Influence of hydrogel coatings on corrosion and fatigue of iron in simulated body fluid

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Abstract
Surface corrosion and fatigue studies of pure iron were performed in a modified simulated body fluid (m-SBF) electrolyte with and without applied agar films as a typical hydrogel film. The electrochemical corrosion rates were analysed using electrochemical impedance spectroscopy. The morphology and surface chemical composition of the samples after exposure were analysed using X-ray photoelectron spectroscopy and Raman microscopy. The swelling process of the agar film was measured by in situ fourier-transform infrared spectroscopy in attenuated total reflection. The combination of the electrochemical and interface analytical approaches allowed for the estimation of the influence of an applied agar film on the corrosion processes. Moreover, the studies clearly reveal a correlation between the surface corrosion process and the fatigue life of the iron samples in m-SBF.

KEYWORDS
corrosion, hydrogel, iron, simulated body fluid

1 | INTRODUCTION

Bioresorbable implants, mostly based on polymers and metal alloys, can safely dissolve in the body within a certain period of time.1 In recent years, bioresorbable metal alloys have received increasing attention as implant materials due to their specific mechanical properties.2 Magnesium, zinc and iron alloys are currently the most studied materials due to their inherent biocompatibility.1 Among them, magnesium alloys show the highest dissolution rates.4 Zinc alloys have also been considered as potential biodegradable materials, but their low tensile strength limits their application.5,6 The mechanical properties of iron-based alloys, on the other hand, present a remarkable advantage in comparison to other metallic materials. Iron-based alloys have thus received increasing attention in recent years. However, their low degradation rate is a major concern and many studies have attempted to address this issue.7,8

To develop suitable medical materials, it is essential to consider the impact of the physiological environment on the material properties. In addition to cells and tissues, the human body contains a large amount of inorganic components such as phosphates, organic molecules such as sugars and biological polymers such as proteins, which are dissolved in various body fluids. Implants in contact with such a complex physiological environment are subject to corrosion, protein adsorption and cell adhesion.9 Therefore, it is necessary to evaluate the effects that these different components possibly exert on the implant in vitro before the implant can be tested in vivo. Simulated body fluid (SBF) is widely used in the in vitro bioactivity assessment of biomaterials because...
its ionic composition is similar to that of human plasma.\textsuperscript{[10,11]} Metal implants in SBF tend to form a CaP layer on their surface.\textsuperscript{[12,13]} For Mg alloys, the formation of this layer can effectively decelerate their corrosion rate and enhance their biocompatibility.\textsuperscript{[14-16]} However, for Fe-based alloys that already have the disadvantage of a comparatively low corrosion rate, the accumulation of corrosion products and the formation of a calcium-containing degradation layer on their surface are detrimental.\textsuperscript{[17,18]} Gebert et al.\textsuperscript{[19]} studied the corrosion behaviour of Fe-30Mn-1C in NaCl, tris-buffered saline and SBF and observed the precipitation of phosphate compounds already at an early stage of immersion. Xu et al.\textsuperscript{[20]} investigated the mechanical properties of Fe-Mn alloys as a function of the immersion time in SBF and found that their tensile strength continuously decreased over 45 days. The degradation mechanism of austenitic Fe-Mn-C-Pd alloys in SBF was studied by Schinhammer et al.\textsuperscript{[21]} They reported that the degradation rate is enhanced by the presence of Pd. However, the surface product layer consisting of hydroxides and carbonates reduced the degradation rate by limiting the diffusion of oxygen and ions to the metal surface.

Concerning the corrosive medium, hydrogel films have been discussed as an alternative to liquid electrolytes.\textsuperscript{[22-25]} Among them, the natural polymer agar is particularly promising, since it is biocompatible, biodegradable and has suitable ionic conductivity.\textsuperscript{[26]} In addition, agar forms stable gels even at low concentrations that adhere well on metal surfaces. Heyn et al. analysed the corrosion of stainless steel\textsuperscript{[27]} and zinc-coated steel substrates\textsuperscript{[28]} in contact with agar-based hydrogel electrolytes. They could show that the application of the hydrogel changes the transport kinetics and thereby typically lowers the overall corrosion reaction kinetics.\textsuperscript{[27]} However, so far, the influence of a hydrogel on the corrosion behaviour of iron alloys in contact with a physiological electrolyte has not been studied in detail.

Since implants are often subjected to cyclic mechanical loading during use, it is also important to investigate the fatigue properties of the alloys for their application as biomaterials.\textsuperscript{[29]} Since these fatigue properties can be influenced significantly by the environmental conditions such as corrosive media, it is also important to test the specimens not only in purely mechanical fatigue tests but also in combined tests involving mechanical loading under the additional influence of corrosion. In previous studies, it was shown that the fatigue properties of titanium alloys could be significantly reduced in a corrosive environment. Repeated cyclic loading breaks down the comparatively stable protective oxide layers and restarts the initial corrosion attack, which leads to a significantly reduced fatigue life.\textsuperscript{[30]}

However, corrosion fatigue of bioresorbable pure iron has rarely been studied under physiological conditions. Various studies have focused on the fatigue behaviour of pure iron under purely mechanical loading and also investigated its very high-cycle fatigue behaviour.\textsuperscript{[31]} Further investigations into the fatigue behaviour using modified microstructures by equal channel angular pressing of pure iron have shown that the fatigue lives can be significantly increased without the addition of further leaching elements.\textsuperscript{[32]}

In the present work, the influence of an applied agar film on the surface corrosion and corrosion fatigue of iron in modified simulated body fluid (m-SBF) was investigated. The corrosion properties of Fe alloys were studied using electrochemical impedance spectroscopy (EIS) in m-SBF with and without an applied agar hydrogel film. The swelling process of the agar film was measured by in situ fourier-transform infrared spectroscopy (FTIR) in attenuated total reflection (ATR). Surface characterization was carried out by field-emission scanning electron microscopy (FE-SEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) with the aim of correlating the surface composition and morphology after the corrosive attack of the corrosive environment. The fatigue tests were carried out under a rotating bending load. A total of three test series were carried out: under purely mechanical load, under mechanical load with an additional corrosion influence of m-SBF and under mechanical load with an additional corrosion influence of m-SBF with an agar hydrogel film on the specimen surface.

2 | Experimental

2.1 | Materials and chemicals

In this study, ARMCO Fe with dimensions of 15 × 15 × 3 mm was cut from a rolled stick. The specimens were electropolished with a Lectro Pol SE system. The removal height was 150 µm, so that further surface defects due to the cutting process could be excluded, analogous to the specimens for fatigue testing. The surface roughness after electropolishing is $R_a < 0.05 \mu m$ and was determined using a Keyence VK-9700K confocal microscope.

SBFs are often used to simulate the inorganic components of the physiological environment. Oyane et al.\textsuperscript{[10]} described in detail the differences between several SBFs and reported that m-SBF not only has an ion concentration similar to that of plasma but also excellent stability, which is considered to be optimum for the in vitro evaluation of biomaterials. In the present study, m-SBF was prepared according to the protocol reported by Oyane et al.\textsuperscript{[10]} The ion concentrations of m-SBF are shown in Table 1. 2-[4-(2-hydroxyethyl)-1-piperazinyl]-ethanesulphonic acid (HEPES) and a 1.0 M NaOH aqueous solution were used for buffering and to adjust the pH.
2.2 | Preparation of hydrogel films

Figure 1 shows a schematic of the preparation of the agar film. Agar films were prepared using agar powder from AppliChem GmbH. 0.25 L of distilled water was boiled in an oil bath, after which 5 g of agar powder was added. After stirring until the agar powder was fully dissolved, 5 ml of the hot agar solution was spread on a Teflon plate and left to stand at room temperature for 3 days. The thoroughly dried films were recovered from the Teflon plates and reimmersed in water for a few seconds to form transparent and malleable hydrogel films. Finally, the produced hydrogel films were applied to the iron sample. They had a film thickness of 300 μm.

2.3 | Surface and corrosion analysis

2.3.1 | Electrochemical impedance analysis

EIS measurements were performed in a three-electrode configuration using a Gamry Ref. 600 galvanostat/potentiostat (Gamry Instruments). The electropolished substrates with and without an applied agar film were used as working electrodes with an exposed area of 0.5 cm². A Ag/AgCl (sat. KCl) electrode was used as the reference electrode and a Pt platinum sheet was used as the counter electrode. The EIS measurements were performed in m-SBF at the open circuit potential (OCP) with and without the applied agar hydrogel film at 37°C for 24 h. The frequency was varied between 100 kHz and 0.1 Hz with 10 points/decade and a perturbation amplitude of ±20 mV. The OCP values were continuously recorded during these studies. The EIS spectra were analysed using Echem Analyst™ software.

2.3.2 | Scanning electron microscopy

FE-SEM was performed using a Zeiss NEON®40 Electron Microscope (Carl Zeiss SMT AG) with an SE2 and an InLens detector.

2.3.3 | Raman spectroscopy

Raman spectra were recorded using an InVia Renishaw Raman microscope (Renishaw) with a CCD detector. A YAG-Laser (532 nm), 1800 L/mm grating, was used to measure iron substrate and an NIR-Laser (785 nm), 1200 L/mm grating, was used to measure the agar film. A 50X objective was used for all measurements.

2.3.4 | XPS

The surface chemical composition was analysed using XPS. XPS was performed in an ESCA + facility (Oxford Instruments). The base pressure of the system was lower than 5.0 × 10⁻¹⁰ mbar. Spectra were measured using monochromatic Al Kα irradiation (1486.7 eV). A take-off angle of 60° with respect to the surface was chosen for all spectra. No neutralization was used. The calibration was performed using the C 1s signal (at 284.6 eV) of adventitious carbon as the internal reference.

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**TABLE 1** Ion concentrations of the used simulated body fluid (m-SBF)

| Concentration (mM) | Value  |
|--------------------|--------|
| Na⁺                | 142.0  |
| K⁺                 | 5.0    |
| Mg²⁺               | 1.5    |
| Ca²⁺               | 2.5    |
| Cl⁻                | 103.0  |
| HCO₃⁻              | 10.0   |
| HPO₄²⁻              | 1.0    |
| SO₄²⁻              | 0.5    |

Abbreviation: m-SBF, modified simulated body fluid.
2.3.5 | Attenuated total reflection FTIR spectroscopy (ATR-FTIR)

The in situ FTIR cell for attenuated total reflection studies (ATR-FTIR) was mounted on an attachment for ATR measurements (IRUBIS) within the sample compartment of a Bruker Vertex 70v FTIR spectrometer, equipped with a narrow-band MCT detector. Spectra were recorded at room temperature at a resolution of 4 cm\(^{-1}\) and 128 scans were co-added. The bare Si crystal served as the reference. The agar film was applied to the Si-ATR crystal in the same way as for the iron samples. Spectra of the agar film were recorded before and after exposure to m-SBF.

2.4 | Fatigue studies

For the investigations of the fatigue life, rotating bending tests (stress ratio \(R = -1\)) were carried out on a Zwick/Roell 200tC rotating bending machine. The set-up was extended by a chamber in which the m-SBF was added by continuously dripping onto the specimen during the test run. The flow rate of the m-SBF was 150 ml/h; the specimen was constantly wetted with the m-SBF during the test. The rotational speed during the test was \(n = 1000\) min\(^{-1}\), which resulted in a test frequency of \(f = 16.7\) Hz. The limiting load cycle number was set to \(N_{\text{D}} = 5 \times 10^6\) cycles; this led to a maximum test duration of 83.3 h until the endurance strength was reached. The tests were performed in a force-controlled mode. The resulting loads were calculated assuming linear elastic material behaviour according to the following equation:

\[
\frac{\Delta \sigma}{2} = 32 \cdot M \cdot \pi \cdot \frac{d^3}{d^3}.
\]  

(1)

The specimen diameter is given by \(d\), and the bending moment is given by \(M\). The assumption of a linear elastic material behaviour results in an increased estimation of stresses above the actual tensile strength of the material, which is about \(R_m = 250\) MPa. Stresses above the tensile strength are released by plastic flow at the beginning of the test. The same test set-up was used in Torrent et al. for the mechanical fatigue testing of pure iron manufactured by electron beam melting.[33]

The specimens for fatigue testing were designed according to DIN 50113. The specimen geometry is shown in Figure 2. The surfaces were electropolished before starting the tests. For electropolishing, the fatigue specimens were anodically contacted with a current density of \(1\) A/cm\(^2\) at a voltage of 35 V. The fatigue specimen was thereby set as the anode. The electrolytic polishing was carried out using a custom set-up, which circulates the electrolyte and at the same time rotates the specimens during the polishing process to ensure uniform removal. The polishing time was 270 s, at an electrolyte temperature of 0°C. The electrolyte used was ATM© K1 part A + B based on perchloric acid. The polishing resulted in roughness values of an average of \(R_s = 0.07\) \(\mu\)m determined by confocal microscopy. The amount of material removed during polishing was about 150 \(\mu\)m, so that no further surface defects or influence on the microstructure are to be expected from preceding steps of the sample manufacturing. For the investigations with an additional hydrogel layer, the layer was applied as a film to the measuring length of the specimen by additionally attaching adhesive strips to the edges. The hydrogel was then allowed to swell briefly. The thickness of the hydrogel layer at the start of the fatigue tests was then approx. 300 \(\mu\)m.

3 | RESULTS AND DISCUSSION

3.1 | Electrochemical corrosion analysis

For the corrosion test, EIS data of iron samples were continuously measured with and without the applied agar hydrogel film for an immersion time of 24 h in m-SBF at OCP. Figure 3a,b shows the impedance spectra obtained for samples with and without agar films at different times. The Bode plots show only one time constant for both samples. In the high-frequency region (\(10^2-10^7\) Hz), the impedance is almost independent of the frequency and can be used to describe the electrolyte resistance (\(R_{\text{ely}}\)). In the low-frequency region, the two samples showed capacitive behaviour at the initial stage of immersion. With increasing immersion time, the low-frequency impedance values decreased in both cases due to the onset of corrosion. According to the measured values at 0.1 Hz, the corrosion rate was higher for the agar-coated surface.

Figure 3c,d shows the development of OCP values and impedance values at 0.1 Hz with incubation time, respectively. The transients of the free corrosion potential and the low-frequency impedance values of the iron
sample in m-SBF show a certain incubation period of about 3 h. Interestingly, the required time for initiating corrosion with the applied agar film is slightly shorter than for the noncoated iron substrate, which indicates fast electrolyte transport through the agar film. Both the measured free corrosion potentials and the impedance values at 0.1 Hz indicate faster corrosion attack for the agar film-coated substrate during the first 3 h of immersion. However, for extended durations of immersion, the free corrosion potentials and impedance values at 0.1 Hz are similar for both samples (Figure 3c,d), indicating that the applied agar film does not lead to any preferential inhibition of anodic or cathodic reactions.

The equivalent electrical circuit (EEC) in Figure 4 was used to analyse the EIS data. The nonideal capacitive behaviour was described by the constant phase element (CPE) in the model EEC. $R_S$ represents the electrolyte resistance. $CPE_{dl}$ and $R_{ct}$ are the capacitive and resistive elements of the electrolyte/metal interface, respectively. $CPE_{film}$ and $R_p$ are the capacitive and resistive elements of the surface film, respectively. The surface film is either the formed corrosion product layer on the base iron substrate or the combination of the agar film and the formed corrosion product layer in the case of the agar-coated substrate. The simulated equivalent circuit parameters for iron with and without an agar hydrogel film at different immersion times in the m-SBF solution are presented in Table 2.

The presence of the hydrogel film leads to a higher electrolyte resistance. In agreement with Figure 3, the $R_{ct}$ values indicate slightly higher corrosion current densities in comparison to the film without an applied agar film.

### 3.2 ATR-FTIR spectroscopy of electrolyte uptake in hydrogel films

For an improved understanding of the transport properties of the agar film, in situ FTIR-ATR studies were performed. The agar film was applied to a Si-ATR crystal in the same way as for the iron samples. Figure 5 shows the absorption spectrum of the agar film.
The characteristic bands of agar are consistent with those reported in the literature. The adsorption bands of agar at around 3230 and 2890 cm\(^{-1}\) are attributed to the stretching vibrations of \(-\text{OH}\) and \(-\text{CH}\), respectively.\(^{[34]}\) The band at about 1635 cm\(^{-1}\) is assigned to the stretching mode of \(-\text{C}=\text{O}\) and also the absorption band of H\(_2\text{O}\).\(^{[35]}\) The peaks between 880 and 1150 cm\(^{-1}\) are typical vibrations of the 3,6-anhydro-galactose networks.\(^{[34]}\)

The difference spectra after the exposure of the agar film to m-SBF are shown in Figure 5. Positive absorption bands were observed only in the \(-\text{OH}\) stretching and the H\(_2\text{O}\) absorption region. It is known that agar can reach 160\% swelling at room temperature within 12 h.\(^{[36]}\) The difference spectra indicate that the m-SBF electrolyte rapidly penetrates the agar film and does not influence the incubation time. It is assumed that the applied agar film not only acts as a barrier but also that the interfacial interaction with the oxide influences the stability of the passive film.

### 3.3 Interface characterization after exposure to m-SBF

After immersion in m-SBF over 24 h, both samples were analysed using microscopic and spectroscopic techniques. The agar film was peeled off the substrate before this characterization. Samples without agar films were just rinsed with pure water and blown dry with nitrogen to remove loosely bound corrosion products. For comparison, the removed agar film was analysed in terms of its interface to the iron sample and the interface to the m-SBF.

The FE-SEM images of the corroded samples with and without an agar film are shown in Figure 6. Obviously, the iron sample with an applied agar film shows significantly fewer corrosion products in comparison to...
the iron surface that was in direct contact with m-SBF. However, as shown in Figure 6, corrosion products formed at the interface between the agar film and iron were partly transferred to the underside of the agar film.

The thick layer of corrosion products on the surface of the sample directly exposed to the m-SBF was, however, only weakly binding to the iron surface and could be easily washed off. The resulting surface (see Figure 6c) rather resembles that already shown in Figure 6a. This means that the corrosion product layer formation is not completely inhibited by the agar film, but the transfer of released ions into the adhering agar film prevents the formation of thicker oxide scales at the iron interface. This assumption is supported by the FE-SEM image of the outer surface of the agar film (see Figure 6d), which indicates the formation of insoluble corrosion products.

Microscopic images and Raman spectra on different sites of both samples are shown in Figure 7. The observed Raman bands and assignments are listed in Table 3. Raman measurements of the different areas confirmed

**FIGURE 6** Field-emission scanning electron microscopy (FE-SEM) images of an iron substrate and agar film surfaces: iron substrate after immersion in modified simulated body fluid (m-SBF) for 24 h with (a) and without (b) an applied agar hydrogel film; FE-SEM image of the iron sample shown in (b) after mechanical removal of the corrosion product layer (c); FE-SEM images of the agar film after removal from the corroded iron sample (m-SBF/agar interface to the electrolyte (d), and agar/Fe interface to iron (e) of the agar film. The corresponding high-resolution images are shown on the right (*). m-SBF, modified simulated body fluid.
the assumption that the agar film mainly influenced the distribution and amount of formed corrosion products. The chemical composition, however, remained rather unaffected. In both cases, the Raman peaks of the surface layer were assigned to a mixture of haematite, magnetite, and maghemite.\cite{37,38} In addition, signals of phosphate at around 1040 cm$^{-1}$ were detected on the surface of samples with and without agar hydrogel.\cite{39} The signal of phosphate was prominent for the samples without applied agar films.

Raman spectroscopic analysis of the agar film as shown in Figure 8 supports the interpretation of the FE-SEM results as peaks that can be assigned to iron oxides and more specifically to $\alpha$-FeOOH (388/410 cm$^{-1}$),\cite{38} and phosphates (about 1005 cm$^{-1}$)\cite{39} were mainly observed on the outer surface of the agar film.

XPS was performed for further characterization of the interface chemistry of the iron samples after exposure to m-SBF. Table 4 shows the calculated atomic concentration for the m-SBF/Fe and the m-SBF/hydrogel/Fe interface, that is, the corroded surface with and without an agar film, respectively. The just polished iron surface was used as a reference. The surface layer compositions indicate that residues of agar remained on the Fe surface after the removal of the film. This conclusion is mainly based on the C1s contribution for the m-SBF/agar/Fe sample measured on the iron interface and the FTIR data of the corresponding surfaces shown in the SI (Figure S3). The samples in direct contact with m-SBF formed a phosphate-rich layer of corrosion products on the surface (see Table 4). Interestingly, higher iron concentrations were detected on the outer surface of the agar film (m-SBF/agar) compared to the inner surface in contact with the iron (agar/Fe). In addition, the phosphate concentration at the agar interface was measured to be higher in the case of the m-SBF/agar interface. Both results are in excellent agreement with FE-SEM and Raman data shown in Figures 6d and 7a. It can be assumed that iron ions can diffuse through the

![Figure 7](https://wileyonlinelibrary.com)
agar film, while the oxidic iron species or phosphates formed remain on the surface of the agar film.

### 3.4 Fatigue measurements

Figure 9 shows the results of the fatigue tests. The results for the fatigue tests without corrosive influence on pure Fe are taken from comparable investigations by Bruder. In addition, reference tests were carried out as part of this study; the results for mechanical fatigue testing of the pure Fe have already been shown partly in Torrent et al.

The fatigue tests under purely mechanical loading show at \( \sigma_f = 225 \text{ MPa} \) a runner through for a limit load cycle number of \( N_D = 5 \times 10^6 \) cycles. For the fatigue tests under the additional influence of m-SBF, an influence on the fatigue strength could be shown already after a test duration of several minutes. On average, the fatigue strength is about 75 MPa lower under the influence of m-SBF.

#### Table 3: Raman data of iron with and without agar after 24 h exposure to m-SBF as measured on the iron substrate surface

| Raman shift (cm\(^{-1}\)) | With applied agar film | Bare iron | Assignment\(^{[37-39]}\) |
|---------------------------|------------------------|-----------|----------------------|
| With agar film            |                        |           |                      |
|                           | I                      | II        | III                  | IV                   |
|                           | 246                    | -         | -                    | Haematite            |
|                           | -                      | -         | 269                  | Magnetite            |
|                           | 303                    | -         | -                    | Haematite            |
|                           | 347                    | 355       | -                    | Maghemite            |
|                           | 376                    | -         | 468                  | Haematite            |
|                           | -                      | 620       | Haematite            |
|                           | 663                    | 663       | -                    | Magnetite            |
|                           | 1048                   | -         | 1031                 | Phosphates/apatite   |
|                           | 1316                   | -         | 1380                 | Haematite            |
|                           | 1380                   | -         | 1385                 | Maghemite            |

Abbreviation: m-SBF, modified simulated body fluid.

#### Table 4: Surface elemental composition (at.%) of the relevant interfaces determined by XPS after 24 h immersion in m-SBF

| Interface                                      | Atomic percentages (at.%) |
|------------------------------------------------|---------------------------|
| Iron substrate surfaces                        | O1s  | C1s  | Fe2p | N1s  | Ca2p | P2p  | Na1s  | S2p  | Si2p |
| Polished Fe                                    | 49.5 | 32.9 | 15.0 | 2.6  | -    | -    | -     | -    | -    |
| Corrosion product layer m-SBF/Fe               | 55.2 | 19.4 | 3.6  | 1.1  | 6.3  | 13.9 | 0.5   | -    | -    |
| m-SBF/Fe after removal of the corrosion product layer | 48.2 | 35.1 | 14.7 | 0.7  | -    | 13.9 | 0.5   | -    | -    |
| m-SBF/agar/Fe after removal of the agar film   | 48.4 | 42.0 | 8.8  | 0.8  | -    | -    | -     | -    | -    |
| Interfaces of the agar film                     | O1s  | C1s  | Fe2p | N1s  | Ca2p | P2p  | Na1s  | S2p  | Si2p |
| m-SBF/agar interface to the electrolyte        | 42.6 | 45.6 | 2.0  | 1.4  | 2.3  | 4.9  | 0.5   | -    | 0.7  |
| Agar/Fe interface to iron                      | 32.7 | 62.2 | 0.5  | 1.4  | 0.7  | 1.3  | 0.4   | -    | 0.8  |

Abbreviations: m-SBF, modified simulated body fluid; XPS, X-ray photoelectron spectroscopy.
m-SBF compared to the purely mechanical load. A runner through was determined at $\sigma_f = 150$ MPa. Overall, the measured values under additional corrosion influence are subject to a relatively high scatter. The fatigue tests under the influence of m-SBF with the additional agar hydrogel film also show a lower fatigue strength after a short test period. On average, this is about 75 MPa lower than under purely mechanical loading. For $\sigma_f = 200$ MPa, a runner through was determined.

A general correlation between the corrosion behaviour and the fatigue behaviour has already been demonstrated in various studies.[40,41] In each case, it was shown that the fatigue properties are significantly lower in corrosive media, which can be explained by localized corrosion processes resulting in local defects that can initiate crack formation and promote crack growth.[42,43]

In summary, it was shown that the influence of corrosion has a significant impact on fatigue strength. Overall, the values are subject to relatively high scatter, presumably due to the locally varying corrosion rates and the associated crack lengths that ultimately lead to failure of the specimen. In addition, it was shown that the additional application of hydrogel leads to a slight increase in fatigue strength.

4 | CONCLUSIONS

Surface corrosion studies indicate that the applied agar films prevent the formation of corrosion product layers at the electrolyte/iron interface. While the interfacial corrosion kinetics at extended times of immersion are not significantly affected by the agar film as measured by EIS, the fatigue tests showed a slight increase in the fatigue strength. Combined Raman, XPS and FE-SEM data show that the applied agar film leads to the transport of released metal ions into the swollen hydrogel film. This process leads to the formation of phosphates and iron oxides within the hydrogel film and at the electrolyte/agar interface.

The influence of the agar film on the fatigue strength under corrosive conditions indicates that the prevention of the extended corrosion product layer formation in the case of the agar-coated iron sample leads to a decrease of crack nucleation probability during fatigue testing. The comparison of the EIS studies and in situ FTIR measurements indeed showed that the kinetics of electrolyte transport in the agar film is very fast, which promotes the transfer of dissolved iron into the agar film. Overall, the studies show that the application of agar as a hydrogel film on alloy surfaces for the study of corrosion in physiological electrolytes may affect the interfacial reaction and the formation of interfacial corrosion products. This influence is based on both the macromolecular adsorption and the transfer of dissolved metal ions into the hydrogel film. The development of the surface corrosion products in turn affects the fatigue strength.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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REFERENCES

[1] R. Waksman, J. Interv. Cardiol. 2006, 19, 414.
[2] Y. F. Zheng, X. N. Gu, F. Witte, Mater. Sci. Eng., R 2014, 77, 1.
[3] Y. Li, J. Yan, W. Zhou, P. Xiong, P. Wang, W. Yuan, Y. Zheng, Y. Cheng, Bioact. Mater. 2019, 4, 114.
[4] J. Bennett, Q. de Hemptinne, K. McCutcheon, Expert Rev. Med. Devices 2019, 16, 757.
[5] X. Liu, J. Sun, Y. Yang, F. Zhou, Z. Pu, L. Li, Y. Zheng, Mater. Lett. 2016, 162, 242.
[6] P. K. Bowen, J. Drelich, J. Goldman, Adv. Mater. 2013, 25, 2577.
[7] J. Čapek, J. Kubásek, D. Vojtěch, E. Jablonská, J. Lipov, T. Ruml, Mater. Sci. Eng., C 2016, 58, 900.
[8] P. Liu, D. Zhang, Y. Dai, J. Lin, Y. Li, C. Wen, Acta Biomater. 2020, 114, 485.
[9] V. Wagener, A. Schilling, A. Mainka, D. Hennig, R. Gerum, M.-L. Kelch, S. Keim, B. Fabry, S. Virtanen, ACS Appl. Mater. Interfaces 2016, 8, 11998.
[10] A. Oyane, H.-M. Kim, T. Furuya, T. Kokubo, T. Miyazaki, T. Nakamura, J. Biomed. Mater. Res., Part A 2003, 65, 188.
[11] T. Kokubo, H. Takadama, Biomaterials 2006, 27, 2907.
[12] Y. Chen, S. Zhang, J. Li, Y. Song, C. Zhao, X. Zhang, Mater. Lett. 2010, 64, 1996.
[13] F. Barrère, P. Layrolle, C. A. van Blitterswijk, K. de Groot, MRS Online Proc. Libr. 1999, 599.
[14] S. Keim, J. G. Brunner, F. Fabry, S. Virtanen, J. Biomed. Mater. Res., Part B 2011, 96, 84.
[15] J. G. Acheson, S. McKillop, P. Lemoine, A. R. Boyd, B. J. Meenan, Materialia 2019, 6, 100291.
[16] S. Jiang, S. Cai, Y. Lin, X. Bao, R. Ling, D. Xie, J. Sun, J. Wei, G. Xu, J. Alloys Compd. 2019, 793, 202.
[17] T. Kraus, F. Moszner, S. Fischerauer, M. Fiedler, E. Martinelli, J. Eichler, F. Witte, E. Willbold, M. Schinhammer, M. Meischel, P. J. Uggowitzer, J. F. Löfler, A. Weinberg, Acta Biomater. 2014, 10, 3346.
[18] W.-J. Lin, D.-Y. Zhang, G. Zhang, H.-T. Sun, H.-P. Qi, L.-P. Chen, Z.-Q. Liu, R.-L. Gao, W. Zheng, Mater. Des. 2016, 91, 72.
[19] A. Gebert, F. Kochta, A. Voß, S. Oswald, M. Fernandez-Barcia, U. Kühn, J. Hufenbach, Mater. Corros. 2018, 69, 167.
[20] Z. Xu, M. Hodgson, P. Cao, Metals 2016, 6, 309.
[21] M. Schinhammer, P. Steiger, F. Moszner, J. F. Löffler, P. J. Uggowitzer, Mater. Sci. Eng., C 2013, 33, 1882.
[22] T. M. Di Palma, F. Migliardini, D. Caputo, P. Corbo, Carbohydr. Polym. 2017, 157, 122.
[23] F. Di Turo, P. Matricardi, C. Di Meo, F. Mazzei, G. Favero, D. Zane, J. Cult. Herit. 2019, 37, 113.
[24] W. G. Moon, G.-P. Kim, M. Lee, H. D. Song, J. Yi, ACS Appl. Mater. Interfaces 2015, 7, 3503.
[25] B. Ramírez Barat, E. Cano, ChemElectroChem 2019, 6, 2553.
[26] H. Ueno, Y. Endo, Y. Kaburagi, M. Kaneko, J. Electroanal. Chem. 2004, 570, 95.
[27] A. Heyn, IOP Conf. Ser.: Mater. Sci. Eng. 2020, 882, 12010.
[28] M. Babutzka, A. Heyn, IOP Conf. Ser.: Mater. Sci. Eng. 2017, 181, 12021.
[29] M. Niinomi, J. Mech. Behav. Biomed. Mater. 2008, 1, 30.
[30] C. Fleck, D. Eifler, Int. J. Fatigue 2010, 32, 929.
[31] A. Vshivkov, A. Prokhorov, S. Uvarov, O. Plekhov, Mech. Adv. Mater. Mod. Process. 2016, 2, 2.
[32] E. Bruder, Metals 2018, 8, 191.
[33] C. J. J. Torrent, S. Wackenrohr, J. Richter, C. E. Sobrero, S. Degener, P. Krooß, H. J. Maier, T. Niendorf, Adv. Eng. Mater. 2021, 23, 2100018.
[34] E. A. El-hefian, M. M. Nasef, A. H. Yahaya, E-J. Chem. 2012, 9, 1431.
[35] T. Lpez, M. Picquart, G. Aguirre, G. Arriola, Y. Freile, D. H. Aguilar, P. Quintana, J. J. Alvarado-Gil, F. M. Vargas-Luna, Int. J. Thermophys. 2004, 25, 1483.
[36] M. Mahmoud Nasef, E. A. El-hefian, S. Saalah, A. H. Yahaya, E-J. Chem. 2011, 8, S409.
[37] D. L. A. de Faria, S. Venâncio Silva, M. T. de Oliveira, J. Raman Spectrosc. 1997, 28, 873.
[38] A. P. Kozlova, S. Sugiyama, A. I. Kozlov, K. Asakura, Y. Iwasawa, J. Catal. 1998, 176, 426.
[39] K. Zaghib, C. M. Julien, J. Power Sources 2005, 142, 279.
[40] X. N. Gu, W. R. Zhou, Y. F. Zheng, Y. Cheng, S. C. Wei, S. P. Zhong, T. F. Xi, L. J. Chen, Acta Biomater. 2010, 6, 4605.
[41] P. S. Pao, S. J. Gill, C. R. Feng, K. K. Sankaran, Scr. Mater. 2001, 45, 605.
[42] K. Sadananda, A. K. Vasudevan, Int. J. Fatigue 2003, 25, 899.
[43] R. Jones, Fatigue Fract. Eng. Mater. Struct. 2014, 37, 463.

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