstructure in fatigue crack initiation has been reviewed recently by Chan [25]. The term "crack initiation" may be defined from a scientific or from an engineering point of view. The scientific approach states that initiation is the number of cycles required to generate, nucleate or form the smallest detectable crack. Chan adapted this definition to mean the process of forming a fatigue crack of a length that is of the same order of a grain size or less. The engineering definition is based on the smallest crack that can be determined by reliable non-destructive evaluation techniques, such as X-ray and ultrasonic methods [26,27]. Independently of the definition, it is widely accepted that fatigue crack initiation in ductile metals is the result of localized plastic deformation during cyclic slip processes [28–30]. Plastic strain can be highly concentrated in some regions while the surroundings areas are still in the domain of elasticity. The plastically deformed regions are referred to as persistent slip bands (PSBs). This process is typical of single crystals of face-centered cubic (fcc) metals. A PSB consists of a large number of slip planes, forming a flat lamellar structure divided into channels by a periodic array of dislocations. A complete description of PSBs structure and formation is given by Suresh [9].

A transmission electron microscopy (TEM) image of two slip bands in a failed fatigue specimen of Ni-based superalloy (Udimet 720). The inset shows a low-magnification view of persistent slip bands [31]; reprinted with permission from Elsevier.

Fig. 2. TEM image of two slip bands in a failed fatigue specimen of Ni-based superalloy (Udimet 720). The inset is a low-magnification view of persistent slip bands (from Sangid et al. [31]; reprinted with permission from Elsevier).
Fatigue cracks initiated by the intrusion–extrusion mechanism from PSBs are called Stage I cracks. As these cracks propagate and grow they become Stage II fatigue cracks. In stage I fatigue crack growth the crack and the zone of plastic deformation surrounding its tip are restricted to only a few grain diameters. This is called the short crack propagation stage [36]. As the stresses increase, the plastic zone at the crack tip involves a large number of grains. This stage leads to the formation of the so-called fatigue striations that appear as ripples on the fracture surface [9,36]. A n example of fatigue striations on the fracture surface of a surgical 316L stainless steel plate is shown in Fig. 4. At this point, it is interesting to define the fatigue crack growth mechanism in a more mechanistic basis. The reliable prediction of crack growth under cyclic loadings is a valuable and challenging topic for actual engineering applications of metallic materials. Successful design against fatigue is often determined by the understanding of this topic. In this context, it is important to describe how the fatigue life of a metallic component can be evaluated. The prediction of fatigue life may follow two different approaches: cumulative fatigue damage (CFD) and fatigue crack propagation (FCP) [38]. CFD is related to total fatigue life, safe life or damage-intolerant life design.

In this virtual infinite life design, fatigue data are presented in the form of Wöhler’s or S–N curves, which represent the plot of stress, $S$, vs. number of cycles to failure, $N$ [39]. These curves are determined for high cycle fatigue conditions, i.e. for $N > 10^5$ cycles. The stress level is relatively low and the overall strains are mainly elastic, even though the material undergoes localized plastic deformation. This is a common approach to the evaluation of fatigue resistance of metallic implants [40–42].

A schematic representation of an $S$–$N$ curve is shown in Fig. 5. In this figure, the cyclic stress range ($\Delta \sigma = \sigma_{\text{max}} - \sigma_{\text{min}}$) is plotted against the number of cycles to failure, $N$, in log–log scales. The endurance, or fatigue limit ($\sigma_n$), is defined as the stress range below which there is no crack growth (the material would be subjected to an infinite number of stress cycles without fatigue fracture). The number of cycles corresponding to the endurance limit is often considered to be $10^7$; this represents an infinite fatigue life. However, some materials do not present an endurance limit. For these materials, the stress continuously decreases with increasing number of cycles, and the “fatigue limit" is arbitrarily defined as the fatigue strength at a specific number of cycles, typically $10^6$ or $5 \times 10^6$ cycles [39]. A distinct fatigue limit has been reported for titanium alloys, Co–Cr–Mo and austenitic stainless

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**Fig. 3.** (a) Schematic representation of extrusions and intrusions formed within a PSB as a result of cyclic strain during fatigue of a metallic material (from Schijve [35]; reprinted with permission from Elsevier); (b) SEM image of extrusions within a PSB of high-purity polycrystalline nickel (From Weidner et al. [29]; reprinted with permission from Elsevier).

**Fig. 4.** Fatigue striations on the fracture surface of a surgical 316L plate (from Kanchanomai et al. [37]; reprinted with permission from Elsevier).

**Fig. 5.** Schematic representation of an $S$–$N$ curve (from Plekhov et al. [43]; reprinted with permission from Elsevier).
steel implants [44–46], while biodegradable magnesium alloys do not exhibit an endurance limit [47].

For low numbers of cycles (low cycle fatigue; N < 10⁵ cycles), cyclic stresses are higher than for high cycle fatigue. The resulting plastic deformation makes cyclic stress more relevant than cyclic stress. Hence, fatigue tests are controlled by cyclic stress instead of cyclic stress in the low cycle fatigue regime, plotting plastic strain range (Δεp) vs. the number of cycles to failure. Despite the higher number of investigations on the high cycle fatigue approach of biomaterials, low cycle fatigue data have been reported by some authors [48,49]. This approach is important in applications such as pacemakers or claps for removable partial dentures [50].

The cumulative fatigue design approach has well-established limitations. As pointed out by Zhang et al. [51], the accuracy of life prediction is strongly influenced by the geometry of the component under testing (stress concentration factors), process and load, resulting in a wide scattering of fatigue life data. Furthermore, it ignores the presence of flaws in the material [39]. The fatigue crack propagation (FCP) approach overcomes these drawbacks. This method derives from the linear elastic fracture mechanics (LEFM) concepts developed in the early 1960s, and is also known as damage-tolerant or finite life design. In their pioneering work, Paris et al. [52] proposed that the stress intensity factor range (ΔK = Kmax − Kmin) could be used to characterize the rate of crack advance per cycle (da/dN) during fatigue. The plot of da/dN vs. ΔK allows the interpretation of experimental fatigue data in terms of the well-known power-law relationship called Paris’s law:

\[ \frac{da}{dN} = C \Delta K^m \]  \hspace{1cm} (1)

In Eq. (1), C and m are the Paris coefficient and exponent, respectively, which depend on the material, environment, frequency and stress ratio (R = σmin/σmax). ΔK is expressed as:

\[ \Delta K = Y \Delta \sigma \sqrt{a} \]  \hspace{1cm} (2)

In Eq. (2), Y is a dimensionless parameter that depends on the geometry and size of an existing crack of length a in the material. At this point, it is important to emphasize that the LEFM approach only provides reliable data for the fatigue crack propagation rate of metallic materials when the initial size of a fatigue crack is longer than 1 or 2 mm and the small-scale yielding conditions apply [9]. These fatigue flaws are classified as long cracks. Conversely, the growth rates of small cracks can be much faster at the same ΔK.

Suresh and Ritchie [53] gave a detailed definition of small cracks: (i) microstructurally small cracks if the crack size is comparable to the scale of the characteristic microstructural dimension, such as the grain size for monolithic materials; (ii) mechanically small cracks if the plastic zone around a crack tip is comparable to the crack size; (iii) physically small cracks if the crack is larger than the characteristic microstructural dimension and the scale of the plastic zone is smaller than 1 or 2 mm; and (iv) chemically small cracks when environmental stress corrosion mechanisms become more active below a determined crack size. For these cracks, the use of Eq. (1) is no longer applicable.

The behavior of small fatigue cracks is of prime importance, since a major part of the fatigue life of a metallic component is spent in the propagation of this type of crack. Since the LEFM approach is not valid in this case, the propagation behavior of small fatigue cracks has been described by other criteria. The is invited to consult the reports by Pearson [54], Endo and McEvily [55] and Shyam et al. [56] provide deeper insights into this theme. In spite of the limitations of the LEFM approach to long fatigue cracks, the fatigue propagation rate behavior of biomedical metallic alloys has been widely characterized through da/dN vs. ΔK plots.

A typical da/dN vs. ΔK plot has a sigmoidal shape, as schematically shown in Fig. 6. Three distinct regions may be defined from this curve. Region I corresponds to the regime in which the average crack growth rate per cycle is smaller than a lattice spacing [9]. A threshold value of the stress intensity factor range (ΔKth) is marked on the plot, and determines the end of region I and the start of region II. According to Carpinteri and Paggi [38], this parameter is closely related to the concept of fatigue limit. The conventional definition of ΔKth is taken as the value of ΔK below which the crack growth rate is 10⁻⁹ mm per cycle or less. Paris’s law is valid in region II, which is related to the propagation of long cracks (stage II cracks). Region III denotes fast crack propagation, leading to final failure at very high values of ΔK, approaching Kc. Kc is a particular property of the material, called the fracture toughness, and is related to its resistance to brittle fracture.

FCP philosophy is used by several authors to investigate the crack growth rate of metallic implant materials [58–60]. However, despite the widespread use of the FCP approach, several deviations from the behavior described by Paris’s law have led to the development of other fatigue crack growth criteria. It is not within the scope of this article to give a deep description of these multiple criteria. For a more complete insight, the reader should consult the work by Pugno et al. [61] and references therein. Despite the limitations of both the CFD and FCP approaches, the general bases of these design philosophies are perfectly sufficient for the discussion of the literature on corrosion fatigue phenomena of metallic implants that is presented in the following sections.

2.2. Corrosion-assisted fatigue of metals: general mechanisms

The classification of corrosion-assisted fatigue of metals was primarily given by McEvily and Wei [62]. The environment affects fatigue crack growth depending on the Kmax value applied to the KSCC threshold for a sustained load. Kmax is the stress intensity factor and KSCC is the stress corrosion cracking (SCC) threshold. The classification scheme is separated into three different possibilities according to da/dN vs. Kmax plots, as shown in Fig. 7. Type A behavior is related to the situations where Kmax is reduced by the environment. For high values of da/dN, the curves of aggressive and inert environments are superimposed, that is, the contribution of the environment to fatigue crack growth is reduced with increasing fatigue crack growth rates. It is deduced, then, that corrosion fatigue is a time-dependent process and that such dependency becomes less pronounced with increasing frequency of cyclic stress. This is considered to be a true corrosion fatigue behavior as the
environment affects fatigue crack growth even when $K_{\text{max}} < K_{\text{ISCC}}$. The influence of the environment is less marked for type B behavior than for type A at low crack growth rates ($K_{\text{max}} < K_{\text{ISCC}}$). When $K_{\text{max}}$ exceeds $K_{\text{ISCC}}$, there is a superposition of the stress corrosion process on fatigue. A plateau is then formed, which is typical of the stress corrosion cracking growth mechanism. Crack growth is governed mainly by the applied stress. Type C behavior is a combination of types A and B. Crack growth is dependent on both time (frequency of the cyclic stress) and the applied stress.

Recently, Vasudevan and Sadananda [63] extended this early classification scheme of corrosion-assisted fatigue growth to five types of behavior. The scheme is based on the parameters $\Delta K$ and $K_{\text{max}}$ that are recognized to provide two crack tip driving forces simultaneously required for the propagation of fatigue cracks. In this way, the corresponding threshold values of $\Delta K$ and $K_{\text{max}}$ must be surpassed to allow the growth of a fatigue crack. These thresholds are represented as $\Delta K^*$ and $K_{\text{max}}^*$. Crack growth is controlled by cyclic amplitude in the Paris regime. In this case $\Delta K^* = K_{\text{max}}^*$ and the plot of $\Delta K^*$ vs. $K_{\text{max}}^*$ for different crack growth rates (da/dN) will be a straight line. This is characteristic of a pure fatigue crack growth or ideal fatigue behavior, and may be observed for alloys tested in a very high vacuum. A representation of such a mechanism is shown in Fig. 8. The curve in Fig. 8 may be considered as a trajectory of crack growth mechanism and is known as a trajectory map [64]. Alterations of the mechanism of fatigue crack growth give rise to deviations from this ideal behavior. It has been reported that all deviations from the ideal behavior occur when $K_{\text{max}} > K_{\text{ISCC}}$, i.e. non-ideal behaviors fall below the line $\Delta K^* = K_{\text{max}}$, approaching the x-axis [64]. One main reason for such a deviation is the onset of a corrosion process. According to Vasudevan and Sadananda [63], if a metallic material is in a corrosive environment, $K_{\text{max}}$ controls crack propagation by breaking the crack tip bonds. One possibility is that the environment reduces the $K_{\text{max}}$ required to break the bonds. The trajectory map is influenced by the aggressiveness of the environment. As the environmental effect increases relative to fatigue, the crack growth trajectory can become almost parallel to the x-axis. The trajectory map may thus be used to study the crack growth mechanisms for a given material–environment pair. The classification scheme proposed by Vasudevan and Sadananda [63] can be described from these definitions.

Type I is related to the case where fatigue crack growth is controlled by cyclic amplitude and $\Delta K^* = K_{\text{max}}$, i.e. it is the ideal fatigue behavior typical of materials that are insensitive to the environment. Type II is the true corrosion fatigue behavior as observed in Fig. 7a. Type III behavior accounts for the case where the environmental fatigue crack growth curve in a da/dN vs. $\Delta K$ plot runs parallel to the pure fatigue behavior. The contribution of the environment is nearly constant throughout the range of fatigue crack growth. Type IV is typical of a superimposed stress corrosion behavior on fatigue analogous to the type B behavior proposed by McEvily and Wei [62] (Fig. 7). Type V behavior is an extreme case of Type IV. The slope of $\Delta K^*$ vs. $K_{\text{max}}$ tends to zero as the trajectory crack growth is parallel to the $K_{\text{max}}$ axis. The trajectory maps for these five types of corrosion-assisted fatigue crack growth are shown in Fig. 9. This approach provides an effective method of separating the relative contributions of fatigue and environment to the crack growth of specific materials. Despite the valuable information of trajectory maps to the investigation of corrosion fatigue of metallic materials, we have not encountered environment (from Vasudevan and Sadananda [63]; reprinted with permission from Elsevier).

Fig. 7. Classification scheme of corrosion-assisted fatigue crack growth proposed by McEvily and Wei: solid line refers to aggressive environment; dotted line refers to inert environment (from Vasudevan and Sadananda [63]; reprinted with permission from Elsevier).

Fig. 8. Representation of an ideal fatigue behavior in trajectory map (plot of $\Delta K^*$ vs. $K_{\text{max}}$). In this curve $\text{da/dN}_2 > \text{da/dN}_1$ (from Sadananda et al. [64]; reprinted with permission from Elsevier).
Tribocorrosion is defined as an irreversible transformation of a material from concomitant physicochemical and mechanical surface interactions occurring at tribological contacts [65]. The importance of this phenomenon for metallic implants has been widely recognized [66–68]. This interest arises from the widespread use of total hip arthroplasty as a common surgical intervention. A sliding contact is formed between the femoral head and the acetabular cup during the articulating movements of the hip joints in the human body [69]. The sliding surfaces are then subjected to tribocorrosion. The resulting particulate debris has been found to promote adverse biological effects [70,71]. Furthermore, the small relative displacements between the prosthesis and the surrounding bone tissues lead to deterioration of the biomedical alloys by fretting corrosion [72]. Documented cases of fretting corrosion have been reported in bone plates and screws at the bone–stem interface and stem–cement interfaces of modular hip implants [73]. Titanium alloys are susceptible to fretting damage [74,75]. In the same way, fretting corrosion has been a concern for austenitic stainless steels and cobalt-based alloys [76–78].

Two- or three-body contacts are frequently associated with tribocorrosion [79]. Entrapped wear debris acts as an abrasive and is defined as the third body, while the sliding surfaces are the first and second bodies [80]. The main concerns while one investigates the simultaneous action of corrosion and wear in biomedical systems are the ability of the passive layer to withstand the mechanical stresses arising from wear, the ability of the metal surface to repassivate when the passive film is removed and the resistance of the new repassivated surface to both wear and corrosion [81]. In this regard, fretting has a big influence on the corrosion behavior of orthopedic devices due to the potentially harmful effects that it exerts on the mechanical stability of the passive films. Fretting corrosion is a crucial mechanism of in vivo implant corrosion. Crevice corrosion is frequently associated with this phenomenon [82,83]. Rabbe et al. [84] confirmed the validity of this model for Ti6Al4V and 316L biomedical alloys. Chandrasekaran et al. [85] studied the fretting corrosion behavior of Ti–6Al–4V modular taper specimens and discussed the clinical implications of this phenomenon. The potential adverse effects of fretting damage are the loosening of modular connections and the formation of debris that can lead to osteolysis or accelerate articular wear if entrapped between the contacting surfaces. It is noticeable that fretting motion between modular components in orthopedic implants is typically enhanced by manufacturing-induced discontinuities, such as scratches introduced during machining operations. Hence, the careful control of the surface integrity of the components is highly recommended in order to diminish the fretting corrosion of biomedical alloys.

Barril et al. [86] identified a clear correlation between mechanical and electrochemical parameters by evaluating the fretting corrosion behavior of a Ti–6Al–4V plate against an alumina ball. They showed that the electrochemical activity depends on the third-body behavior in the contact. Current peaks were associated with third-body accumulation in the contact, suggesting that the third-body particle formation occurred due to local depassivation of the metal. The depassivated surface then dissolves and repassivates. The freshly formed metallic wear particles may also dissolve and passivate, contributing to the observed current peaks.

Diomidis et al. [87] also observed the repassivation of biomedical titanium-based alloys during fretting corrosion experiments. Monticelli et al. [88] reported that the corrosion processes of Ti–6Al–4V were stimulated markedly when the material was subjected to combined wear and corrosion conditions, while under pure corrosion the corrosion current density was two orders of magnitude lower.

Recently, Souza et al. [89] brought new knowledge to the field by investigating the influence of oral biofilms on the biotribocorrosion behavior of commercially pure titanium (grade 2). The tests were conducted in vitro by exposing the samples to an artificial saliva solution. The authors reported that the titanium surfaces can be easily colonized by oral biofilms. The presence of biofilms decreased the corrosion potential of the titanium implants probably due to the release of acidic substances that diminished the pH of the test solution in comparison with a condition without the presence of a biofilm on the surface of the samples. During the...
tribocorrosion tests in the absence of a biofilm, the potential dropped due to the removal of the TiO₂ passive film under an applied normal load of 200 mN load. Upon unloading, the potential increased due to the repassivation of the titanium surface. The potential remained almost unchanged after unloading for the samples tested at a normal load of 100 mN, suggesting that repassivation could occur during sliding. The presence of biofilms altered this behavior. The potential drop after starting the sliding tests at 200 mN was also verified, but at longer times than when no biofilms were present. Hence, it is suggested that the biofilm is first removed and then the TiO₂ passive film. The authors noticed that the corresponding coefficient of friction was lower during the time the biofilm remained on the surface of the samples. When the sliding tests were conducted at 100 mN, the potential remained unchanged, as did the coefficient of friction, which remained low throughout the whole test. The wear scars produced on the surface of the samples after the tribocorrosion tests were observed by SEM. It was found that the wear scars were larger in the absence of biofilms, but were also present when a biofilm was present. This result points to a positive effect of the oral biofilm on the wear resistance of the titanium surface, although the passive film was still removed from the surface of the samples covered with a biofilm, especially at high loads. Electrochemical impedance spectroscopy measurements conducted in the absence of wear showed that biofilms decreased the corrosion resistance of the material. It is concluded that a wear corrosion mechanism is developed during sliding of the titanium samples and this process may lead to the failure of dental-implant-supported systems.

Igual-Muñoz and Julián [90] studied the tribocorrosion behavior of a high-carbon CoCrMo biomedical alloy. The current density was found to increase in the passive domain of the alloy.

According to Mischler [91], the corrosion rate of passive metals can increase by several orders of magnitude under tribocorrosion conditions in comparison with pure corrosion. There is a constant depassivation followed by repassivation during the combined wear and corrosion processes. Consequently, a sharp increase in the current follows in tribocorrosion tests at the onset of rubbing, thus accelerating the wear corrosion process of the alloy, leading to progressive consumption of the material.

Sinnett-Jones et al. [92] showed the influence of the integrity of the passive film and of the repassivation kinetics on the tribocorrosion rate of a CoCrMo alloy.

Yan et al. [93] showed that under tribological contact the corrosion rate of high-carbon CoCrMo, low-carbon CoCrMo and 316L stainless steel alloys increased 20–60 times in comparison with static corrosion conditions. The constant depassivation of the alloys by the mechanical forces generated in the tribocorrosion test accelerated the corrosion processes. Similar findings have been reported by the same group in other publications [94,95].

Igual-Muñoz and Mischler [96] studied the influence of different simulated body fluids on the tribocorrosion behavior of CoCrMo biomedical alloys. NaCl and phosphate-buffered saline (PBS) solutions with and without the addition of albumin were used in the tests. The wear ranking of the alloy depended significantly on the test electrolyte. The composition of the solution influences the surface chemistry of the metallic material. Consequently, mechanical wear is also affected. The nature of the passive film depends on the electrolyte, and can alter the mechanical response of metals in sliding tribocorrosion systems [97].

The adsorption of ions or molecules from the electrolyte may affect the repulsion/attraction forces between wear particles and solid surfaces, modifying the response of the material to wear. The presence of proteins in the electrolyte solution during tribocorrosion test has been reported to decrease wear-induced corrosion currents of CoCrMo alloys [98]. Indeed, Igual-Muñoz and Mischler [96] suggested that in the NaCl–albumin solution the pulling out of carbides is suppressed and wear becomes less intense for a high-carbon CoCrMo. However, this effect was not observed in the PBS–albumin solution. The authors recognize the complexity of the interaction between the electrolyte solution and the tribocorrosion behavior of CoCrMo alloys, and the necessity for further investigations to clarify the mechanisms involved in this process.

In addition to the tribological and chemical aspects depicted above, the concomitant action of cyclic stresses should not be disregarded. Fretting fatigue develops under the combination of wear and fatigue processes when two contacting surfaces experience small oscillatory relative motions while enduring a normal load and at least one of them carries bulk stress [99,100]. In this regard, Hoeppner and Chandrasekaran [101] reviewed the fretting-related damage of orthopedic implants. Fretting causes a local increase in strain on the surface of the metallic material that is a preferable site for the nucleation and early growth of fatigue cracks, leading to premature fatigue failure. Fretting fatigue life is typically divided in two parts, the first of which is referred to as stage I propagation. In this stage, the crack initiates along a slip direction in a grain. The second part is stage II crack propagation, where the fatigue crack growth can be predicted by the Paris law. Stage II evolves into fast propagation when the fatigue crack is longer than a critical size [100], which was experimentally shown to be 1.5–2.0 times the grain size of the metallic alloy [102]. Waterhouse and Dutta [103] recognized a long time ago that the corrosive nature of the body fluids affects the fretting fatigue behavior of biomedical titanium alloys. The importance of considering the interaction of biomedical alloys with living tissues for a complete understanding of corrosion fatigue phenomena has also long been recognized by Morita et al. [104]. They observed a remarkable reduction in the fatigue strength of austenitic stainless steel biomedical alloys when the fatigue tests were conducted in vivo. Although the authors did not evaluate the influence of fretting on the in vivo corrosion fatigue of the biomedical alloys, this phenomenon is likely to be present. Chandra et al. [100] recently studied the fretting corrosion behavior of Ti–6Al–4V. They observed that the wear volume depends on the stress state of the alloy and on the pH of the electrolyte in contact with the surface of the metallic material. They also evaluated the fatigue crack growth under fretting conditions, and proposed a model to predict the critical crack length and the life expectancy of the component under fretting fatigue. According to Chandra et al., fretting motion in the transverse direction of the throat stem in a modular hip joint decreases the crack length that is critical for fast crack propagation. Moreover, both the critical crack length and life expectancy diminish with the progression of wear. Furthermore, the amount of wear depends on the pH of the electrolyte. Hence, the corrosive conditions of the fluid in the joint of a modular orthopedic device are strictly related to the critical crack size under fretting fatigue conditions.

The tribocorrosion and fretting corrosion mechanisms discussed to this point are mainly referred to in vitro laboratory investigations. However, the in vivo behavior of metallic implants under combined wear corrosion or fretting corrosion has been hardly studied. Lomholt et al. [105] gave a recent contribution towards the understanding of the in vivo behavior of Ti–6Al–4V biomedical alloy under tribocorrosion conditions. They compared results from laboratory tribocorrosion tests with those from retrieved acetabular cups with appurtenant polymer liners from patients that suffered from pain. The implants were part of artificial hip joints. SEM images of the retrieved implants and the laboratory-tested specimens evidenced similar features. A pattern of light and dark contrast was found on the failure surfaces of the retrieved implants and the specimens evaluated in vitro. Higher microhardness values were found in the dark regions that also presented cracks for both conditions (in vivo and in vitro). Metallic particles were found to be adhered to the polymer liners of the retrieved implants and on the
electrolyte solution used in the tribocorrosion tests. A mechanism for the failure of the retrieved implants has been proposed based on the experimental observations. The movement of the femoral head within the acetabular cup after the polymer liner has been worn through generates wear debris from the acetabular cup. The accumulation of the wear debris from the Ti–6Al–4V acetabular cup forms large flakes. These flakes are then pressed into the surface during the sliding between the femoral head and the acetabular cup. The dark contrast on the failure surface of the acetabular cup would arise from this mechanism. As these dark regions are brittle, cracks are formed and yield fine particulate debris upon further sliding in the hip joint. The transport of the debris through the body can then cause inflammation of the peri-prosthetic tissue and loosening of the implant. Moreover, the debris also acts as three-body wear particles, increasing the deterioration of the sliding surfaces. Although this mechanism makes a valuable contribution to the understanding of the failure of titanium-based acetabular cups under in vivo tribocorrosion conditions, it does not encompass the influence of fatigue on the failure process.

Indeed, the synergism between wear, fatigue and corrosion of metallic implants is as yet unexplored in the literature. However, this gap in our knowledge has started to be filled by the investigations performed by von der Ohe et al. [106,107]. This group proposed a multi-degradation mechanism of passive metals that combines the simultaneous influence of wear, corrosion and cyclic loading. The mechanism is proposed as a model for the behavior of metallic structural materials in seawater; however, as it is related to the degradation of passive metals under the combined action of wear, corrosion and fatigue, it could be extended to other environments, such as body fluid. This approach could hence prompt further contributions to the understanding of the influence of wear on the corrosion fatigue of metallic implants.

2.4. Titanium alloys

2.4.1. General aspects

Pure titanium has two different allotropic phases: below 883 °C its crystalline structure is hexagonal close-packed (α phase), while above this temperature it is body-centered cubic (β phase). Depending on the alloying elements and the heat treatment used, the final microstructure can be conveniently tailored, according to the desired mechanical products. Titanium alloys are classified as α, near-α, α + β and β alloys according to their chemical composition, the content and nature of alloying elements and the resultant microstructures [108]. Aluminum is an α-stabilizer element. Vanadium, niobium, molybdenum and tantalum are β-stabilizers. Zirconium is considered a neutral element [109]. Alloys that consist of a large fraction of the less ductile α phase, such as the widely used biomedical alloy Ti–6Al–4V, have a modulus of elasticity (E) around 110 GPa. This value is significantly higher than that of a typical human bone (30 GPa) [110]. Such a stiffness mismatch is associated with an insufficient load transfer from the metallic implant to the bone tissue that may lead to the loosening of the prosthesis. This phenomenon is referred to as the stress shielding effect [111]. In order to avoid such complications, the development of new biomedical titanium alloys was concentrated on β alloys that are typically less stiff than α and α + β alloys (modulus of elasticity as low as 50 GPa [112]).

The fatigue behavior of biomedical titanium alloys has been found to be dependent on microstructure [113–115]. A wide variety of microstructures can be produced depending on the combination of mechanical processing and heat treatment [116,117]. The fatigue and corrosion fatigue behaviors of titanium alloys vary accordingly. Representative data taken from selected references are referred to in this section. The aim is to provide a clear correlation between microstructural features and corrosion fatigue behavior of biomedical titanium alloys based on either the CFD or FCP approach.

2.4.2. The CFD approach

Akahori et al. [118] investigated the fatigue and corrosion fatigue behavior of Ti–29Nb–13Ta–4.6Zr (TNTZ) alloy in air at 22 °C and in Ringer’s solution at 37 °C. The material was tested under different conditions: (a) solutionized at 1063 K for 3600 s in argon atmosphere; (b) the same treatment described in (a) followed by cold rolling up to a reduction ratio of 87.5% at room temperature; (c) same treatment described in (a) followed by water quenching. The specimens were then aged at different temperatures, followed by water quenching. The main goal of this procedure was to obtain distinct microstructures and to evaluate their effect on the fatigue and corrosion behavior of the alloy. The specimens were tested under plain and fretting fatigue conditions. The authors used only the CFD approach, showing their results as S–N curves for each set of test conditions. They found that the fatigue strength of both the solutionized and aged specimens was equal in air and in Ringer’s solution. Hence, the contact with the physiological solution did not degrade the fatigue behavior of the TNTZ alloy from the standpoint of the cumulative fatigue design approach. However, the fatigue crack growth behavior was not assessed. It is possible that the immersion in Ringer’s solution can lead to an increase in the crack growth rates (da/dN) in comparison with the rates obtained in air. This effect cannot be ignored if the corrosion fatigue behavior of the metallic biomaterial is to be fully characterized.

The fatigue behavior of another β alloy, Ti–13Zr–13Nb, was characterized by Baptista et al. [119]. They used the CFD approach, obtaining S–N curves for the alloy in air and in 0.9 wt.% NaCl solution. The alloy was found to be insensitive to the environment. The curves obtained in air and in the saline solution were equivalent. Similar findings were reported by Akahori et al. [117] for TNTZ β alloy in air and in physiological solution, as depicted above. Boehler et al. [120] have also demonstrated such insensitivity for Ti–15Al–33Nb and Ti–21Al–29Nb alloys, the microstructures of which consisted mainly of the body-centered cubic β phase. Based on these results, Majumdar et al. [121] disregarded the evaluation of the fatigue behavior of Ti–13Nb–13Zr and Ti–13Nb–13Zr–0.5B in simulated body fluids, performing the fatigue tests only in air.

Azevedo [10] investigated the failure of a commercially pure titanium (grade I) reconstruction plate for osteosynthesis. The microstructure of the material consisted of equiaxed α-grains and intergranular β-platelets. Failure occurred as a consequence of intergranular corrosion attack on the β-platelets due to the contact with body fluids and fatigue caused by high stress concentrations at lateral notches in the titanium plate. Azevedo emphasized that the loosening of the plate-screws in the bone due to a technical error of the surgeon or bone resorption also contributed to the failure. In another report, Azevedo and dos Santos [122] showed that the number of cycles to failure of a commercially pure titanium plate (grade I) was reduced during laboratory fatigue testing when the tests were conducted under immersion in serum at 37 °C. Papakyriacou et al. [123] used the CFD approach to study the fatigue behavior of Ti–6Al–7Nb alloy and commercially pure titanium in air and in 0.9 wt.% NaCl solution. The number of cycles to failure was found to decrease in the saline solution for both materials. Zavanelli et al. [124] found a similar trend for Ti–6Al–4V and commercially pure titanium dental implants when exposed to synthetic saliva and fluoride synthetic saliva.

2.4.3. FCP approach

Bache and Evans [125] studied the fatigue crack growth behavior of Ti–6Al–4V in air and in 3.5 wt.% NaCl solution at room temperature. This alloy is typically used as an implant material, and its microstructure is classified as α + β. The authors evaluated three
distinct microstructures obtained from different heat treatments: mill annealed, bimodal $\alpha + \beta$ and transformed lamellar. These are shown in Fig. 10. The transformed lamellar microstructure is formed by colonies of aligned, elongated grains separated by a continuous retained $\beta$ phase. It is interesting to note that the mill annealed and bimodal alloys were nearly insensitive to the environment, with only a slight increase in crack growth rates ($da/dN$) upon immersion in the saline solution in comparison to the rates obtained in air. Conversely, transformed lamellar alloys presented a marked increase in crack growth rates under immersion in the saline solution. This result points to a clear and decisive influence of microstructure on the corrosion fatigue behavior of Ti–6Al–4V. The fatigue crack propagation approach successfully indicated this influence. According to the classification scheme of corrosion-assisted crack growth proposed by Vasudevan and Sadananda [63], Ti–6Al–4V with mill annealed and bimodal microstructures are type I materials, that is, they present ideal fatigue behavior. Transformed lamellar microstructure is a type II material at low stress ratios ($R$) and a type IV material for increasing values of $R$. The increment of crack growth rates with the increase in the stress ratio is typical of environmentally assisted crack growth. Under high $R$ the crack does not “close” during the unloading cycle. As a consequence, a constant supply of the corrosive species reaches the crack tip and the reaction products are transported away. Such knowledge is essential to the design of biomedical implants against fatigue. The most favorable microstructure should be preferred in order to avoid premature failures.

Gregory [126] reviewed the corrosion fatigue crack growth behavior of titanium alloys and commented on the expected increase in crack growth rates when the material is in contact with an aggressive environment. An interesting aspect described in the text is the influence of crystal orientation (texture) on the fatigue behavior of titanium alloys. When the basal planes of the hexagonal $\alpha$ phase are subjected to a tensile load, corrosion fatigue crack growth depends on the frequency of the cyclic stress. The crack growth rates increase when the frequency is decreased. If no basal planes are subjected to a tensile load, then corrosion fatigue crack growth is independent of the frequency of the oscillating stress. Conversely, if the basal planes are subjected to a perpendicular tensile stress, the environmental effects on fatigue crack growth are marked. This result was also reported by Hall [127] for a Ti–6Al–4V alloy. The control of crystallographic texture of plates and bars can be done through thermo-mechanical processing such as rolling and extrusion. Furthermore, the microstructure of the alloy is also important as the crystallographic effect is only related to the hexagonal $\alpha$ phase, not the cubic $\beta$ phase. In this respect, corrosion fatigue crack growth of $\beta$ titanium alloys is insensitive to variations in the frequency of the cyclic stress. For these alloys, fatigue data obtained in air could be used to predict fatigue life. Moreover, low- to medium-strength $\alpha$ and $\alpha + \beta$ alloys (yield strength less than 700 MPa) behave in the same way as $\beta$ alloys. The corrosion fatigue crack growth behavior of laser melted (LS) and ingot metallurgy (IM) Ti–6Al–4V under a vacuum, in air and in a 3.5 wt.% NaCl solution was studied by Lee et al. [128]. They found that crack growth rates are much higher in air and saline solution than in a vacuum for both LS and IM alloys. It is noteworthy that the behavior in air and in the saline solution is equivalent when $R = 0.1$. Nevertheless, when $R = 0.9$ the crack growth rate in
3.5 wt.% NaCl increases more rapidly than in air. The authors state that a pure corrosion fatigue behavior operates at $R = 0.1$. The alloys may then be classified as type II according to the classification scheme of Vasudevan and Sadananda [63]. At $R = 0.9$, a stress corrosion cracking process would be present in addition to corrosion fatigue, leading to substantial differences between the $da/dN$ curves of the materials exposed to air and in the saline solution. In this case, the corrosion-assisted fatigue crack growth behavior of both materials would be classified as type IV.

In addition to the effect of the environment on the fatigue crack growth behavior of the alloys, Lee et al. [128] also assessed the influence of microstructure. The LS alloy microstructure consisted of large $\beta$ grains (diameter of 600 $\mu$m) containing $\alpha$ platelets, while the IM alloy had much smaller, equiaxed $\alpha$ grains (diameter of 15 $\mu$m) in a matrix of transformed $\beta$, containing $\alpha$ platelets (Fig. 11). The IM alloy was found to present higher fatigue crack growth rates. This behavior was attributed to its large $\beta$ grains. The authors also expressed their data as trajectory maps ($\Delta K^* \text{ vs. } K_{\text{max}}$ plots), as shown in Fig. 12 for $R = 0.9$. It can be seen that the trajectories of both alloys in air and in 3.5 wt.% NaCl solution start at lower values of $\Delta K^*$ and $K_{\text{max}}$ than in a vacuum.

There is a clear divergence from the ideal fatigue behavior even in a vacuum. The environment provides an additional driving force of chemical nature to fatigue crack propagation. The main effect of the environment seems to be a reduction in the mechanical stresses needed to propagate the fatigue cracks. It is noticeable that the trajectory of the crack growth runs almost parallel to the $K_{\text{max}}$ axis in the high crack growth regime for the alloys exposed to air and saline solution. This behavior is typical of type V fatigue crack growth [63], and is related to stress corrosion control; that is, crack growth is governed rather by $K_{\text{max}}$ than $\Delta K^*$, meaning that the stress level is more important than its frequency.

Even though the article by Lee et al. [128] is not focused directly on biomedical applications, it exposes the crucial role that environment and microstructure play on the fatigue crack growth behavior of titanium alloys. Such an approach is hardly ever found in the literature regarding biomedical metallic materials. In this respect, it is evident that the development of new titanium-based orthopedic implants should encompass a more detailed analysis of fatigue crack growth behavior. The use of the methodology developed by Vasudevan and Sadananda [63] is efficient at identifying the mechanisms involved in fatigue crack growth at specific environments for a given material and microstructure.

Leinenbach et al. [129] proposed a different approach to evaluate the influence of corrosion on the fatigue behavior of titanium alloys. According to the authors, corrosion potential measurements can give in situ information on surface damage during rotating bending in a corrosive environment. The formation of intrusions and extrusions during cyclic stresses lead to the creation of new non-passivated surfaces in metallic implants. Crack initiation and propagation act in the same manner. When the material is in contact with an aggressive environment, the passive film is damaged, thus creating fresh new passive film-free surfaces. Consequently, the open circuit potential is shifted to more negative values.

Leinenbach et al. [129] employed electrochemical noise to simultaneously follow the potential and corrosion current variations of a Ti–6Al–7Nb biomedical alloy under cyclic deformation. In this electrochemical technique, the working electrode (the specimen under testing) is electrically connected to a counter electrode. The counter electrode consists of the same material with the same surface finishing condition as the working electrode. Hence, the
counter electrode will be in the same electrochemical state as the working electrode and no net current will flow between them while the surface of the loaded specimen is undamaged. Upon starting the test, the local destruction of the passive film on the surface of the working electrode gives rise to variations in both the potential and the corrosion current. If oxygen is dissolved in the electrolyte, a new oxide film may develop immediately after activation of the surface. As a result, the ion flux into the electrolyte is reduced, the corrosion current drops and the potential increases. A constant decrease in potential and a constant increase in the corrosion current indicate that more new surfaces are created and subsequently repassivated within a certain period of time. Thus, the evaluation of fatigue crack nucleation and growth can be carried out through potential and current measurements during the number of stress cycles in a fatigue test.

An example of this approach used by Leinenbach et al. [129] with their Ti–6Al–7Nb orthopedic alloy is shown in Fig. 13. First, the crack grows along the surface of the alloy. The small current peaks indicate that the crack growth rate is low. This would denote that only a reduced fraction of the surface of the titanium alloy is activated during each stress cycle. As the crack becomes longer, the load at the crack tip increases and so does its growth rate. This regime is evidenced by a sudden rise of the current peaks and a sharp reduction in the corrosion potential. Final fracture leads to a distinct peak of the corrosion current due to the relatively large activated surface characteristic of the last stress cycle before failure. The validity of this mechanism was confirmed through microscopic investigations by scanning electron microscopy. This approach was further developed by the same group in other publications [130,131].

Niinomi et al. [132] investigated the fatigue crack growth behavior of Ti–5Al–2.5Fe alloy in air and in Ringer’s solution. They tested the material with a microstructure composed of equiaxed α grains and fine α precipitates (denoted as material B). The fatigue behavior was compared to that of a Ti–6Al–4V ELI alloy with a typical Widmanstätten microstructure (denoted as material F). Both microstructures are shown in Fig. 14. For both materials, da/dN was higher in Ringer’s solution than in air in the Paris law regime. The crack closure effect was smaller in Ringer’s solution than in air. The fracture surface would become smoother in Ringer’s solution as a consequence of corrosion. Thus, when a fatigue crack is nucleated, the fracture surface is more easily dissolved in physiological solution than in air. Based on the da/dN vs. ΔK plots, the corrosion-assisted fatigue crack growth of both materials may be classified as type II behavior (pure corrosion fatigue process) according to the classification scheme of Vasudevan and Sadananda [63].

2.4.4. In vivo corrosion mechanisms and failure analysis

In addition to the study of the fatigue properties of biomedical alloys through laboratory testing, failure analysis of prematurely fractured implant materials is also of prime importance to the understanding of the mechanisms that govern environment-assisted fatigue failure of metallic implants under real conditions. Currently, fracture of modern orthopedic implant devices is considered a rare complication in total hip arthroplasty [133]. However, contemporary modular designs used in this type of surgical procedure allow micromotion at the Morse taper junctions during mechanical loading [134]. Furthermore, crevices are formed between the taper junctions, creating conditions for the penetration of body fluids that remain stagnant. As a consequence, crevice corrosion may develop. As corrosion advances in this confined area, oxygen concentration drops, leading to an excess of metallic ions. Negatively charged chloride ions migrate from the physiological solution to the crevice. Hydrochloric acid then begins to form inside the crevice, dissolving the protective oxide film on the surface of the implant. This type of corrosion has been found in stainless steel, cobalt–chromium and titanium implants [135,136].

The combination of crevice corrosion and fretting fatigue is a critical issue in the event of mechanical failure of metallic implants. A recent report by Paliwal et al. [137] confirmed the association of fretting fatigue and corrosion in the fracture of three uncemented Ti–6Al–4V alloy modular total hip stems. The general mechanism of failure begins with the formation of microcracks on the surface of the implant during fretting corrosion. Microcracks then propagate because of fatigue until the load reaches the fatigue strength of the material, leading to brittle fracture. Rodrigues et al. [138] observed the susceptibility of Ti–6Al–4V/Ti–6Al–4V modular taper interfaces in the stem to fretting and crevice corrosion. Moreover, hydrogen embrittlement was also found due to the typical mechanism of crevice corrosion in these devices.
Variable frequency of oscillating stresses, patient's health and lifestyle, and accuracy of the surgical procedure are factors that pose serious difficulties at reproducing real service conditions of an implant through in vitro tests. Recent developments of titanium-based implants have attempted to give a step in this direction [140,112,141]. However, a complete evaluation of fatigue life of metallic implants has not been performed to date. Accurate simulation of the complex natural body fluid, composed of proteins, enzymes and saline species that act and interact simultaneously, and of the stresses that combine fretting and fatigue conditions is still to be done, as noted by Fleck and Eifler [3]. There is a clear need to drive future developments of biomedical alloys along this route. Moreover, the lack of studies on fatigue crack propagation of titanium alloys in simulated body fluids is surprising. There has been no systematic investigation of the correlation between microstructures, surface finishing and fatigue crack growth of biomedical titanium alloys under real service conditions, i.e., simulating crevice corrosion in the physiological medium composed of a mixture of proteins, enzymes and saline species at 37 °C, and with different conditions of wear and frequency of the cyclic stresses. This lack of information is not exclusive of titanium alloys. The same deficiency is encountered in the literature concerning stainless steels, cobalt–chromium and biodegradable magnesium alloys, as described in the next sections.

2.5. Stainless steels

The stability of the passive films formed on the surface of stainless steels strongly affects the corrosion fatigue behavior of these materials [142]. Thus, the chemical composition is decisive in determining fatigue properties. In this context, it has been reported that the addition of molybdenum and nitrogen to austenitic stainless steels is an effective method for improving their corrosion fatigue resistance. Analytical studies by means of Auger electron spectroscopy and X-ray photoelectron spectroscopy show that the oxide layer on austenitic stainless steels has a duplex structure [143,144]. It is known that the composition of the passive film is strongly influenced by the composition of the alloy and the pH of the solution [145,146]. It is also well documented that the passive layer on these materials is composed of an inner chromium-rich region of a few atomic layers in contact with the metallic substrate and an external iron-rich layer at the interface between the film and the electrolyte [147,148].

Molybdenum is known to have beneficial effects on the pitting corrosion resistance of austenitic stainless steels [149]. The high energy of Mo–Mo bonds increases the activation energy barrier for dissolution, thus enhancing resistance to pit initiation. Nitrogen influences passivity of austenitic stainless steels [150,151], increasing the stability of the passive layer. This effect has been explained through several mechanisms. Jargelius-Petersson [152] found that the primary role of nitrogen is in pit repassivation rather than in the onset of pitting corrosion. A synergism between molybdenum and nitrogen was also proposed based on the fact that the combination of these elements was effective at eliminating current transients during passive current density measurements in molybdenum-bearing stainless steels. Other mechanisms are based on the formation of ammonium ions or nitrate/nitrite ions [142,153] and the enrichment of nitrogen on active surfaces [154].

The specific mechanism through which nitrogen acts may depend on the characteristics of the electrolyte in contact with the stainless steel such as pH. However, it is well recognized that nitrogen alloying increases pitting corrosion resistance of austenitic stainless steels in neutral and acidic environments [155]. This effect has been discussed by many authors [156–158].

Fatigue crack initiation has been correlated to the presence of pits in metallic materials [8,159]. Repassivation of mechanically depassivated slip steps may not occur when the material is at a potential in the metastable pitting range. Localized attack is then likely to occur at these active sites. This mechanism is known as the slip step dissolution model [160]. Pits are formed in the process, acting as stress raisers and preferential sites for fatigue crack initiation. Thus, as molybdenum and nitrogen improve the pitting corrosion resistance of austenitic stainless steels, adding such elements would also be an effective way of improving corrosion fatigue resistance of stainless steel implants. Additionally, as depicted by Begum et al. [142], the low stacking fault energy (SFE) of nitrogen is closely related to its positive effect on the corrosion fatigue resistance of austenitic stainless steels. Low SFE is associated with an increase in the amount of planar slip. This, in turn, increases the resistance of the material to localized strain and hinders the formation of PSBs, thus hindering fatigue crack initiation [161].

In spite of the widespread use of austenitic stainless steels as load-bearing devices in biomedical applications [162], there are relatively few investigations on the corrosion fatigue phenomena associated with fatigue life, especially the fatigue crack growth of these materials. One exception is the report by Giordani et al. [12]. They investigated the corrosion fatigue crack initiation of a high-nitrogen ISO 5832-9 austenitic stainless steel. This type of steel was developed to replace the conventional ASTM F-138 grade, owing to its higher pitting corrosion resistance [163]. Their fatigue data were expressed as S–N curves obtained in air and 0.9 wt.% NaCl solution at 37 °C. The saline environment reduced the fatigue life of the specimens. The mechanism of failure was not attributed to the primary onset of pitting corrosion. No evidence of pitting was observed on the surface of the specimens tested in the aqueous environment. The preferential sites for crack initiation were coarse precipitates, composed mainly of Nb and Cr (a complex nitride of Nb and Cr called the Z-phase), and Al-rich non-metallic inclusions, as shown in Fig. 15. This mechanism operates for both fatigue and corrosion fatigue failure. According to the authors, the first cycles of stress plastic deformation lead to the fracture of many coarse precipitates, forming geometric discontinuities at these sites. The electrolyte then penetrates through such discontinuities, reaching the bare metal underlying the fractured passive film. As a result, a crevice corrosion mechanism is developed.
continuously impeding repassivation inside the discontinuities. Consequently, anodic dissolution of the metallic material proceeds with the evolution of the cyclic loading, giving rise to an autocatalytic process. Therefore, corrosion accelerates fatigue failure by intensifying the concentrations of stress and strain at the precipitates and non-metallic inclusions.

The corrosion fatigue failure of an orthopedic stainless steel implant was studied by Amel-Farzad et al. [164]. The device was a DCS barrel plate, which had been implanted in the patient's thigh for two years. A top view of the fractured plate is shown in Fig. 16. Pits and cracks are visible on the surface of the implant with unaided eye. Failure was found to be due to corrosion fatigue assisted by a crevice corrosion mechanism. The material used to manufacture the plate had a chemical composition that was totally inadequate for such biomedical applications, with much lower nickel, chromium and molybdenum contents than those recommended by the ASTM F-138 standard. The low quality of the material led to the onset of pitting corrosion inside the crevices between the screws and the plate. Then cyclic loadings nucleated cracks at the localized corrosion sites. Cracks propagated with the increase in stress cycles and, when a critical size was reached, the final fracture occurred.

Swarts et al. [165] carried out a retrieval study of fractured high-nitrogen stainless steel tapered hip stems. The authors emphasize the superior corrosion resistance of this grade to conventional 316L surgical materials and point that the occurrence of failure is rarely reported for these devices. However, six different cases of failure of tapered hip stems manufactured from this material had been forwarded to the authors' laboratory for an accurate evaluation of the main causes involved in the fractures. The failure mechanism was identified as corrosion-initiated fatigue for all stems. The authors conducted potentiodynamic polarization measurements to assess the pitting corrosion resistance of the materials. The results pointed to a high resistance to the onset of pitting. The presence of localized corrosion attack at the surface of the stems was thus considered surprising by the authors. The combined effect of wear and crevice corrosion was hypothesized as a possible cause for the localized corrosion signs on the stems: fatigue cracks had initiated at these sites, leading to catastrophic failure.

A further explanation for the failure mechanism was given based on the microstructure of the stems, especially the grain size. The microstructure of the stems was found to present an average ASTM grain size in the range specified by the ISO 5832-9 standard (the maximum allowable grain size is ASTM 4, based on the measurements described in ASTM E-112 standard). However, the grain size distribution was heterogeneous, and some grains at the surface of the stems were coarser than the maximum size specified by the standard. The authors suggest that grain size heterogeneity has the potential to reduce the fatigue strength of the alloys, increasing the probability of fatigue failure. A careful control of the grain size through the combination of specific mechanical processing (cold work) and heat treatment (recrystallization) operations is suggested to avoid this problem. The analyses by Swarts et al. [165] highlight the importance of controlling specific microstructural aspects of austenitic stainless steel in order to attain optimized corrosion fatigue properties.

Tavares et al. [166] investigated the causes of failure of stainless steel orthopedic implants (dynamic compression plates) removed from patients after premature fracture. Failure was related to a combined corrosion fatigue process accelerated by the poor surface finishing of the prostheses that acted as stress concentration sites to the nucleation of fatigue cracks. Crevice corrosion in the bolt/plate contact also contributed to the corrosion-assisted fatigue failure. This article reveals the decisive role that surface finishing plays on the corrosion fatigue behavior of metallic implants. Even when surface corrosion is not present, fatigue failure of stainless steel compression plates may occur as a result of cleavage decoherence, as reported by Triantafyllidis et al. [167].

Xie et al. [168] extended the analysis of the mechanisms that govern corrosion fatigue of stainless steel implants. They concluded that the initiation of corrosion fatigue cracks is due to intergranular corrosion inside pits. The initial cracks are generated along attacked grain boundaries and propagate intergranularly. In a next step, transgranular cracks are formed from the initial intergranular ones due to the local stress field at the crack tip. One of the transgranular cracks dominates fatigue crack propagation, leading to the final failure. Dislocation pile-up is also closely related to this mechanism. The authors observed that dislocations multiply and pile up along grain boundaries during corrosion fatigue tests of surgical stainless steels in laboratory. The longer the cyclic stress, the more pronounced is this effect. As a result, the chemical activity of stainless steels will increase along the high dislocation density grain boundaries. Intergranular corrosion is facilitated at these sites and propagates rapidly to become a dominant transgranular crack under cyclic stresses.

Bolton and Redington [169] conducted an investigation of the fatigue crack growth behavior of two surgical grade (316L and 316LVM) stainless steels in physiological solution. This is a rare example of the use of the FCP approach to the evaluation of the fatigue behavior of surgical stainless steels. For both materials, crack growth rates increased in the presence of the saline solution in comparison with air at low stress intensities. This trend was reversed at high stress intensities. The da/dN vs. AK plots for 316L stainless steel in air and in Ringer’s solution is shown in Fig. 17. The crack growth behavior of the materials may be classified as type II, i.e. a true corrosion fatigue, according to the classification scheme of Vasudevan and Sadananda [63]. The decrease in da/dN with increasing AK may be related to the secondary cracking that occurred along striations. The authors found that above \( AK = 30 \text{MPa.m}^{0.5} \) a fully developed striation appearance formed across the fracture surface and the striation spacing increased with stress intensity. Consequently, the opening up of a fatigue crack along the base of striations suggests that changes took place during the reversed plastic flow. As a result, the shape of the fatigue cracks was altered, as was the morphology of the striations, leading to a decrease in the crack growth rate. This analysis was supported by SEM images of the fractured surfaces.

The number of scientific investigations of the fatigue behavior of stainless steel implants is very low in comparison with those of titanium-based alloys, especially during the last decade. This is probably related to the well-documented limitations of stainless steels owing to corrosion resistance in body fluids, the release of potentially damaging ions to adjacent tissues and the stress shielding effect [170–173]. Titanium-based biomaterials are known to behave better in all these aspects [48,174]. However, permanent prostheses made of stainless steel are still widely used due to cost savings [175,176]. This scenario is likely to continue for an indefinite period. While the study of fatigue crack growth behavior of the stainless steels used in nuclear power or chemical plants has received considerable attention [177–179], a systematic investigation of this subject regarding biomedical applications has been neglected.

Fig. 16. Top view of the stainless steel fractured plate (from Amel-Farzad et al. [164]; reprinted with permission from Elsevier).
2.6. Co–Cr–Mo alloys

Co–Cr–Mo alloys are known to present high wear resistance and good mechanical properties under static loadings [180]. In addition to these features, intrinsic biocompatibility and excellent corrosion resistance are also key factors that determine the use of these alloys for orthopedic applications [181]. Moreover, the fatigue strength of cobalt-based biomaterials exceeds that of titanium alloys and austenitic stainless steels, depending on the manufacturing methods employed to produce the alloys [182,183]. Nevertheless, fatigue failures of Co–Cr–Mo orthopedic devices have been reported [184–186]. Corrosion processes are often associated with these catastrophic failures.

Gilbert et al. [187] analyzed the fracture causes of two modular total hip prostheses, consisting of a wrought cobalt alloy (ASTM F799) head coupled to a wrought cobalt alloy stem. The two fractures occurred in the neck region, outside of the taper junction between the head and neck components.

Modularity is known to favor the onset of crevice corrosion in orthopedic metallic implants [188]. In fact, Collier et al. observed several pits on the fracture surface of the prostheses which were created inside the crevices between the head and the stem. Manufacturing defects such as porosity and segregation may have also contributed to the corrosion-assisted fatigue failure of the prostheses.

Sudhakar [189] reported on the corrosion fatigue failure of a Co–Cr–Mo alloy (Vitallium 2000) used as a bone plate. The fracture was found to occur at the interface between the screws and the plate, a typical site for the onset of crevice corrosion. Sudhakar showed that pitting corrosion was present at the fracture surface as well as fatigue striations.

It is not only the design of Co–Cr–Mo implant devices influences the fatigue behavior of these components; their microstructure is also of prime importance. A typical as-cast microstructure of cobalt-based surgical alloys presents a dendritic α-fcc metastable matrix and precipitates composed mainly of blocky M23C6 carbides, which appear in interdendritic regions and grain boundaries [190]. A lamellar phase has also been observed in the grain boundaries. Furthermore, an intermetallic sigma (σ) phase and MσC carbides may be present as minor constituents of the secondary phase aggregates [191]. An example is shown in Fig. 18.

Carbide precipitation accounts for the main strengthening mechanism of the alloys in the as-cast condition. Coarse blocky carbides act as sources of dislocations and stacking faults when the material is subjected to mechanical loads. As suggested by Dobbs and Robertson [192], the lamellar constituent is the most detrimental phase of the microstructure. When it is removed by heat treatment, the tensile strength, ductility and fatigue life are increased. Hence, it is possible to improve the fatigue behavior of cobalt-based implants through the careful control of alloy composition and heat treatment operations. Alloy composition is primarily related to the carbon content in the alloy, which provides the basis for carbide formation during cooling from the melt. However, other elements can improve the overall mechanical properties of Co–Cr–Mo biomedical alloys and, consequently, their fatigue properties. Zhuang and Langer [193] observed that nickel additions...
improved the fatigue crack growth resistance of a Co–Cr–Mo biomedical alloy by increasing its stacking fault energy. This prevents the reduction of ductility of the alloy [194] and is beneficial to the workability during subsequent cold working operations, such as forging [195]. Heat treatments, in turn, provide specific microstructural alterations that are directly related to the mechanical behavior of the material under both static and cyclic stresses [196].

Despite the well-documented failures of cobalt-based implants due to a corrosion fatigue mechanism, few attempts have been conducted to predict the fatigue crack growth of these materials under the influence of a corrosive environment or even in air [197–199]. Marrey et al. [200] conducted an investigation into this subject. They developed a damage-tolerant analysis for the fatigue crack growth behavior of a Co–Cr–Mo alloy used as a cardiovascular stent. The mathematical model was compared with experimental results obtained in Ringer’s solution at 37 °C. The authors predicted that, provided that all flaws greater than 90 μm were detected prior to the implantation of the stent, in vivo fatigue failure was unlikely to occur. Niinomi [1] reported such a reduction in fatigue strength of Co–Cr–Mo alloys in physiological solution in comparison with fatigue tests conducted in air. However, Niinomi’s report is based on the CFD approach, ignoring the fatigue crack growth behavior of the metallic implants. If one considers the widespread use of cobalt-based orthopedic devices, it is clear that research on the corrosion fatigue behavior of these materials needs to evolve. In particular, the fatigue crack propagation approach simulating crevice corrosion conditions in physiological solutions has been hardly considered in the literature.

2.7. Magnesium-based alloys

Magnesium alloys are currently considered for applications as load-bearing implant devices such as plates, screws and pins for repairing bone fracture [201]. This trend arises from the low corrosion resistance of magnesium alloys in aqueous environments [202]. While for most engineering applications the susceptibility to corrosion is a critical limitation of these materials, for biomedical purposes it is a desirable property. If the material is employed as a fixture device, degradation may be beneficial to the patient, since the device will be absorbed by the body and hence the need for a new surgical procedure to remove the device will be avoided [203].

From this standpoint, biodegradable magnesium-based implants are very attractive since the in vivo corrosion of these materials generates mainly soluble, non-toxic products. This has been well studied in the literature [204–206]. However, hydrogen gas also evolves during in vivo degradation of Mg alloys. If the degradation is too fast, hydrogen may accumulate as subcutaneous gas bubbles. Moreover, the implant device may lose its mechanical integrity before the effective healing of the fractured bone [207,208]. Hence, controlling the corrosion rate of magnesium-based biomedical alloys is of utmost importance.

Several studies have concentrated on this subject, investigating the effect of different alloying elements and coatings on the corrosion properties of biodegradable magnesium alloys [209–212]. Reports have focused mainly on aluminum- and rare earth (RE)-containing magnesium alloys due to the overall positive effect that these elements have on the corrosion resistance of magnesium [213]. However, Witte et al. [201] have recently recommended that MgAl and MgRE systems should not be used for biomedical applications due to indications of possible harmful effects of these elements to osteoblasts and the onset of Alzheimer’s disease or cytotoxicity to specific cell lines [214–216]. Consequently, new Al- and RE-free biodegradable magnesium alloys have recently been developed for biomedical purposes and their in vitro corrosion resistance in physiological fluids have been evaluated [217–219].

The corrosion fatigue of structural magnesium alloys has been studied by several authors in NaCl and borate-buffered solutions. These investigations have generally focused on applications of magnesium alloys in the electronic, automotive and aerospace industries [220–223], and have used the cumulative fatigue damage (CFD) approach to assess the corrosion fatigue behavior of magnesium alloys. However, it is known that crack initiation life is significantly reduced due to pit formation in a corrosive environment [224]. The fatigue strength of magnesium alloys is significantly reduced in humid environments, and the fatigue limit drops drastically in NaCl solution. This reduction is caused by the formation of pits on the surface of the alloy, the initiation of fatigue cracks at these sites and their subsequent growth [225], leading to final catastrophic fracture. Thus, the CFD approach, which focuses on fatigue strength and fatigue life rather than on crack growth, is not suitable to fully understand the corrosion fatigue behavior of magnesium alloys.

Despite this, an alternative approach – the fatigue crack propagation (FCP) approach – has been used by only a few authors [223,224]. Rozali et al. [224] studied the fatigue crack growth of AZ61 alloy in NaCl 3.5 wt.% solution at different frequencies. They observed that the fatigue crack growth rate was higher when the alloy was immersed in the NaCl solution in comparison with a low humidity environment. Moreover, fatigue cracks were shown to propagate under lower load amplitudes in the saline environment. Nan et al. [223] proposed a mathematical law to model the corrosion-assisted fatigue crack growth of AZ31 alloy in 3 wt.% NaCl solution. Experimental da/dN vs. ΔK plots and modeled data corresponded well.

Despite the relatively high number of scientific reports on the corrosion behavior of biomedical magnesium-based alloys, corrosion fatigue has received little attention. Although these materials are designed to dissolve within the human body in accordance with their application as temporary fixation components, they have to maintain suitable mechanical strength during the healing of the fractured bone [226]. Hence, corrosion fatigue should be thoroughly evaluated to ensure that the orthopedic device will perform suitably and safely. Recently, Gu et al. [227] provided a proper analysis of this problem and took a step towards a deeper understanding of this phenomenon by evaluating the corrosion fatigue behavior of AZ91D and WE43 biomedical magnesium alloys. They compared the fatigue properties of both materials in air and in simulated body fluid (SBF) at 37 °C through S–N curves. The fatigue limit was found to significantly decrease for both alloys in SBF solution, as shown in Fig. 19 for the AZ91D alloy. The mechanism of fatigue failure was associated with the stress concentrations in casting defects such as internal pores, and with crack initiation and growth at surface pits formed in the SBF solution. Chamos et al. [228] also showed the major role played by pitting corrosion in the fatigue failure of AZ31 magnesium alloy.

The report by Gu et al. [227] clearly shows the harmful effect physiological solutions can have on the fatigue behavior of magnesium alloys. The importance of low cycle fatigue is also outlined, since final failure may occur within the typical number of cycles that a temporary implant may be expected to withstand during the healing of the fractured bone. In this scenario, in addition to the evaluation of the corrosion fatigue behavior by the CFD approach, it is very important to consider fatigue crack propagation, analyzing the da/dN vs. ΔK plots with regard to the growth of fatigue cracks under simulated physiological conditions. This approach is not found in the literature for the modern Al-free biodegradable magnesium alloys or even for the conventional Al-containing materials such as AZ91D, AZ31 or AZ61.
From the foregoing context, it is clear that research on the corrosion fatigue behavior of magnesium-based biomaterials is still incipient. The interaction between pitting corrosion and fatigue failure is clear and relatively well known from investigations in NaCl solution. However, fatigue crack propagation behavior needs to be studied for a wide variety of biodegradable Mg alloys. Even reports on the CFD approach are not found for Al-free alloys. Furthermore, the relationship between microstructure and corrosion fatigue behavior in physiological medium has been ignored in the literature. Several aspects, such as grain size, cold work, twinning, crystallographic texture and the content of specific alloying elements such as Ca, Zn and Mn, have been evaluated separately, i.e. focusing on their individual effects on corrosion or fatigue behavior [203,229–231], whilst their combined action has been ignored. This scenario should be modified by combining FCP and CFD approaches through the investigation of the relationship between the microstructure and corrosion fatigue mechanisms of biodegradable magnesium alloys. This is an imperative step towards the development of fail-safe orthopedic components.

3. Mitigation

According to Bayraktar et al. [232], the microstructures of alloys and their manufacturing processes are closely related to fatigue failure. Prevention of fatigue failure starts through the careful control of alloy composition and processing. Microstructure-related influences have been addressed in the previous section. Surface effects also determine the fatigue behavior of metallic materials [233]. It is widely recognized that surface finishing operations may be favorably used to increase the fatigue strength of metallic materials [234–236]. Conventional methods for fatigue life improvement are based on the introduction of surface compressive residual stresses and the deposition of hard thin films [237–240]. Metallic implants have benefited from both of these methods. A hot topic has emerged in the last decade: surface nanocrystallization as an alternative way to increase the corrosion resistance of metallic alloys. This approach has proved to be efficient in a variety of materials, such as stainless steels, zirconium, titanium alloys and nickel alloys [241–244], regarding their applications as biomaterials or not.

Despite the large number of investigations on the effect of nanocrystallization on the corrosion resistance of specific metallic materials, corrosion fatigue has hardly been evaluated at all; and if one considers metallic implants, the lack of information is still more pronounced. Therefore, this section deals with the analysis of prevention and mitigation methods used to improve the fatigue properties of biomedical alloys. The more conventional methods, based on compressive residual stresses and hard coatings, are depicted in the first two subsections, then the potentialities of surface nanocrystallization are discussed. As will become evident the reader, there is an undeniable scarceness of corrosion fatigue studies even for the conventional mitigation methods. This scarceness is still more significant for alloys with a nanocrystallized surface.

3.1. Compressive residual stresses

Compressive residual stresses are created by finishing processes that impart localized plastic deformation to the material surface. At the surface, deformed regions tend to expand, but the unstrained regions more distant from the surface restrain this expansion [245]. Thus, compressive strains are generated at the deformed surface. The compressed surface is effective at preventing fatigue failure since the fatigue cracks are generally initiated at zones subjected to tensile stresses at the free surface of a metallic material [237].

The most widespread method to obtain compressive residual stresses is shot peening. This is based on the bombardment of a metallic surface with small glass, ceramic or metallic spherical particles (shots), which undergo multiple and repeated impacts (peening) against the surface of the alloy [246]. As a consequence, the dislocation density is increased in the near-surface zones, as are the roughness and hardness [247]. Surface roughening is considered to be deleterious to the fatigue strength of shot-peened materials [248]. Hence, shot peening has both beneficial and harmful effects on the fatigue properties of metallic alloys. The optimization of parameters such as peening intensity, peening coverage, saturation, shot material, shot size, shot velocity, shot hardness and time of peening is essential to reach the best conditions of compressive residual stresses and surface roughening [249]. The determination of the optimum parameters is a time-consuming task. Laser shock peening (LSP) has been developed as an alternative finishing process in order to achieve deeper compressive residual stresses and avoid the deleterious effect of exaggerated surface roughening after shot peening [250]. LSP imparts plastic deformation to the treated surface through the formation of a plasma cloud that is generated by a laser pulse and travels into the workpiece as a shock wave, creating compressive residual stresses [251].

Both shot peening and LSP have been used to increase the fatigue strength of metallic implants, LSP being investigated more recently [252–255]. Semlitsch et al. [252] assessed the fatigue behavior of Ti–6Al–7Nb hip stems through S–N curves. The endurance limit of shot-peened components was increased in comparison with polished oxygen-diffusion-hardened specimens. Furthermore, the fatigue strength was found to be sensitive to surface roughness, with a reduction associated with the rougher surface.

Papakyriacou et al. [123] compared the corrosion fatigue behavior of Ti–6Al–7Nb and commercially pure Ti specimens with two different surface conditions: ground and shot peened. The fatigue tests were conducted in a physiological solution that simulated inflammatory conditions at the oral cavity. The shot-peened specimens were less sensitive to fatigue fracture in the corrosive solution than ground materials.

Azar et al. [253] investigated the effect of the time of peening on the corrosion and fatigue behavior of a surgical AISI 316L stainless steel. These properties were evaluated separately, i.e. some specimens were subjected to fatigue tests by a rotating, bending method in laboratory air and others underwent the electrochemical measurements in Ringer’s solution at 37 °C. Hence, the study was not focused on the assessment of the combined action of cyclic loading...
and corrosion attack on the shot-peened material. Nevertheless, it provides information useful in elucidating the influence of the shot-peening process on the performance of surgical stainless steel regarding its corrosion and fatigue behavior. The number of cycles to failure increased with the time of peening, as observed in the fatigue tests. This result was due to the high compressive residual stresses introduced for longer times of peening, postponing the initiation of fatigue cracks. Electrochemical measurements pointed to an increase in the corrosion rate and a reduction in the breakdown potential after up to 15 min of shot peening. The increase in surface roughness associated with the plastic deformation caused by the impact of the peening medium was closely related to the reduction in corrosion resistance observed with up to 15 min of peening. However, the surface roughness was found to decrease for longer times of peening, and the compressive residual stresses increased.

These two effects have been correlated with a reduction in the corrosion rate in austenitic stainless steels [254,255]. This approach reveals the strong effect of process parameters on the performance of shot-peened biomedical alloys. Nevertheless, despite the usefulness of these findings, the actual material response could only be perceived if the simultaneous effect of fatigue and corrosion had been investigated by the authors. Wieser [254] made a valuable contribution to this topic by studying the effect of conventional shot peening on the corrosion fatigue of the austenitic X2CrNiMo-18-15-3 surgical steel. Wieser conducted fatigue tests in laboratory air and in 0.9 wt.% NaCl solution at 37 °C with shot-peened specimens and electrolytically polished specimens. The effect of the combined surface treatments (shot peening followed by electrolytic polishing) on the fatigue behavior of the specimens was also evaluated. Without the influence of corrosion, the shot-peened specimens presented higher fatigue strength than the electrolyte-polished ones. By combining the two finishing processes, the fatigue strength was further improved. The results obtained in the physiological solution evidenced a pernicious effect of shot peening under corrosion fatigue conditions. The fatigue strength of the shot-peened specimens was reduced by 30% in the saline solution, while for the electrolyte-polished specimens the reduction was only 13%. According to the author, after shot peening, the surface roughness increases as well as the specific surface area of the material. As a result, localized corrosion attacks occur at the narrow depressed sites in the rough surface, making the material more susceptible to the initiation of fatigue cracks. Moreover, the dislocation density increases due to the strain hardening effect of the shot-peening process, shifting the corrosion potential toward the anodic direction and further decreasing the corrosion resistance of the peened surface. The specimens subjected to the combined action of shot peening and electrolytic polishing presented the best behavior under the corrosion fatigue conditions. The fatigue strength was decreased by only 4% in comparison with the result obtained in air. Surface smoothing due to electrolytic polishing was very important in preventing the harmful effects of corrosion-assisted fatigue crack initiation.

Pazos et al. [256] evaluated the fatigue strength of annealed commercially pure grade 4 Ti subject to acid etching (9 M sulfuric acid solution at 60 °C for 15 min), shot blasting with Al2O3 particles and a dual treatment consisting of the shot blasting treatment followed by the acid-etching treatment. The as-machined surface was used as a reference condition. The results are summarized in Fig. 20. The tests were conducted in air at room temperature. Hence, only the fatigue behavior of the biomedical material was assessed, without any information on the corrosion-assisted fatigue crack initiation. Despite the absence of investigations regarding corrosion-related phenomena, the results nevertheless showed that surface finishing operations can be detrimental to the fatigue properties of metallic implants. From the S–N curves shown in Fig. 20 it is clear that the acid-etching treatment led to a significant decrease in fatigue strength. This was caused by the introduction of several surface defects, mainly represented by microholes and intergranular corrosion, as observed through SEM micrographs. These defects acted as stress raisers, giving rise to the early initiation of fatigue cracks. The treatments that involved plastic deformation, i.e. shot blasting and the dual treatment, introduced compressive residual stresses in the surface of the metallic material. Consequently, fatigue strength was higher in comparison with the etched material. However, the as-machined material was more resistant to fatigue than the shot-blasted one. Shot blasting created notch-shaped surface defects that were preferential sites (stress raisers) for the nucleation of fatigue cracks. This effect counteracts the benefit of the compressive residual stresses generated during the treatment. The combination of shot blasting and acid etching produced the best performance amongst the three surface treatments. This result resembles the findings by Wieser [254], who showed that a dual treatment consisting of shot peening and electrolytic polishing increased the corrosion fatigue resistance of a surgical stainless steel.

The increase in fatigue resistance reported by Pazos et al. [256] was only marginal in comparison with the reference as-machined finishing. In addition, it is important to emphasize that the results were obtained in air. Thus, it is not unlikely that, under a combined corrosion fatigue mechanism, the performance of the biomedical material would be further reduced. It is notable, then, that surface treatments have to be carefully evaluated regarding their influence on the fatigue behavior of metallic implants and, most importantly, corrosion processes should always be considered in order to achieve reliable results.

Shot peening has also been performed on magnesium-based alloys. Most reports are concerned with aerospace or automotive engineering applications [257–259], while biomedical use has received only minor attention [260]. Irrespective of the application, it is important to concentrate on the outputs of the shot-peening process regarding its effect on the fatigue properties of magnesium alloys. In this respect, Zhang et al. [257,258] evaluated the effect of shot peening on the fatigue performance of a high-strength wrought Mg–Al–Zn–Mn alloy (AZ80). The authors used the CFD approach and the tests were conducted in air. The results indicated that the fatigue strength and fatigue life of the AZ80 alloy could be improved by the compressive residual stresses introduced by shot peening. The extent to which the fatigue performance can be improved depends on the peening medium and is directly
related to the degree of compressive stresses generated during the process.

The influence of corrosion on the fatigue strength of the shot-peened magnesium alloy was not assessed by Zhang et al. [257,258]. However, Khan et al. [259] provided a contribution to this field by investigating the corrosion fatigue behavior of a die-cast Mg–Al–Si–Cu–Mn–Zn alloy (AM60) subjected to shot blasting. They showed that shot blasting was effective at improving the fatigue performance of the alloy. S–N curves indicated that the fatigue strength was increased for the shot-blasted specimens in comparison with the die-cast alloy in an NaCl solution. Fatigue cracks originated from corroded areas at the surface of the material. The authors gave further insight into the fatigue behavior of the AM60 by evaluating the fatigue crack growth rate of the die-cast material through da/dN vs. AK curves. The threshold stress intensity range (AKth) was found to decrease when the material was in an NaCl environment (5 wt.% NaCl solution) in comparison with low aggressive humid environments. The humid environments consisted of a low relative humidity (55%) air atmosphere and a high relative humidity (80%) air atmosphere. These results are reproduced in Fig. 21. It is concluded, then, that the fatigue crack propagation rate is faster in a saline solution. This behavior may be classified as pure corrosion fatigue (type II), according to the classification scheme of Vasudevan and Sadananda [63]. Unfortunately, this approach was not shown for the shot-blasted specimens.

3.2. Coatings

In addition to the introduction of compressive residual stresses at the surface of metallic implants by using shot peening and laser shock peening, other surface modification methods have been extensively used to improve the fatigue performance of these components. Passivation, electropolishing, chemical oxidation and nitriding have been reported by several authors [261–263]. However, perhaps the most versatile surface modification method is based on the deposition of protective coatings on metallic implants, and involves the improvement of a variety of material properties, such as biocompatibility, fatigue strength, corrosion and wear resistance. Dealing with all the possible deposition processes and types of materials that may be employed as protective films for biomedical alloys is not within the scope of this section. Instead, we aim to discuss representative data of selected examples, including titanium alloys, austenitic stainless steels, Co–Cr–Mo and biodegradable magnesium alloys.

Even though the fatigue properties of metallic implants can be greatly altered by a coating layer, it is not uncommon that the primary goal of designing a coated orthopedic component is to increase its osteointegration capability rather than its fatigue strength [264,265]. In the same way, corrosion and wear resistances are frequently focused on because of the direct relationship between these properties and the biocompatibility of the biomedical device [266–269], while the evaluation of the fatigue behavior of the coated material is disregarded. However, several authors have recognized the importance of considering the response of coated metallic implants to cyclic loadings [270–272]. For example, Wang et al. [270] studied the effect of titanium nitride (TiN) and diamond-like carbon (DLC) coatings on the fatigue, wear and corrosion properties of AISI 316L surgical stainless steel specimens. The TiN layer was deposited using electron-beam plasma-assisted physical vapor deposition while the DLC film was produced by a plasma-assisted chemical vapor deposition (PACVD) method. Fatigue tests were performed with a ball-on-plate impact tester, as schematically shown in Fig. 22. The test does not consider the influence of corrosion on the cyclic loads applied to the coated biomedical alloy; however, it shows the superior behavior of DLC-coated specimens in comparison with TiN-coated ones. Corrosion tests were performed separately in a simulated body fluid. Both coatings significantly improved the corrosion resistance of the substrate.

The increase in fatigue strength of metallic alloys due to the presence of PVD films has been reported by other authors [46,273–276]. Recently, Puchi-Cabrera et al. [277] showed that a DLC coating deposited by magnetron sputter ion plating increased the fatigue strength of 316L stainless steel in air and in 3 wt.% NaCl solution.

Fig. 21. Fatigue crack growth curves for as-cast AM60 alloy under different environments (from Khan et al. [259]; reprinted with permission from Elsevier).

Fig. 22. Representation of the impact tester used to assess the fatigue response of TiN and DLC-coated surgical stainless steel (from Wang et al. [270]; reprinted with permission from Elsevier).
solution. Most importantly, the improvement in fatigue properties was more pronounced in the corrosive environment, as shown in Fig. 23. According to the authors, the benefit of PVD layers arise due to the combination of high mechanical strength, compressive residual stresses in the coating and good adhesion to the substrate. Other reports have demonstrated that PVD films enhance the wear and fatigue strength of Co–Cr–Mo and Ti-based biomedical alloys [278–280]. However, if the coating delaminates because of poor adhesion to the substrate, then the presence of the PVD film may reduce the fatigue strength of the coated metal instead of improving it [281].

The results of Puchi-Cabrera et al. [277] show the good performance that a thin, hard coating, such as a PVD film, can achieve against corrosion fatigue in metallic alloys. Nevertheless, it is important to bear in mind that such layers have intrinsic limitations regarding their application as protective films on load-bearing implants. These include the formation of wear debris and the intrinsic brittleness of PVD thin films [282,283]. An overview of such drawbacks and how to overcome them is given by Antunes and De Oliveira [7].

The suitability of using plasma-based technology of thin film deposition to enhance the fatigue properties of a magnesium-based alloy was investigated by Uematsu et al. [284]. This work focuses on the application of AZ80A alloy as a structural material in the aerospace and automotive industries. Biodegradable magnesium alloys are not intended for application in highly wearable parts of an orthopedic device, such as a femoral head, nevertheless, the results are important in that they evaluate the corrosion fatigue behavior of a CVD-coated metallic material. Few reports provide information on this subject. Thus, even though the work by Uematsu et al. [284] is not directly related to the biomedical area, it provides a valuable contribution to the understanding of the mechanisms involved in the corrosion fatigue of CVD-coated alloys.

Uematsu et al. evaluated the corrosion fatigue behavior of a multilayer DLC film deposited on the AZ80A alloy (of which Al, Zn and Mn are the main alloying elements) by a PACVD technique. Fatigue tests were performed in air and in distilled water using the cumulative fatigue design approach. Fatigue crack propagation was not studied. The main achievement of this work is the verification of a direct relationship between the thickness of the coating layer and the resistance to corrosion fatigue failure. The authors observed that a 3 µm single DLC layer did not enhance the corrosion fatigue strength of the magnesium alloy in distilled water, whereas a 12 µm multilayer DLC film enhanced it to nearly the same level as in air. It is thus speculated that the thickening of multilayer DLC films could completely suppress corrosion fatigue in aqueous environments. This finding may be applied to enhance the corrosion fatigue properties of biomedical metallic alloys in physiological medium. However, this approach is not found in the literature. Moreover, it is of fundamental importance in evaluating the fatigue crack growth behavior of coated implants, yet very few such studies are reported in the literature.

In an effort to enhance the wear and corrosion resistances of orthopedic devices such as femoral heads, alternative techniques to the PVD and CVD methods have been developed, focusing mainly on achieving better surface coverage (non-line-of-sight processes) and lower processing temperatures. In this regard, sol–gel, electrolytic deposition and plasma immersion ion implantation have been used to deposit ceramic-based hard films on biomedical metallic alloys [285–288]. Although some successful applications are described in the literature regarding the improvement of wear and corrosion resistances imparted by films deposited by these techniques, the corrosion fatigue behavior is often ignored, as occurs for the PVD- and CVD-coated metallic implants.

### 3.3. Surface nanocrystallization

The mechanical strength of metallic alloys can be controlled through grain refinement. The conventional way to do this is to combine plastic deformation and heat treatment. This is limited to the microcrystalline scale; however, and the dependence of the static mechanical strength on the grain size is given by the well-known Hall–Petch relationship [289,290]. Typical average grain sizes are larger than 1 µm. The fatigue limit is often increased as well as the tensile yield strength after grain refinement at the microcrystalline scale [291]. The utmost barrier to this approach is related to the development of nanocrystalline metallic materials. The basic goal is to span the microcrystalline scale and reach grain sizes smaller than 100 nm [292]. However, hardly any true bulk nanocrystalline metals have been produced due to the difficulty in producing yields that are sufficiently large to undergo the standardized mechanical tests [293]. Because of this, other processes have emerged as viable engineering alternatives to circumvent this problem. One example is

![Fig. 23. Relative increase in fatigue life as a function of maximum alternating stress for DLC-coated 316L stainless steel in air and in 3 wt.% NaCl solution (from Puchi-Cabrera et al. [277]), reprinted with permission from Elsevier).](image-url)
the production the so-called ultrafine-grained (UFG) metals with an average grain size between 100 nm and 1 μm. Today, severe plastic deformation processes, such as equal channel angular pressing (ECAP), are routinely employed to produce bulk submicron-grained metallic materials [294].

In addition to the well-known effect of severe plastic deformation on the mechanical properties of metallic materials, the biological response of a UFG alloy may also be positively affected by this structure modification. An interesting example of this was reported by Kim et al. [295]. They showed that ECAP processing enhanced the biocompatibility of a grade 2 Ti rod in comparison with a conventional Ti–6Al–4V alloy by providing greater cell proliferation and adhesion. This behavior was due to the high surface energy and the presence of nanosized grooves on the severely plastic deformed material.

Surface nanocrystallization has also arisen as a method to enhance the fatigue properties of metallic materials. The development of this was motivated by the fact that fatigue failure is very sensitive to the microstructure and properties of the material’s surface. Thus, the optimization of the surface microstructure can be effective at enhancing the performance of metallic materials under cyclic stresses [296]. Moreover, other surface-related phenomena, such as wear and corrosion, can also benefit from this approach [297]. Surface nanocrystallization can be achieved by surface mechanical attrition treatment (SMAT) or shot peening [298,299]. The fatigue properties of biomedical metallic materials have been improved by UFG and surface nanocrystallization methods. In this section the mechanisms that govern this enhancement are reviewed. Furthermore, the potential of using surface nanocrystallization to mitigate the corrosion fatigue failure of metallic implants is discussed.

Saitova et al. [300] studied the fatigue behavior of a UFG Ti–6Al–4V ELI alloy. The ultrafine structure was obtained by combining heat treatment, ECAP and conventional extrusion. Two different processing conditions were used to produce the UFG alloys: varying the heat treatment temperature and varying the number of ECAP steps. The materials yielded in the two conditions were identified as UFG1 and UFG2, respectively. The fatigue behavior of the UFG materials was compared with a conventional coarse-grained (CG) alloy through stress-controlled tests in the two conditions. The materials yielded in the two conditions were identified as UFG1 and UFG2, respectively. The fatigue behavior of the UFG materials was compared with that of a conventional coarse-grained (CG) alloy through stress-controlled tests in the high cycle fatigue regime, thus obtaining S–N curves. The results are shown in Fig. 24. The fatigue lives of the UFG specimens were significantly improved in comparison with the CG ones. The fatigue endurance limit increased by 70 MPa for both UFG conditions. The severe plastic deformation imparted by the ECAP process is responsible for the increase in the fatigue strength. The authors speculate that ECAP can be used to produce Ti–6Al–4V ELI alloy for biomedical applications. However, the influence of corrosion on the fatigue properties of the UFG materials was not assessed.

Wang et al. [301] investigated the corrosion properties of a nanocrystalline austenitic stainless steel in a 3.5 wt.% NaCl solution. A combination of shot peening and heat treatment was used to produce surface nanocrystallization. Nanocrystallization was found to decrease the anodic current density and passive current density of the treated specimens in comparison with the as-received ones. Furthermore, the surface treatment had a marked beneficial effect on the pitting corrosion resistance of the alloy. It greatly extended the passive region of the stainless steel and increased the breakdown potential of the passive film. It is hypothesized that this effect is related to an increase in the density of diffusion paths available for the migration of alloying elements and rapid formation of a protective passive film in the nanocrystalline surface material. Similar results were reported by Wang and Li [255].

Hu et al. [302] studied the corrosion behavior of a surface nanocrystalline NiTi alloy produced by SMAT. They observed that the corrosion potential of the nanocrystalline material was shifted to more positive values in comparison with the untreated alloy. Furthermore, the corrosion current density was reduced by one order of magnitude after the surface treatment. Despite the attractive indications of these reports from a corrosion standpoint, the fatigue behavior of the nanocrystalline materials was not assessed.

Roland et al. [303] investigated the fatigue behavior of a surface nanostructured 316L stainless steel subjected to SMAT. The results obtained from S–N curves showed that the fatigue strength of the nanostructured material was significantly higher than that of the untreated specimens in both the low and high cycle fatigue regimes. Using TEM analysis, the authors could distinguish a nanocrystalline surface layer and a plastically deformed sub-surface layer containing twins and high dislocation densities. The deformed sub-surface presents high compressive residual stresses, while the nanocrystalline layer at the surface accounts for an increase in mechanical strength by grain size reduction. Under these conditions, fatigue crack initiation and propagation are prevented. The authors additionally showed that a post-annealing step after SMAT can further enhance the fatigue strength of the material by increasing the surface ductility through a recovery process, without leading to grain size growth. The influence of corrosion processes on the fatigue behavior of the SMAT-processed material was not assessed.

Surface nanocrystallization of magnesium alloys has been successfully achieved by a variety of processes, such as ECAP, SMAT and high-energy shot peening [304–307]. Despite the positive effects that have been reported for the wear resistance and surface microhardness of nanocrystalline magnesium alloys, a detailed investigation of the effect of nanocrystallization on the fatigue properties of these materials is still awaited. Moreover, the corrosion behavior, whether associated with fatigue or not, has not been investigated in the literature. This is especially true for alloys specifically developed for biomedical applications, such as Mg–Ca alloys.

From the analysis of the current literature, it can be concluded that nanocrystallization may be a powerful tool for enhancing the fatigue behavior of biomedical metallic materials. Nevertheless, it is imperative to extend the scientific investigations toward a concomitant evaluation of corrosion and fatigue. Only isolated studies of each of these processes have been reported. Moreover, the fatigue crack growth behavior of nanocrystallized biomedical alloys is often ignored in the literature. This approach becomes more important if one considers that severe plastic deformation processes such as ECAP may decrease the fatigue strength of Mg.

![Fig. 24. S–N curves for Ti–6Al–4V ELI alloy in CG and UFG conditions (from Saitova et al. [300]; reprinted with permission from Elsevier).](image-url)
and Ti alloys in the low cycle fatigue regime [296]. The inferior performance of UFG and nanocrystalline metals is related to their limited ductility under cyclic deformation, which leads to early crack initiation and a greater number of grain boundaries that are favorably oriented for crack propagation. Even though this problem can be prevented by the combination of ECAP with further mechanical treatments [308,309], it is important to consider early crack initiation when designing nanocrystalline biomedical alloys. In this respect, the assessment of crack growth rate through da/dN vs. ΔK curves is of prime interest. This is evident from an analysis of the results presented in Fig. 25 [240]. The plots in this figure were obtained for microcrystalline (mc) and ultrafine-crystalline (ufc) grade 2 Ti. It is clear that the ΔKth values are lower for the ufc material. This effect may be related to the grain refinement and strain hardening of the ECAP-processed material. Consequently, dislocation mobility is limited and this inevitably results in suppression of the crack tip blunting effect (limited crack tip plasticity), leading to faster propagation of fatigue cracks. Microstructural changes due to specific alloying additions and heat treatments may alter this behavior. Systematic studies of such possibilities for different biomedical metallic materials are lacking in the literature.

4. Recommendations for future work

It is well recognized that corrosion fatigue impairs the performance of biomedical metallic alloys and is still responsible for most of the catastrophic failures of these components, despite the evolution of both material quality and design over the years. Therefore, it would be expected that the development of new materials and the enhancement of the existing ones would be driven by this issue. Indeed, there is a huge amount of information on the isolated aspects of this problem, i.e. works devoted only to corrosion or to fatigue of metallic biomaterials. Many authors have reported on the combined action of corrosion and fatigue of biomedical alloys in physiological solutions, facing the challenge of understanding the synergism between them. However, while cumulative fatigue design has received much attention, fatigue and wear processes of the orthopedic device without consideration of microstructure and surface finishing on the isolated aspects of this problem, i.e. works devoted only to corrosion or to fatigue of metallic biomaterials. Many authors have reported on the combined action of corrosion and fatigue of biomedical alloys in physiological solutions, facing the challenge of understanding the synergism between them. However, while cumulative fatigue design has received much attention, fatigue crack propagation has barely been investigated. There is hence a strong need to investigate the crack growth behavior of metallic biomaterials in corrosive physiological environments, composed not only of saline species, but also of proteins and enzymes. Studies that correlate the mechanisms of corrosion fatigue crack growth of biomedical alloys with microstructural features such as grain size, crystalline phase composition and distribution are very scarce, while experimental investigations that also include different heat treatments and mechanical processing operations are not encountered in the literature at all.

Predicting the fatigue lives of metallic biomaterials in a reliable manner will only be possible through the development of unequivocal models based on extensive experimental data. As can be inferred from the literature reviewed within this work, this research field has the potential to be greatly expanded to all the typical metallic materials used for biomedical applications.

The same scarceness of systematic investigations occurs with the methods of preventing and mitigating corrosion fatigue failure. Even for traditional techniques such as shot peening and hard thin coatings there is an insufficiency of corrosion fatigue studies. This shortcoming is still more pronounced with the most up-to-date methods, which produce UFG or surface nanocrystalline materials. More than just a fertile research field, corrosion fatigue of biomedical metallic materials is also a phenomenon that demands significant technological advancements to be fully understood and prevented.

5. Conclusions

Mechanical failure of metallic biomaterials is often related to corrosion fatigue phenomena. Pitting corrosion is often considered to be the active mechanism through which fatigue cracks initiate. The way nucleated cracks propagate depends on the surface and internal (defects, phases) characteristics of the metallic material. Microstructural aspects are closely related to the corrosion fatigue strength of biomedical alloys. This property can be significantly altered through the careful control of alloy composition and by the use of thermo-mechanical processing. The CFD approach is often used to characterize the corrosion fatigue behavior of biomedical alloys. FCP investigations through da/dN vs. ΔK curves are often ignored in many studies. This common practice yields an incomplete assessment of the corrosion fatigue behavior of metallic biomaterials as the presence of pre-existing flaws is very likely and should not be disregarded during the development of a biomedical device. The lack of investigations devoted to this approach is surprising. Moreover, the contribution of wear processes to the corrosion fatigue failure of orthopedic components such as modular total hip stems has been recognized. This poses a further difficulty to the simulation of actual in vivo conditions during laboratory tests. The complexity of this task is to simultaneously encompass corrosion, fatigue and wear processes of the orthopedic device without ignoring the influence of microstructure and surface finishing on the material response.

The most commonly used methods of preventing fatigue failure of metallic materials are based on the introduction of compressive residual stresses or on the deposition of hard thin coatings. Successful examples of these approaches have been outlined throughout the text. Protective coatings may also influence the corrosion resistance of the material, as well as processes that introduce residual stresses. The corrosion fatigue behavior of metallic alloys subjected to different surface modification methods has been studied by several authors. The CFD approach is very frequent, while the FCP approach is not. More recently, UFG or nanocrystalline alloys have emerged as promising materials for biomedical applications. Despite some valuable reports on the suitability of achieving high fatigue strength and corrosion resistance through surface nanocrystallization, the systematic study of this method as a means of improving the corrosion fatigue performance of biomedical metallic alloys is only just beginning.

Fig. 25. Crack growth rates for grade 2 Ti after ECAP process (from Hanlon et al. [289]; reprinted with permission from Elsevier).
Appendix A. Figures with essential colour discrimination

Certain figures in this article, particularly Figures 9, 16, 19 and 24, are difficult to interpret in black and white. The full colour images can be found in the on-line version, at doi: 10.1016/j.actbio.2011.09.012.

References

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