Full length article

Controlling the dissolution of iron through the development of nanostructured Fe-Mg for biomedical applications

Muhammad Mudasser Khan a, Kashif Mairaj Deen b, Ishraq Shabib a,c, Edouard Asselin b, Waseem Haider a,c,∗

a School of Engineering and Technology, Central Michigan University, Mount Pleasant, MI, United States of America
b Department of Materials Engineering, The University of British Columbia, Vancouver, V6T 1Z4 Canada
c Science of Advanced Materials, Central Michigan University, Mount Pleasant, MI, United States of America

ABSTRACT

In the field of biodegradable metallic materials, rapid and non-uniform biodegradation, caused by uncontrolled corrosion rates, is a potential shortcoming. Among the prominent biodegradable materials, magnesium is an attractive choice, however, it is prone to rapid dissolution. In contrast, iron possesses a slow dissolution rate. To approach the middle ground, instead of making magnesium more corrosion-resistant, the less-explored approach of making iron less corrosion-resistant is employed here. In this study, iron, and magnesium, having contrasting corrosion rates, are combined via magnetron co-sputtering. The idea of combinatorial synthesis is employed to fabricate two model nanostructured Fe–Mg samples, i.e. CSFM-1 (Fe58Mg42), and CSFM-2 (Fe56Mg44), exhibiting a controlled and uniform degradation in phosphate-buffer saline solution. The structural characterization of the two samples demonstrates a substitutional solid solution of bcc-Fe–Mg in CSFM-1 and an amorphous short-range-ordered structure in the CSFM-2 sample. Electrochemical investigation shows increased corrosion rates for the two Fe–Mg samples in comparison to pure Fe, validated by relatively active corrosion potentials, higher corrosion current densities, faster anodic dissolution, and lower charge transfer resistances, governed by chemical composition and non-equilibrium nanostructures. Finally, nano-indentation testing of the two samples reveals relatively higher hardness and lower elastic moduli, a suitable combination for bio-implants.

Statement of Significance

The use of Mg as a biodegradable in-vivo implant material is problematic because of its high dissolution rate and potential for hydrogen gas generation. This is the first time that the idea of combinatorial synthesis is employed to fabricate two model nanostructured Fe–Mg systems, i.e. CSFM-1 (Fe58Mg42), and CSFM-2 (Fe56Mg44), exhibiting a controlled and uniform degradation. The structural characterization of the two systems demonstrates a substitutional solid solution of bcc-Fe–Mg in CSFM-1 and an amorphous short-range-ordered structure in the CSFM-2 system. Electrochemical investigation shows increased biodegradation rates for the two Fe–Mg systems in comparison to pure Fe, validated by relatively active corrosion potentials, higher corrosion current densities, faster anodic dissolution, and lower charge transfer resistances, governed by chemical composition and non-equilibrium nanostructures.

© 2020 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Biodegradable materials are emerging as a new class of biomaterials for a multitude of applications including osteosynthesis devices [1–3], cardiovascular stents [4,5] transient bioelectronics [6–9] and programmable drug delivery applications [10,11]. The main purpose of a biodegradable material is to perform its intended function for a specific period as well as safely degrade in vivo, thereby ruling out post-implantation surgery and any resulting complications.

Among biodegradable metallic materials, magnesium (Mg), which is the fourth most abundant cation in the human body [12], has been trending in research studies [5,13,14]. It possesses
excellent biocompatibility properties, a relatively higher recommended daily intake [15] as well as low mass density and an elastic modulus approaching that of human bone [16]. Mg and its alloys have been clinically applied [17,18], however, there are certain potential shortcomings regarding in vivo biodegradation, notably the high degradation rate and substantial evolution of hydrogen gas. Rapid degradation can adversely affect the mechanical integrity of biomimics as demonstrated by Zhang et al. [19] wherein the bending strength of Mg-Zn dropped to 390 MPa from 625 MPa after the mass loss of only 6 wt.%. The inhomogeneous and rapid degradation results in local stress concentrations leading to premature mechanical failure [4]. Additionally, Mg possesses limited ductility [20,21], and low mechanical strength [22,23].

To address the aforementioned issues, three approaches have been reported, namely, alloy development [4,24,25], surface engineering [26,27], and metallic glass development [28,29]. Among these approaches, metallic glasses have been partially successful in resolving the potential issues of rapid biodegradation, poor mechanical strength, and hydrogen evolution because of their homogeneous, grain-boundary-free, microstructure, and compositional flexibility that allows the addition of beneficial species without thermodynamical constraints. Nonetheless, each approach faces some challenges that are, consequently, impeding the clinical success of Mg-based biodegradable systems for transient implantable medical devices [24,25].

In parallel to extensive research towards addressing the issues associated with Mg, the scientific community is also exploring other possibilities: for instance, Ca-based [28,30], Zn-based [31,32], and Fe-based [1,3–35] biodegradable alloy systems. Among these less-explored candidate materials, iron-based alloy systems are intriguing. Iron (Fe) is an essential nutrient element in the human body that plays a vital role in a multitude of biochemical reactions, e.g. induction and transportation of oxygen, electron transfer and catalysis [36]. Additionally, Fe possesses good mechanical properties and is biocompatible [37–39]. However, the main obstacle in its clinical success is its slow rate of biodegradation [40,41], – a characteristic exactly opposite to Mg.

To address the issue of slow dissolution of Fe, two approaches have been attempted, i.e. alloy development [1,33–35] and surface engineering [36,41–43]. In alloy development, the degradation rate of Fe can be increased via the addition of species that are either more or less noble than Fe [34]. In the case of alloying with more-noble species, (Pd, Pt [43] for instance), Fe is preferentially leached out due to the formation of galvanic cells at the micro/nanoscale. In the case of alloying with less-noble species (Mn [44] for instance), the corrosion potential of the sample can be negatively shifted and the overall degradation rate of the matrix can be accelerated. Schinhammer et al. [34] have explored a Fe-Mn-Pd, having one order of magnitude higher degradation rate than pure Fe, which was attributed to the combined role of Mn and Pd. Surface engineering has also been adopted to raise the dissolution rate of Fe. For example, patterning of Fe with arrays of Pt discs [36] has been reported to accelerate the degradation of Fe via galvanic corrosion. Similarly, micro-patterning of Fe with arrays of Au discs has resulted in faster degradation in comparison to uncoated Fe [40]. Among the aforementioned strategies, alloy development, though it successfully elevates the dissolution rate of Fe, may also introduce non-biodegradable and/or non-biocompatible species into the alloy system. Furthermore, it faces limitations in the form of solid solubility limits of alloying elements as well as the human body’s tolerance to the added species [34]. Surface engineering, on the other hand, may not ensure uniformity of the degradation rate across the bulk material.

Despite the rise of biodegradable materials, the main impediment in their clinical implementation is the lack of a tailor-made material having the appropriate blend of physical, mechanical, and electrochemical properties. For instance, for many biomedical applications that necessitate biodegradable alloy systems, the material must be biocompatible, provide sufficient mechanical strength and, most importantly, safely dissolve in a uniform and controlled manner over the intended service life. To achieve such multi-property requirements, there is a need for a robust technique to efficiently fabricate and screen out alloy systems having a combination of requisite characteristics from a wider compositional space by circumventing the thermodynamics constraints. Combinatorial fabrication via co-sputtering is one such technique to identify novel alloy systems [45–47] having a blend of appropriate properties, even from species that are immiscible under equilibrium conditions [48–50].

Fe and Mg, possessing contrasting dissolution kinetics, are, under equilibrium conditions, immiscible in the solid and liquid state with a positive enthalpy of mixing (+18 kJ/mol). According to the thermodynamic phase diagram, Mg possesses very limited solubility in Fe in the crystalline state. This rules out the possibility of using conventional fabrication methods to develop Fe-Mg alloys under equilibrium conditions. Among the non-equilibrium methods, Berziou et al. [51], for instance, have employed co-sputtering of Fe and Mg to fabricate Fe-Mg samples for prospective applications as sacrificial coatings in the protection of steel structures. Other non-equilibrium methods have also been adopted to fabricate Fe-Mg samples; for example mechanical alloying [52,53], ion implantation [54,55], and thermal co-evaporation [56]. These studies are mainly focused on the immiscibility of Fe and Mg and microstructural characterization. To our knowledge, there has been no study conducted with a view to in-vitro use of Fe-Mg samples in transient implantable medical devices. In this paper, combinatorial magnetron co-sputtering is employed to synthesize two fully biodegradable nanostructured Fe-Mg samples, exhibiting controlled and uniform dissolution rates in phosphate-buffer saline solution. The microstructural, electrochemical, morphological, and mechanical characteristics of the co-sputtered samples, in comparison to pure iron, are discussed in detail in light of prospective applications for transient implantable medical devices [9,57].

2. Experimental procedure

2.1. Magnetron sputtering

Fe (99.99%) and Mg (99.95%) sputtering targets from the Kurt J. Lesker Company were individually sputtered as well as co-sputtered using a magnetron Sputterer (Nano-36, Kurt J. Lesker Company) to develop thin films on 2-inch diameter silicon wafers (100) (universitywafers.com). Instead of glass slides, the thin films were deposited on the silicon wafers owing to their appreciable electrical conductivity as necessary for the electrochemical testing. The silicon wafers were mounted on a rotating disk (20 rpm) to ensure deposition uniformity. The sputtering chamber was first evacuated to a base pressure of 1 × 10⁻⁶ Torr and then filled with high purity Argon maintaining a working pressure of 8 × 10⁻³ Torr. DC and RF guns, employed for Fe and Mg, respectively, were operated at different power levels to develop different samples. Prior to sputter deposition, target conditioning was carried out via a 5-min pre-sputtering, to remove the airborne surface oxides present on both Fe and Mg targets. The pre-sputtering was carried out in a closed-shutter configuration to constrain the plasma and let the deposition occur on the inside of a shutter cap. Following target conditioning, the deposition was carried out on the silicon wafers. A DektakXT stylus profiler (Bruker) was used to calculate the film thicknesses of the co-sputtered samples. The sample(s)
designations, experimental conditions used to develop Fe, Mg, and co-sputtered Fe-Mg (abbreviated as CSFM-1 & CSFM-2) samples and film thickness are given in Table 1. It can be noticed that the thickness of the specific composition film depends on the sputtering parameters. The sputtering conditions were optimized to control the uniform film composition; however, the thickness of the sputtered film can be effectively controlled by varying DC and RF power. The chemical composition of these samples was also determined via EDX at different spots and the average values are reported with a variation of ±2% in the nominal composition.

2.2. Grazing-incidence x-ray diffraction

Grazing-Incidence X-Ray Diffraction (GI-XRD) was conducted using a Rigaku SmartLab Multipurpose Diffractometer that utilizes the parallel beam optics for in-plane grazing incidence X-ray diffraction analysis. The diffractometer was equipped with 1.54 Å Cu Kα radiation source and Ge-220 2-bounce monochromator. GI-XRD was done in a grazing incidence 2θ-ω mode, using a scan rate of 1°/min. ω’ is set at 1° to avoid interference from the silicon substrate by minimizing the X-Ray penetration depth. The diffraction patterns were processed via Fourier Transformation and interpreted using PANalytical X’Pert HighScore.

2.3. High-resolution transmission electron microscopy

Aberration-corrected High-Resolution Transmission Electron Microscopy (Cs-corrected HR-TEM) was carried out using a JEM 3100HR with double aberration correctors operated at 300 kV acceleration voltage, in a scanning transmission electron microscopy (STEM) mode. The lens settings were set to define a probe size of ~1.5 Å. High-resolution imaging and selected-area-electron-diffraction (SAED) were conducted to reveal the atomic-scale structure of the two co-sputtered samples. High-resolution images were taken using a Gatan Ultrascan 1000 CCD TV camera. Specimens for HR-TEM were made via a focus ion beam (FIB) in-situ lift-out method (FEI Helios FIB/SEM system) to prepare a cross-sectional view of the specimens. The high-resolution images were further processed using Fast Fourier Transformation (via Gatan Microscopy Suite).

2.4. Electrochemical characterization

The electrochemical testing was carried out in a three-electrode-cell connected to a potentiostat (Reference 1000, Gamry Instruments). Saturated Calomel Electrode (SCE, +0.240 V vs SHE) and graphite were used as reference and counter electrode, respectively, while the sputtered samples were used as working electrodes. A special paint cell (PTC-Gamry Instruments) [58] was used for the electrochemical testing of the thin-film samples. In this cell, the film was covered by a masking tape (Gamry Instruments) leaving a 1cm² round area exposed to the electrolyte. Beneath one end of the mask, the copper tape was placed on the film for electrical connection. The working electrode (sputtered samples) was exposed to Phosphate Buffered Saline solution (PBS, Thermofisher Scientific, pH 7.4 ± 0.1 at 25 °C) for 1 h to achieve a relatively stable open circuit potential (OCP, potential variation ± 0.1 mV/min) prior to potentiodynamic polarization. Potentiodynamic polarization scans were obtained in PBS solution within a ± 0.3 V potential range (versus OCP) using a sweep rate of 1 mV/s. Electrochemical impedance spectroscopy (EIS) was carried out in PBS solution using a sinusoidal potential perturbation of 10 mVrms (at DC = 0 V, vs OCP). For EIS measurements, where the spectra were recorded after every 1 h, the frequency was scanned in the range of 10² to 10⁻² Hz. The electrochemical tests were repeated three times to ensure reproducibility.

2.5. X-ray photoelectron spectroscopy

To examine the surface chemistry of the post immersion co-sputtered samples, i.e. CSFM-1 and CSFM-2, X-Ray Photoelectron Spectroscopy (XPS) was conducted using Kratos Axis Ultra DLD X-Ray Photoelectron Spectrometer with monochromated Al source having an energy resolution of 0.6 eV (at 20 eV pass energy). The photoelectrons emitted from the surface of the samples were analyzed at a take-off angle of 45°. Survey spectra (0–1000 eV) were acquired for qualitative and quantitative analysis, while high-resolution spectra were obtained to characterize the chemical states of different species on the surfaces. The high-resolution spectra were deconvoluted using the Gaussian-Lorentzian function after applying the Shirley method for background subtraction.

2.6. Nanoindentation testing

Due to the film-substrate nature of the co-sputtered samples, a TribolIndenter, TI 980 Performech II (Bruker) with a Berkovich Diamond indenter, was used for the nanoindentation testing for CSFM-1 and CSFM-2. Two different modes, quasi-static and dynamic, were conducted to assess the mechanical properties. In the quasi-static mode, the indenter was driven into the surface up to a peak load (10 mN), held for 2 s and then unloaded to zero (trapezoidal-shape load-unload cycle). In the dynamic test, a continuous stiffness measurement (CSM) mode was performed on the specimens by superimposing a 220 Hz oscillating load on top of the quasi-static load. The phase and amplitude of the oscillations were used to continuously measure the stiffness during the loading segment. Mechanical properties, i.e. elastic modulus and hardness, were calculated from dynamic CSM mode by averaging in a specific range of contact depth (accounting for around 10–15% of film thickness) to avoid substrate interference. For each specimen, indentations were made at 18 different locations to ensure reproducibility.

Table 1

<table>
<thead>
<tr>
<th>Sample(s)</th>
<th>Composition* (at%)</th>
<th>DC Power (W)</th>
<th>RF Power (W)</th>
<th>Film Thickness** (nm)</th>
<th>Deposition Time (min)</th>
<th>Throw Distance*** (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>100</td>
<td>210</td>
<td>0</td>
<td>423±10</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>CSFM-1</td>
<td>Fe (85), Mg (15)</td>
<td>210</td>
<td>55</td>
<td>327±10</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>CSFM-2</td>
<td>Fe (65), Mg (35)</td>
<td>200</td>
<td>90</td>
<td>527±5</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>Mg</td>
<td>100</td>
<td>0</td>
<td>90</td>
<td>360±15</td>
<td>20</td>
<td>7</td>
</tr>
</tbody>
</table>

*As confirmed via EDX analysis, (for simplicity only the composition of Fe and Mg species, excluding O, are reported with ± 2% error margin).
**Measured via DektakXT stylus profiler (Bruker).
***Gun-to-substrate.
3. Results

3.1. Structural characterization

3.1.1. Grazing-Incidence X-Ray diffraction

For the structural characterization of individually sputtered samples, Fe and Mg, as well as the co-sputtered samples, CSFM-1 and CSFM-2, GI-XRD was conducted. Fig. 1 shows the diffraction patterns of the four samples. The individually sputtered Fe and Mg both exhibit distinct sharp peaks characteristic of fully crystalline bcc-Fe (JCPDS card no. 00–006–0696) and hcp-Mg (JCPDS card no. 00–035–0821), respectively. In the case of pure Mg, however, some peaks are missing as compared to the diffraction pattern of Mg fabricated through conventional equilibrium methods [59,60]. The missing peaks may be due to crystallographic texture formation [61], i.e. preferred orientation of crystallites, as reported elsewhere [62] for pure Mg thin films fabricated via sputtering.

Upon simultaneous co-sputtering of Fe and Mg, (Fe–Mg 210 W – 55 W), designated as CSFM-1), the diffraction pattern still demonstrates bcc-Fe, as shown in Fig. 1. However, in comparison to pure bcc-Fe, some aberrations appear in the diffraction pattern of CSFM-1, namely peak broadening and peak shifting. The peak broadening, characterized by an increase of full-width-half-maximum (FWHM) suggests a decrease in the crystallite size of the resulting co-sputtered sample, CSFM-1, according to the Scherrer equation. The decrease in crystallite size may occur because the ordered arrangement of atoms may not progress as they would normally under equilibrium cooling conditions and/or single-component sputter deposition. Under the applied settings, the growth of nucleating phases is intercepted at shorter distances leading to lower crystallite size. The second aberration in the form of peak shifting towards lower diffraction angles suggests an increase in the lattice parameter of bcc-Fe. This increase in the lattice parameter is most likely caused by the substitution of Mg atoms, having a comparatively larger atomic radius, in the bcc-Fe lattice forming a substitutional solid solution. When the Mg content is increased by the application of a higher deposition power, (Fe–Mg (200 W – 90 W), CSFM-2), the diffraction pattern exhibits only a broad peak suggesting a loss of full-/medium-range crystallinity, thus pointing towards amorphization.

Overall, in both co-sputtered samples, there is no peak indicative of crystalline Mg, that validate single-phase structures. The GI-XRD study, therefore, demonstrates the formation of a single-phase substitutional solid solution in the case of CSFM-1 and an amorphous structure in the case of CSFM-2.

3.1.2. High-resolution transmission electron microscopy

The microstructures revealed by the GI-XRD study may not provide detailed information about structures at the nanoscale, especially in the case of the co-sputtered samples, CSFM-1 and CSFM-2. Because of the availability of spherical-aberration-corrected (Cs-corrected) atomic imaging in HR-TEM, local atomic structures can be directly observed. Thus, it is widely employed for sub-angstrom atomic imaging, atomic arrangements, and local crystallinity in amorphous materials [50,63,64]. In this work, Cs-corrected HR-TEM is employed to further explore the substitutional solid solution (CSFM-1) and amorphous structure (CSFM-2) as demonstrated by GI-XRD. HR-TEM observations are carried out in a cross-sectional view to probing the structures of both co-sputtered samples.

Fig. 2 shows the HR-TEM images of CSFM-1 along with selected-area-electron-diffraction (SAED) and Fast Fourier Transformation (FFT). It is clear from Fig. 2(a) that the sample exhibits...
structural order at the nanoscale, indicative of a nanocrystalline configuration. To further explore these ordered regions, some selected areas from Fig. 2(a) were processed via FFT, inverse-FFT, and filtered-FFT. FFT is an image analysis tool that can extract information regarding periodicities, as any small-scale periodicity in the HR-TEM image is susceptible to this analysis [65]. FFT represents the reciprocal space, equivalent to the diffraction pattern of the image, while inverse-FFT carries out an inversion back into the real space. The FFT, Fig. 2(c, j), shows well-defined pairs of diffraction spots, indicative of structural order. The inverse-FFT, Fig. 2(b, i), shows the high-resolution nanocrystallites from which the interplanar spacings are calculated, as shown in Fig. 2(e, g). From the interplanar spacings, the region does not exactly correspond to the pure bcc-Fe (110) phase [66]. The SAED pattern, (Fig. 2a, inset), also demonstrates dotty rings deviating little from the pure bcc-Fe [67]. The increased values of interplanar spacing of Fe (110) (2.15 Å vs 2.02 Å) suggested lattice expansion caused by the substitution of Fe atoms by Mg in the bcc-Fe lattice. Similarly, the d-spacing of 1.84 Å cannot be associated with the pure bcc-Fe phase but attributed to the lattice expansion and formation single-phase Fe-Mg solid solution. This is in agreement with the GI-XRD study (Section 3.1.1), where the diffraction angles are observed to shift to lower values with the incorporation of Mg.

Fig. 3 shows the HR-TEM images, SAED pattern, and FFT analysis of CSFM-2. CSFM-2 has a predominantly amorphous structure, as shown in Fig. 3a. The SAED pattern, Fig. 3a (inset), also shows a ring superimposed on a diffused halo pattern indicative of a predominantly amorphous phase. The FFT, Fig. 3(c, f, i), and filtered-FFT images, Fig. 3(d, g, j), all demonstrate a combination of halo rings and spots that are indicative of a mixture of amorphous phase and ordered domains. The inverse-FFT images, Fig. 3(b, e, h) further justify amorphous configuration with ordered regions on the scale of few nanometers, as shown in Fig. 3e. These HR-TEM findings of CSFM-2 also agree well with the GI-XRD study (Section 3.1.1). Such short-range ordered structures or nanocrystallites in an amorphous matrix have previously been identified in various studies using HR-TEM [64,68-70].

Thus, both GI-XRD and HR-TEM studies confirm a single-phase solid solution in the case of CSFM-1 and an amorphous short-range ordered structure in the case of CSFM-2.

3.2. Electrochemical characterization

Electrochemical characterization is carried out to probe the degradation behavior of the two co-sputtered samples, CSFM-1 and CSFM-2, in PBS solution and the results are compared with the electrochemical degradation tendency of sputtered Fe. Since the thinness of the co-sputtered films limits the practical evaluation of bulk corrosion for an extended period [71], only the electrochemical tests appropriate for determining the degradation behavior at short-time scales are reported in this study.

3.2.1. Potentiodynamic polarization

Potentiodynamic polarization was conducted to evaluate the electrochemical behavior and to quantify the degradation tendency. In this technique, corrosion potential (Ecorr) and corrosion current density (Icorr) are determined to calculate the degradation rate by sweeping the potential below and above OCP. Individually, Fe, CSFM-1, and CSFM-2 samples are first immersed in PBS solution to stabilize their OCPs prior to polarizing them cathodically, as shown in Fig. 4.

The cathodic polarization trend for Fe up to -0.45 V (vs. SCE) represents the total current related to the reduction of dissolved oxygen. Further increase in cathodic overpotential results in a limiting current density attributed to limited mass transfer of
dissolved oxygen to the electrode surface. Based on the polarization trends, it is estimated that under normal conditions, the dissolution of pure Fe is controlled by dissolved oxygen in the PBS solution according to reaction 1. However, at more negative applied potential (< −0.65 V vs. SCE), a large increase in cathodic current on the Fe surface is observed, which is due to H₂O reduction via reaction 2.

On the other hand, in the case of CSFM-1 and CSFM-2 (at more negative potentials than their corresponding OCPs), both dissolved oxygen and water may reduce at the surface. However, at such negative applied potentials (< −0.8 V vs. SCE in case of CSFM-1 and −1.0 V vs. SCE), the cathodic polarization trends highlight the dissolution tendency of these sputtered samples possibly associated with the H₂O reduction (reaction 2). Both CSFM-1 and CSFM-2 have a shift in Ecorr (−0.723 V and −0.910 V vs SCE, respectively) towards more negative potentials compared to Fe (−0.340 V). In simple words, this negative shift in Ecorr represents the relatively active state of the sputtered samples than pure Fe, which is an indication of their larger tendency to dissolve in PBS solution. At such negative potentials, there is an obvious possibility of H₂O reduction on the surface, however, the kinetics of these reactions strongly depends on the catalytic activity of the microstructural phases.

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^- \quad (1) \]

\[ 2\text{H}_2\text{O} + 2e^- = \text{H}_2 + 2\text{OH}^- \quad (2) \]

It is predicted from these results that the shift in Ecorr towards negative potential would correspond to water reduction on the surface, which may ultimately control the degradation tendency of CSFM-1 and CSFM-2 samples. In simple words, under normal conditions, the relatively more negative OCP of CSFM-1 and CSFM-2 compared to Fe highlights the anodic dissolution of these samples is caused by H₂O reduction reaction. Although the reduction of dissolved oxygen on CSFM-1 and CSFM-2 is possible during extended OCP stabilization period, the concentration of this species may decrease at the surface and the dissolution process strongly depends on H₂O reduction reaction.

The anodic polarization trends of CSFM-1 and CSFM-2 were also recorded up to +0.3 V (vs OCP). During anodic polarization at low applied potentials (η < +0.2 V), both samples had similar anodic polarization trends to pure Fe. Compared to the anodic behavior of Fe, the relatively small increase in current registered by CSFM-1 and CSFM-2 possibly correspond to the formation of iron oxide/hydroxide species on the surface. However, these surface species do not form a uniform protective film as evident from the continuous increase in current at the large anodic potential. For instance, the increase in anodic potentials beyond a certain threshold (η > −0.44 V (vs SCE) for CSFM-1 and > −0.72 V for CSFM-2), both CSFM-1 and CSFM-2 demonstrated an abrupt increase in current densities, which highlighted the accelerated degradation rate of these co-sputtered samples.

The corrosion current density (Icorr), extracted from the potentiodynamic scans via Tafel extrapolation, increases in the order of Fe < CSFM-1 < CSFM-2, which further confirms the relatively higher degradation rates of CSFM-1 and CSFM-2.

Overall, the potentiodynamic scans show a monotonic negative shift in Ecorr and an increase in Icorr with the addition and
subsequent increase of Mg content, both trends describing the enhanced degradation of the co-sputtered samples. The corrosion parameters along with standard deviations, determined from the polarization curves, are presented in Table 2.

Interestingly, though the highest negative shift in $E_{\text{corr}}$ for CSFM-2 (−0.910 V vs SCE) is significant in comparison to Fe (−0.340 V vs SCE), it is still much nobler than pure Mg Ecorr in PBS (−1.6 V vs SCE) as reported elsewhere [73]. The relatively more noble $E_{\text{corr}}$ of both CSFM-1 and CSFM-2 in comparison to Mg-based samples also carry additional significance over Mg-based alloys that exhibit higher degradation rates under anodic conditions described by the negative difference effect (NDE) [74,75]. The NDE is associated with the formation of Mg$_2^+$ facilitated by water reduction, leading to chemical interaction of Mg$_2^+$ with the OH$^-$ species with hydrogen evolution, according to reaction 3.

$$\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{HO}_2\text{Mg}^{2+} + \text{OH}^- + \text{H}_2$$ (3)

3.2.2. Electrochemical impedance spectroscopy

The EIS tests of Fe, CSFM-1, and CSFM-2 samples were carried out as a function of time during 6 h immersion in PBS. For the EIS, done to evaluate the immediate-to-short-term changes, the frequency is adaptively scanned up to 10$^{-1}$ Hz, to shorten the experiment time and therefore, avoid any irreversible change at the surface of the samples [76] (ca. 7 min duration for a scan to 10$^{-1}$ Hz). The shorter experimental time avoids a shift from the quasi-equilibrium state of the Fe-Mg samples under investigation. However, once the time-dependent EIS is completed, the final scan is recorded up to 10$^{-2}$ Hz (completed in approximately 24 min) to evaluate the overall interfacial electrochemical reactions of the samples.

Fig. 5 (a, b) shows the Bode and Nyquist plots of Fe in PBS solution as a function of exposure time. From the Bode-impedance spectra of Fe, Fig. 5(a), the phase shift from 0 to −70° (at $f < 1$ kHz) is related to the non-faradaic current contribution, mostly associated with double-layer charging. From the Nyquist plot of Fe, Fig. 5(b), the decrease in both real impedance ($Z_{\text{real}}$) and imaginary impedance ($Z_{\text{imag}}$) at 10$^{-1}$ Hz as a function of exposure time suggests the specific adsorption of ionic species and possible faradaic reactions at the surface. Fig. 5(c−f) shows the Bode and Nyquist plots of CSFM-1 and CSFM-2 recorded as a function of exposure time. Related to the very negative corrosion potentials (active) of both co-sputtered samples compared to Fe, the decrease in the $Z_{\text{real}}$ upon extended exposure is expected, Fig. 5(d, f), due to the progress of water reduction supplemented by Fe-Mg oxidation. The formation of resultant oxide/hydroxide on the surface of CSFM-1 and CSFM-2 changes the surface conditions after extended exposure, as validated from the variations in phase shift and decrease in area-normalized total impedance, $Z_{\text{mod}}$, at a frequency lower than 10$^{-2}$ Hz, Fig. 5(c, e). In the Nyquist plots of CSFM-1, Fig. 5(d) and CSFM-2, Fig. 5(f), the appreciable decrease in $Z_{\text{real}}$ with exposure time is evident (in comparison to pure Fe), which confirms the increased degradation tendency of the two co-sputtered samples. However, the obvious change in the impedance behavior of CSFM-2 in the low-frequency regime compared to CSFM-1 after 3 h exposure is related to the relatively large concentration of Mg (35 at.% and its more active OCP (−0.792 V vs SCE) vs −0.668 V for CSMF-1). The significant decrease in $Z_{\text{mod}}$ (at $f = 10^{-2}$ Hz) of CSFM-2 after 3 h is related to the dissolution of Mg according to reaction 3, in addition to lesser oxidation of Fe in the amorphous structure.

Fig. 6 shows the comparative Bode and Nyquist plots of co-sputtered samples and Fe, obtained after 7 h immersion in PBS solution and simulated with an equivalent electrical circuit (EEC) to quantitatively estimate the corrosion parameters. As shown in the Bode plot, Fig. 6(a), compared to pure Fe, the CSFM-1 and CSFM-2 samples presented relatively lower $Z_{\text{mod}}$ (at $f = 10^{-2}$ Hz) and more positive phase angle shift (esp. CSFM-2), which is directly related to their larger degradation tendency in PBS solution. Likewise, from the Nyquist plots, Fig. 6(b), CSFM-1 and CSFM-2 demonstrate a decrease in the diameter of the semi-circles (after extrapolation to intersect the $Z_{\text{real}}$-axis) that manifest relatively improved charge transfer processes at the electrode/electrolyte interface.

In all three samples, (Fe, CSFM-1 and CSFM-2), the phase angle shift $\sim 90^\circ$ and semi-circle in the Nyquist plots, (obtained by the dissociation of $Z_{\text{mod}}$ into $Z_{\text{real}}$ and $Z_{\text{imag}}$ components) reveal a single time constant [50,65] associated with the parallel contributions of charge relaxation in the electrical double layer (non-faradaic response), represented as a constant phase element (CPE$_A$), and faradaic processes as charge transfer resistance ($R_{\text{ct}}$), as shown in the EEC model, Fig. 6(c). Table 3 presents the EIS parameters along with standard deviations after simulating the experimental impedance spectra with the EEC model by constraining the chi-squared values ($\chi^2$) below 10$^{-3}$. CSFM-1 and CSFM-2 exhibit slightly higher solution resistance, $R_s$, compared to Fe that is possibly related to the surface oxidation and specific adsorption of ionic species and reaction products at the electrode/electrolyte interface due to the more negative $E_{\text{corr}}$ of these samples in the PBS solution. Thus, the reaction products forming on the surface of CSFM-1 and CSFM-2 may change the concentration and type of species at the interface and affect the solution resistance. CSFM-1 and CSFM-2 also have lower $R_{\text{ct}}$, (lowest in the case of CSFM-2) due to their Mg contents. Additionally, CSFM-1 and CSFM-2 have relatively higher values of CPE$_A$ that may be associated with the relatively high affinity of the surface towards polar water molecule i.e. OH$^-$ species and cations H$^+$ specific adsorption as H$^+$ at the surface prior to H$_2$ evolution (reaction 2). Among the co-sputtered samples, the slightly lower CPE$_A$ (2.7 mS/cm$^2$) and phase coefficient, $\alpha$ (0.61) of CSFM-2, as compared to CSFM-1 (3.4 mS/cm$^2$), are likely due to the formation of reaction products at the surface. The increase in interfacial pH due to H$_2$ evolution and increase in OH$^-$ concentration may result in Mg(II) complexes (reaction 3) that settle on the surface. These species along with iron oxide/hydroxide may alter the electrochemical response of the surface, specifically to the adsorption/desorption process.

From the EIS study, the degradation tendency follows an increasing trend, Fe < CSFM-1 < CSFM-2, which is in agreement with potentiodynamic polarization (Section 3.2.1).

3.3. Nano-indentation of the sputtered samples

Nano-indentation, equipped with high-resolution load and displacement data, was employed to study the nano/micro-scale mechanical properties of the two co-sputtered samples, CSFM-1 and CSFM-2. As an experimental technique possessing sufficient spatial and temporal resolution, nano-indentation can be used to
Fig. 5. Bode and Nyquist plots of pure Fe (a, b), CSFM-1 (c, d), and CSFM-2 (e, f) samples as a function of time exposed to PBS solution for 6 h. The EIS spectra are recorded after every 1 h time duration.

Table 3
EIS parameters calculated by simulating and fitting the Equivalent Electrical Circuit (EEC) to the experimental EIS spectra.

| Sample(s) | $R_s$ (Ω.cm²) | $R_{ct}$ (kΩ.cm²) | $CPE_{dl}$ (mS.s^α cm^-2) | Alpha $\alpha$ | $|Z_{real}|_{f=0.1}$ (kΩ.cm²) |
|-----------|----------------|-------------------|--------------------------|---------------|------------------|
| Fe        | 10.4 ± 1.4     | 4.5 ± 0.05        | 2.0 ± 0.1                | 0.76 ± 0.03   | 2.5 ± 0.07       |
| CSFM-1    | 12.4 ± 2.1     | 2.9 ± 0.07        | 3.4 ± 0.2                | 0.81 ± 0.03   | 1.7 ± 0.08       |
| CSFM-2    | 15.0 ± 2.8     | 2.1 ± 0.03        | 2.7 ± 0.2                | 0.61 ± 0.04   | 1.2 ± 0.05       |

Please cite this article as: M.M. Khan, K.M. Deen and I. Shabib et al., Controlling the dissolution of iron through the development of nanostructured Fe-Mg for biomedical applications, Acta Biomaterialia, https://doi.org/10.1016/j.actbio.2020.06.014
Fig. 6. Bode (a), and Nyquist plots (b) of the Fe, CSFM-1 and CSFM-2 samples in PBS solution obtained after 7 h immersion. (c) An equivalent electrical circuit (EEC) used to calculate quantitative parameters from the impedance spectra.
Fig. 7. (a) Quasi-static load-unload curves for CSFM-1 and CSFM-2. (b, c) Dynamic nanoindentation tests, showing the trends of hardness (b) and elastic moduli (c) as a function of contact depth.

explore the fundamental deformation mechanisms of nanocrystalline and amorphous samples [77]. Nano-indentation was carried out in both quasi-static and dynamic modes. The elastic modulus of both CSFM-1 and CSFM-2 samples were calculated from the quasi-static load-unload curves as shown in Fig. 7(a).

It is clear from Fig. 7(a), that CSFM-1 has a higher slope during initial unloading and lower maximum displacement ($h_{\text{max}}$) under the same settings, indicative of relatively higher elastic modulus and hardness, respectively. However, although a quasi-static test might reveal the general deformation behavior, it is not suitable for accurate assessment of elastic modulus and hardness for film-substrate samples. Analysis as a function of contact depth is then essential.

In order to study the depth-dependence variations in mechanical properties, dynamic nanoindentation [50,78–80] was carried out. Fig. 7(b) shows the hardness profiles as a function of contact depth for CSFM-1 and CSFM-2, demonstrating two apparent transition points. The hardness values at the very beginning (initial few nanometers) may have come from the contribution of both surface oxides/hydroxides [81] and the underlying non-oxidized sample. The highest hardness values at the first transition point (20–30 nm) are due to the similar indentation size effect [77], according to which high hardness values might arise at small contact depths (or equivalently lower indentation loads). Following the first transition point, the hardness values decrease with increasing contact depth until a second transition point is reached (65–75 nm), after which the hardness values continue to rise. This rise is due to the substrate effect [82] now becoming prominent. The values of elastic moduli, Fig. 7(c), initially drop slightly, (as reported by Attar et al. [83]) before becoming independent to the contact depth.

4. Discussion

4.1. Formation of single-phase structures

The formation mechanism of the two co-sputtered samples, i.e., substitutional solid solution (CSFM-1) and amorphous structure (CSFM-2) is related to the sputtering parameters and material properties. During the deposition of a single-component sample, the phase nucleation of the deposited species commences with stable clusters of ad-atoms growing in the forward direction instead of dissolving back. When the cluster size approaches a critical value, the crystallography of the nucleating phase is defined. As growth proceeds, the crystallographic orientations minimizing specific surface and interface energies, are favored. The growth rate, however, is a function of temperature and deposition rate, both of which are prime significance [84]. In the deposition of a multi-component alloy system, the crystallographic aspects are, however, more complicated. In this study, the temperature was held constant at ambient, which significantly suppresses ad-atom mobility, whereas the deposition rates of both sputtering guns were varied to modify the resulting Fe-Mg structures.

Fe and Mg, under equilibrium conditions, are immiscible both in the solid and liquid state with a positive enthalpy of mixing (+18 kJ/mol). According to the thermodynamic phase diagram, Mg possesses very limited solubility in Fe, in the crystalline state. This rules out the possibility of using conventional fabrication methods to develop Fe-Mg alloys under equilibrium conditions. However, under non-equilibrium conditions, Mg can be made to occupy substitutional positions in bcc-Fe lattice [53]. Among such non-equilibrium methods, sputtering is one technique to fabricate homogeneous crystalline or amorphous alloy systems from species that are, otherwise, immiscible under equilibrium conditions [49].

In the case of CSFM-1, a low deposition power for Mg (55 W, based on sputtering yield calculations) was chosen to ensure a controlled amount of Mg in the deposited sample. Unlike co-sputtering, pure Fe can form a fully crystalline when individually deposited using magnetron sputtering [67], as shown in Fig. 1. However, the incorporation of another species in the form of co-sputtering can affect the crystallography of the resulting binary alloy system, depending on the species type and composition. In the stated settings of CSFM-1, Fe with a much higher deposition power (210 W) can proceed to nucleate and grow to form a bcc-lattice, while Mg with a much lower deposition power (55 W), may substitute the Fe atoms, overall forming a substitutional solid solution. Moreover, since sputtering is characterized by limited ad-atom mobility under ambient-substrate temperatures, the formation of a single-phase under the given conditions is highly likely as reported for Mg-Ti [58] and Mg-Zr [85] alloys. In the GI-XRD study, Fig. 1, the incorporation of Mg leads to deviations from
a near-ideal diffraction pattern of a pure bcc-Fe. The ideal diffraction pattern demonstrates narrow, symmetrical delta-function-like peaks with Bragg’s angles according to a well-defined unit cell. The deviations from the ideal pattern in the form of peak broadening and peak shifting in the case of CSFM-1, reveal key information. Peak broadening in for CSFM-1 is due to the smaller crystallite size in comparison to pure sputtered Fe, and possibly increased lattice defects and inhomogeneous micro-strains caused by the non-equilibrium mixing. The peak shift, on the other hand, is due to lattice expansion caused by the substitution of Mg atoms having comparatively larger atomic size. The lattice expansion in this work is in contrast to a study conducted by Song et al. [58], where a shift of diffraction peaks towards higher angle was observed with the incorporation of titanium during co-sputtering of Mg-Ti. The shift towards higher angles was attributed to lattice contraction caused by the smaller unit-cell dimensions of Ti substituting Mg. Thus, as demonstrated by the GI-XRD and HR-TEM studies, in the stated range of deposition powers and sputtering conditions, a homogeneous solid solution formation results for the two metals.

In the case of CSFM-2, the Mg content is raised from 15 to 35 at.% by the application of a higher deposition power (90 W compared to 55 W for CSFM-1). Given the fact that Mg has a higher sputtering yield than Fe, the increased deposition rate of Mg is expected to result in a competing effect between Fe and Mg ad-atoms on the substrate. Owing to the different crystal structures and extensive miscibility gaps between Fe and Mg, the competing effect for the formation of a viable crystal structure makes amorphization highly probable, analogous to a confusion principle [86] put forward by Greer for the formation of metallic glasses. On top of that, the high-rate nature of co-deposition would further suppress the long-range crystallinity by ensuring a higher ad-atom arrival rate. Consequently, under the applied conditions of CSFM-2, the growth of the nucleating phase of the majority species (Fe) is intercepted at short distances, disrupting the establishment of a full-scale crystallinity, and leading to amorphization with short-range order. The appearance of amorphization in CSFM-2 is very interesting since the formation of amorphous phase is thermodynamically unfavorable in this sample having large positive enthalpy of mixing, here Fe and Mg, for instance. Classic glass-forming alloy systems usually consist of constituents having higher negative enthalpy of mixing [48]. There are, nevertheless, some immiscible alloy systems having positive enthalpy of mixing, where the formation of amorphous phases have been reported, e.g. Cu-Nb [87], Ag-Fe [49], Cu-Ta [88]. To shed some light on this idiosyncrasy, Michaelaens et al. [87] have reported that the stability of amorphous phases in the immiscible Nb-Cu alloy system may have come from the change of sign of heats of mixing as a function of temperature, being positive in the liquid state and negative in the amorphous state.

4.2. Degradation behavior of the sputtered samples

The higher corrosion rate of the two co-sputtered samples, CSFM-1 and CSFM-2, may be explained in terms of various aspects. For instance, the specific adsorption and formation of reaction products at the surfaces, the chemical composition of the samples and the unique nanoscale structures, with the exclusion of galvanic corrosion (as both CSFM-1 and CSFM-2 possess single-phase structures). Based on the active dissolution in anodic-polarization (as shown in Fig. 4) and decreasing impedance arcs (decrease in $R_{ct}$) was evident from EIS trends obtained during 6 h immersion (Fig. 5), the role of a corroded surface film in governing the degradation behavior may be considered insignificant because of its likely non-protective nature. This leaves the chemical composition aspects and the unique non-equilibrium nanostructures being the two determinants of the elevated degradation rates in PBS solution.

The role of chemical composition is related to the preferential dissolution of electrochemically active Mg from the homogeneous solid solution (CSFM-1) and amorphous short-range ordered sample (CSFM-2). The role of non-equilibrium nanostructures is, however, complex and may be further linked to several aspects.

The first aspect linked to the nanostructures may be related to the electrochemical inhomogeneity associated with a higher degree of disorder, i.e. crystalline defects, as well as the presence of internal stresses following the non-equilibrium mixing of otherwise immiscible Fe and Mg. Crystalline defects, i.e. grain boundaries and dislocations, etc., can affect the kinetics of corrosion, as well as its form and location. Such defects are regions of higher energy in comparison to the adjacent crystal and therefore, possess relatively higher chemical activity, which may lead to accelerated degradation via preferential attack under conditions of active dissolution. The density of such crystal defects and their effects on increasing degradation rates has earlier been discussed for a Mg-based alloys [58]. The CSFM-1 is likely to exhibit high density of such defects in comparison to pure Fe, as demonstrated by the aberrations in X-Ray diffraction pattern (peak broadening and shifting, Fig. 1). The structural transition to a lower-crystallite-size upon co-sputtering is, thus, expected to raise the degradation tendency as per the traditional viewpoint of nano-crystalline structures, though contradictory behavior upon nano-crystallization is also reported [89,90]. Generally, in the case of active dissolution, nano-crystallization is expected to increase corrosion rates, especially if the corrosion products are soluble [91]. Additionally, the non-equilibrium mixing of Fe and Mg can create internal stresses, possibly via substitution of Fe by larger-atomic size Mg atoms, that may increase the reactivity of the samples [92].

The second aspect arising out of the non-equilibrium nanostructures may be explained in terms of atomic mobility that influences electrochemical properties, as put forward by Tang et al. [93] to describe the corrosion properties of metallic glasses. According to this approach, the two co-sputtered samples are thermodynamically in a metastable state exhibiting higher energy, and therefore higher atomic mobility, as opposed to fully crystalline materials that stay in lower energy wells corresponding to an equilibrium state. Therefore, the atoms in the Fe-Mg co-sputtered samples may be considered electrochemically more active leading to the faster dissolution of both Mg and Fe species.

The third aspect linked to the nanostructures may be described in terms of bond length [65,94]. Bond lengths (or bond strengths) can influence the degradation kinetics from the perspective of bond-cleavage energy. Wang et al. [94] have reported that a longer bond length (and correspondingly lower bond strength) in the Zr$_2$Ni single-crystal as compared to a shorter bond length in an amorphous Zr-Ni counterpart, lead to rapid dissolution in the former. This perspective is further validated by Tailleart et al. [95], in a comparative study of Al-Co-Ce as-quenched-amorphous, thermally-oxidized-amorphous, and devitrified alloy systems. In this comparative study, the authors attribute the highest corrosion resistance of the thermally relaxed amorphous structure to the shorter bond length. As reported by Marcus, higher metal-metal bond strength may result in reducing the dissolution rate by raising the activation energy barrier for the disruption of metal-metal bonds [96]. The non-equilibrium mixing leading to lattice expansion can affect the Fe-Fe and Fe-Mg bonds, in contrast to a near-equilibrium bcc-Fe, consequently influencing the degradation properties.

However, it is important to mention that though the aspects of chemical composition and crystalline defects influencing the degradation behavior are widely studied, the approaches of atomic mobility and bond length may need further investigation. One might consider the comparison of CSFM-1 and CSFM-2 to their full equilibrium counterparts (via controlled annealing, for instance),
however, the high positive enthalpy of mixing in the Fe-Mg alloy may result in phase separation if an attempt is made via heat treatment, which precludes such comparisons. Nevertheless, as per the aforementioned discussion, instead of relying on an individual role, a composite effect governed by chemical composition and unique nanostructures may be considered to be operative, overall leading to higher degradation rates of CSFM-1 and CSFM-2 in PBS solution.

The Fe-Mg alloy samples studied here would require a detailed biocompatibility study to ensure that the degradation products are within the safe tolerance limits of the human body and are not causing any adverse reactions. Also, the thin-film nature needs to be translated into bulk form (via mechanical alloying route, for instance) to ensure the fabrication of bulk implants. These alloy also face challenges in the form of necessitating strict control of experimental conditions to avoid segregation and formation of galvanic couples that lead to detrimental degradation rates. Further research work is needed to prevent the occurrence of such electrochemically dissimilar regions. Additionally, for implants that need mechanical integrity during functioning, a detailed analysis

Please cite this article as: M.M. Khan, K.M. Deen and I. Shabib et al., Controlling the dissolution of iron through the development of nanostructured Fe-Mg for biomedical applications, Acta Biomaterialia, https://doi.org/10.1016/j.actbio.2020.06.014
of the loss of mechanical properties as a function of degradation is a must before such alloys find practical applications.

4.3. Post-immersion morphological analysis sputtered samples

Though higher degradation tendencies are demonstrated by the two co-sputtered samples, it is also important to investigate the degradation patterns, as these affect the durability of implant materials. Therefore, Scanning Electron Microscopy (SEM) is employed to study the pre- & post-immersion co-sputtered samples, CSFM-1 and CSFM-2. The CSFM-1 pre-immersed sample, Fig. 8(a & b), has a random fine grainy morphology typical of sputter-deposited films [67,97]. However, CSFM-2 has a smooth featureless appearance, Fig. 8(c & d), possibly due to its amorphous structure [46,98].

Fig. 8(e-g) shows the post-immersion SEM images of CSFM-1 after 6 h exposure to the PBS solution. The corrosion products demonstrate a cracked loose-sheet-like morphology. Such surface cracking of the corroded layer is likely due to Pilling-Redworth ratio effects and/or dehydration of the aqueously formed film [58,99,100]. Below the corroded layer, however, CSFM-1 appears uncompromised showing no delamination from the Si wafer, Fig. 8(g). Fig. 8(f) shows a high magnification image of the cracked sheet fragment where fine-scale globular-shaped corrosion products are observed. The post-immersion SEM images of CSFM-2, on the other hand, show relatively finer cracks, Fig. 8(h–j), in comparison to CSFM-1. For CSFM-2 the corrosion products are more uniform over the surface area and are indicative of a more homogeneous degradation.

From a thermodynamic perspective, it is reasonable to assume that the corrosion products in both samples would be predominantly composed of iron-based ox/hydroxides, that are commonly formed in physiological solutions [41,73]. The corrosion products of Mg, mainly hydroxide, may or may not be stable depending on the local pH at the surface. According to the Eh-pH diagram for the Mg-H2O system at pH 7.4 and for Ecor in the range of −0.6 to −0.8 V vs SCE, magnesium hydroxide is unstable. However, due to H2 evolution a local increase in pH at the surface could facilitate the precipitation of magnesium hydroxide.

The apparently non-protective nature of the corroded surface films, as surmised from SEM imaging, is consistent with the EIS characterization (Section 3.2.2), where no rise in total impedance and charge transfer resistance occurred within 6 h of exposure. A continuous passive film formation would have resulted in slower degradation rates after initial exposure, unlike the trends seen with EIS. The corroded film, being penetrable to the electrolyte and thus non-protective, can grow by the dissolution of the underlying sample leading to product accumulation with time. This also points towards the fact that the degradation mechanism is, by and large, governed by the chemical composition and nanoscale structures, as earlier discussed in Section 4.2.

Fig. 9(a–d) shows the post-immersion co-sputtered samples after 24 h exposure in PBS solution. There is no significant change in the morphology of the corrosion products from those observed after 6 h of exposure. Thus, both co-sputtered samples undergo uniform degradation under open-circuit conditions. This uniformity in dissolution can be linked to the structural homogeneity and absence of Mg segregation in these samples. A separate study but with the similar goal of achieving uniform degradation is reported by Mao et al. [4], where a Mg-Nd-Zn-Zr alloy lead to nano-phasic highly uniform biodegradation. The uniform dissolution of the CSFM-1 and CSFM-2 can also be predicted from the potentiodynamic polarization trends (absence of current fluctuations in the anodic polarization) as shown in Fig. 4. However, without cross-sectional data and/or images, it is not possible to confirm the uniform dissolution of the samples. The presence of cracks on the surface are expected due to natural dehydration process after removal from PBS solution. These surface cracks may also form during sample storage and delay in the surface characterization. Moreover, no sign of localized dissolution (pitting) was observed on the surface of both samples after exposure in PBS solution as evident in the SEM images (Figs. 8 and 9).

The uniformity in dissolution is very crucial for biodegradable implants, whether the material is in bulk form or as a thin film. Non-uniform degradation of material employed for a certain biomedical application, e.g. vascular stents, can lead to local stress concentration that may compromise mechanical integrity leading to unexpected failure. Similarly, in the case of thin films, aggressive non-uniform degradation can lead to delamination (for a film-substrate sample) or complete failure (in the case of monolithic systems, such as electrode materials for biodegradable thin-film batteries [8]). Therefore, a homogeneous degradation pattern, that governs the durability of the implant material, along with a controlled degradation rate, is highly crucial for suitable performance of these materials.

The deposited film are approximately 300 and 500 nm for CSFM-1 and CSFM-2, respectively. XPS analysis was carried out to investigate the surface chemistry of the uppermost corrosion product (up to a few nm thick layer) for both samples after 24 h immersion in PBS solution. Fig. 10a shows the survey spectrum
Fig. 10. (a) Survey spectra of CSFM-1 and CSFM-2. (b & c) Deconvolution of high resolution spectra of Fe 2p, Mg 2p and O 1s species present on the surface of CSFM-1 (b) and CSFM-2 (c) samples.
of CSFM-1 and CSFM-2, displaying photoelectron signals of Fe 2p, Mg 2p, O 1 s and pronounced Auger peak of Mg KLL. The high-resolution spectra are deconvoluted in Fig. 10(b,c). Pure Fe and Mg, that are the main constituents of the CSFM-1 and CSFM-2, have strong tendency to form a of oxides/hydroxides upon exposure to PBS solution. From the high-resolution spectra of Fe 2p of both co-sputtered samples, Fig. 10(b,c), three states can be distinguished, i.e. Fe, Fe$^{2+}$ and Fe$^{3+}$. The Fe 2p$3/2$ peak splits into two peaks corresponding to metallic Fe and Fe$^{2+}$ species at 707.43 eV and 709.77 eV, respectively. A satellite Fe$^{3+}$ peak also appears at 716.43 eV (FWHM = 1.322 eV), which is related to the surface oxidation of CSFM-1. However, the broad Fe 2p$3/2$ peak (FWHM = 4.956 eV) affiliated with the metallic Fe appeared in CSFM-1 is absent in CSFM-2. The signatures of high oxidation state Fe species (Fe$^{2+}$, Fe$^{3+}$ species in Fe–O and oxy-hydroxide, FeO$\text{OH}$) and corresponding O 1 s deconvoluted peaks validate the surface oxidation of these sputtered films. Generally the satellite peak of Fe 2p$3/2$ is located at a position of 8 eV higher binding energy than the main Fe 2p$3/2$ peak that validates the presence of Fe$^{3+}$ species on the surface [101,102]. Analysis of the high-resolution peaks of Fe 2p suggests the presence of metallic Fe in the CSFM-1 and CSFM-2 samples.

Mg, due to its high affinity towards oxygen and water (than Fe), develops a film upon exposure to PBS solution under ambient conditions, usually a mixture of MgO and Mg(OH)$_2$ that may form on the surface. The spectra of Mg 2p, in both CSFM-1 and CSFM-2, Fig. 10(b, c), are composed of several metallic species, Mg (at lower binding energy at or below 49.6 eV), and oxidized species, Mg–O and Mg–OH at higher binding energies [103-105]. The sub-peak of Mg 2p spectra of both sputtered films at ~50.3 eV related to Mg–O is originated due to the adsorption of O$^{2-}$ species on the surface. Comparatively, it is observed that for this species, the FWHM of 1.71 eV is found to be larger than 1.33 eV in case of CSFM-2 compared to CSFM-1. However, the intense and broad peak at 52.62 eV (FWHM 2.78 eV) is evident in CSFM-1 in addition to collar peak at large binding energy (54.64 eV) that are associated to Mg–OH species. In case of CSFM-2 only broad peak at 51.57 eV is originated, which is possibly related to the hydration of the surface due to adsorption of moisture on the surface during storage or transfer of sample before XPS analyses. From the O 1 s spectra of CSFM-1 and CSFM-2, Fig. 10(b,c), two peaks are distinguished. The peak located at lower binding energy, denoted by OM, is assigned to oxygen in a Fe–O component of ferric oxides and/or Mg–O, while the peak located at higher binding energy, denoted by O$^{2-}$, is assigned to oxygen in an O–H component of ferric oxyhydroxides and magnesium hydroxide. As evaluated from the XPS analysis, the top surface layers were mostly composed of oxides and hydroxides of Fe and Mg, however, these top layers might have covered the phosphates, which could have formed during corrosion process. Therefore, the existence of phosphate species can not be overruled.

4.4. Mechanical behavior of the sputtered samples

As shown in Fig. 7, the mechanical behavior of the sputtered film was determined via nano-indentation tests. To avoid substrate interference and determine the ‘film-only’ properties, a widely adopted rule of thumb is to limit the indentation depth below 10% of the film thickness [82,106]. Based on the thickness of the co-sputtered films, a range of 10–15% of film the thickness was selected in this study to ensure enough indentation depth as well as to avoid substrate interference. On the other hand, the influence of surface oxidation of the sputtered samples (when exposed to open environment) cannot be overlooked. Based on these effects, the values for hardness and elastic moduli were taken as the average through the film thickness range of 32–49 nm for CSFM-1 and 52–79 nm for CSFM-2 (accounting for ~10–15% of the film thickness of both samples). Through CSM dynamic nanoindentation, the average hardness values were determined to be 7.23 GPa (CSFM-1) and 6.2 GPa (CSFM-2), while the average elastic modulus is found to be 123.62 GPa (CSFM-1) and 94.76 GPa (CSFM-2).

Generally, the influence on micro/nano-mechanical properties can come from topological features i.e. surface oxides of films composed of highly active elements and/or, intrinsically, from the local atomic bonding and packing [107, 108]. From the perspective of topological microstructure, the generally higher hardness values are associated with the effects of solid solution in CSFM-1 and possibly the absence of a normal deformation mechanism in CSFM-2 (due to the absence of an extended crystalline lattice). The lower elastic moduli of the two samples, however, may be related to the intrinsic non-equilibrium structures and local bonding. The parameters used in nanoindentation (e.g. the applied load) also affect the values of hardness and modulus and should be optimized as discussed in [106].

For bio-implant applications, the elastic modulus plays a crucial role as high values can lead to stress shielding effects and implant loosening. Since pure Fe possesses very high elastic modulus (160 ± 11 GPa for sputtered bcc-Fe film, [109]), the much lower values demonstrated by the two co-sputtered samples, especially CSFM-2, can be of particular interest if they are translated into bulk form (via mechanical alloying for instance, [53]). Further reduction may be possible by tuning the percent concentration of individual species, as discussed by Ehtemam-Haghighi et al. [110] for a Ti-Nb–Fe alloy system. High hardness of the two co-sputtered samples, in comparison to bcc–Fe (1.9 GPa, [109]), is likewise important since it plays a role in reducing wear-induced degradation. The mechanical properties of Fe–Mg in the pre-immersion state are reported above. However, a detailed study of the changes in mechanical properties as a function of degradation process in a physiological medium (PBS) would reveal the actual performance of the two co-sputtered samples and should be the subject of future work.

5. Conclusions

1. Single-phase nanostructured Fe–Mg samples are successfully fabricated from immiscible Fe and Mg. GI-XRD and HR-TEM analysis demonstrate the formation of a substitutional solid solution of bcc–Fe–Mg (CSFM-1) and amorphous short-range ordered structure (CSFM-2) caused by the increase in Mg contents.

2. CSFM-1 and CSFM-2 undergo relatively faster degradation in PBS solution in comparison to pure Fe, validated by a more active $E_{\text{corr}}$, higher $I_{\text{corr}}$, and lower $R_{\text{ct}}$, attributed to the combined role of chemical composition and non-equilibrium nanostructures. However, compared to CSFM-1, the relatively more negative $E_{\text{corr}}$ (~0.910±0.01 V vs. SCE) and larger $I_{\text{corr}}$ (12.4 ± 0.6 μA/cm$^2$) values presented by CSFM-2.

3. CSFM-1 and CSFM-2 exhibit non-localized uniform dissolution patterns as predicted from the potentiodynamic polarization scans and are ascribed to their homogeneous single-phase nanostructures.

4. Nanoindentation studies reveal that compared to pure Fe, the CSFM-1 and CSFM-2 sputtered samples presented higher hardness and lower elastic moduli. Owing to the short range ordered (amorphous) microstructure of the CSFM-2, its hardness and elastic moduli (6.2 GPa, 94.76 GPa, respectively) were found to be lower than the CSFM-1 (7.23 GPa, 123.62 GPa, respectively) which was composed of Fe–Mg solid solution single phase.

5. Through a comparative look of CSFM-1 and CSFM-2, an increase in Mg content from 15 to 35 at.% induces amorphization, accelerates dissolution, decreases hardness and elastic modulus.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Bruker is acknowledged for the nano-indentation data. David Escobar, Michigan State University, is acknowledged for SEM/EDX. Authors would like to thank Zia ur Rahman for his valuable help during experimental design.

References

[12] X.-N. Gu, Y.-F. Zheng, A review on magnesium alloys as biodegradable mate-

Please cite this article as: M.M. Khan, K.M. Deen and I. Shabbir et al., Controlling the dissolution of iron through the development of nanosuctioned Fe-Mg for biomedical applications, Acta Biomaterialia, https://doi.org/10.1016/j.actbio.2020.04.014