Conversion Coatings for Magnesium and its Alloys
Conversion Coatings for Magnesium and its Alloys
Magnesium (Mg) and its alloys have attracted significant research attention due to their striking characteristics, such as high specific strength, good thermal and electrical conductivity, vibration and shock absorption, castability, weldability, biodegradability, and biocompatibility. Mg alloys are considered an ideal choice for several technological applications, including automotive, aerospace, defence, electronics, construction, and biomedical. They are promising alternatives to aluminium alloys in automobile and aerospace applications and biodegradable polymers in implant applications. However, their acceptance is substantially limited by the rapid rate of degradation, which undermines their mechanical integrity.

Surface modification is a viable choice to improve the corrosion resistance of Mg alloys. Among the various methods hitherto available, conversion coatings are simple, cost-effective, and amenable for coating complex-shaped objects with high conformal uniformity. The conversion coating method involves forming a film/coating on the surface of the metal by chemical or electrochemical reactions. During this treatment, the immediate surface layer of the metal is changed into a film of metallic oxides/other compounds, which are chemically bonded to the surface. A part of the metal substrate is also converted into a part of the coating, which serves as a supporting base, improving the adhesion of subsequently deposited top coating and providing high corrosion resistance.

This book is dedicated to chemical and electrochemical conversion coatings of Mg and Mg alloys. The book covers both fundamentals and state-of-the-art advancements in these areas.

The first two chapters (Chaps. 1 and 2) of Part I provide fundamentals, categories, mechanisms, and paint adhesion of chemical conversion coatings. Chapters 3, 4, 5, 6, 7, 8, and 9 deliver detailed accounts of various inorganic chemical conversion coatings, including chromate, phosphate, permanganate, molybdate, vanadate, fluoride, carbonate, rare-earths, and zirconium- and titanium-based conversion coatings. The Chapter 10 gives an account of layered double hydroxide coatings, which are highly significant for Mg alloys.
The following three chapters focus on organic compounds–based chemical conversion coatings, viz phytic acid (Chap. 11), tannic/gallic acids (Chap. 12), and hydroxy benzene/phenolic acids and carboxylic/fatty acids (Chap. 13) conversion coatings.

The first two chapters of Part II (Chaps. 14 and 15) provide interesting accounts of self-healing chemical conversion coatings. The section also has chapters on ionic-liquid-based conversion coatings (Chap. 16) and chitosan-based conversion coatings (Chap. 17). The last chapter of the section (Chap. 18) accounts for superhydrophobic surfaces fabricated by different conversion coating methods.

Part III of the book focuses on electrochemical conversion coatings. Chapters 19 and 20 elucidate the fundamentals of electrochemical anodic oxidation and plasma electrolytic oxidation processes. Chapter 21 gives an account of recent approaches to enhancing the corrosion resistance of electrochemical conversion coated Mg alloys, whereas Chaps. 22 and 23 deal with micro-arc oxidation-based composite coatings and biomedical-grade electrochemical conversion coatings. Chapters 24 and 25, respectively, provide concise accounts of various sealing treatments and pre-treatments for electrochemical conversion coatings.

This book has tried to bring together all the important sections of chemical and electrochemical conversion coatings under one roof. We hope that the present book will be a handy reference tool for students and researchers working in different areas of corrosion and surface coatings.

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Part I
Chemical (Inorganic and Organic) Conversion Coatings
1.1 Introduction

Magnesium (Mg) alloys, the lightest metal structural materials, with high heat conduction, casting properties, excellent electromagnetic shielding properties, and biocompatibility (Wei et al., 2020), have wide applications in the biomedical, aerospace, automotive, and electronics industries (Esmaily et al., 2017). However, the most critical shortcomings that hinder widespread usage of Mg alloy are poor corrosion resistance and wear resistance. In general, Mg alloys are prone to corrosion in an aqueous environment. The corrosion of Mg alloy depends on the pH and the electrode potential, as exhibited in Pourbaix diagram (Fig. 1.1). Mg$^{2+}$ ions from the dissolution of Mg occur at the anode, where electrons are released to reduce water at the cathodic sites (i.e., impurities elements (Fe) or intermetallic compounds) and thus forming ions of H$^+$ and OH$^-$ (Kiani et al., 2020). Simultaneously, Mg$^{2+}$ and
OH⁻ are combined to produce a porous Mg(OH)₂ film on the surface of the Mg alloy; thereby the total chemical reaction (Eq. 1.1) takes place at these locations.

\[ \text{Mg} + 2 \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \uparrow \]  

(1.1)

In Fig. 1.1 the lines divide the diagram into three regions: corrosion (dissolved Mg²⁺), immunity (unreacted Mg alloy), and passivation (formation of passive film, e.g., Mg(OH)₂). In neutral and low-pH environments, Mg alloy suffers from the dissolution of Mg (Eq. 1.2) and hydrogen evolution (Eq. 1.3). In the vicinity of the Mg alloy surface, the accumulation of OH⁻ ions can rapidly increase the pH, which facilitates the precipitation of the chemical conversion coatings.

\[ 2 \text{Mg} \rightarrow 2 \text{Mg}^{2+} + 2 \text{e}^- \]  

(1.2)

\[ 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2 \uparrow \]  

(1.3)

As far as basic environments are concerned, the corrosion rate may remain constant approximately. In basic solutions, the surface of the Mg alloy is passivated by the formation of a Mg(OH)₂ film (Eq. 1.4). A by-product of that reaction is the production of OH⁻ with a concomitant increase of the pH and the stabilization of the local Mg(OH)₂ film and a decrease in corrosion tendency of Mg alloy. Since the MgO and Mg(OH)₂ films that form on the surface of the Mg alloy are slightly soluble in water, they do not provide long-term corrosion protection. When chloride, bromide, and/or sulfate ions are present in the solution, the surface film breaks down easily. Likewise, as CO₂ in the air acidifies water, the films are also unstable (Dhanapal et al., 2012).
It is worth noting that the lower pH or acidic solution is in favor of the formation of a thick coating, but a large number of micro-cracks may exist on the coating. On the contrary, when the pH of the solution is high, the micro-cracks become relatively less. That is to say, high solution pH leads to an increase in the compactness and corrosion resistance of the coating (Zai et al., 2019). For example, Zhang et al. investigated the effect of total acidity (TA)/pH on the microstructure and corrosion property of the phosphate conversion coating on Mg alloys. Figure 1.2a shows that a bath with a high TA/pH leads to a low nucleation density and high growth rate, resulting in the formation of coarse particles and some uncovered area as shown in Fig. 1.2b. In contrast, the solution with a low TA/pH corresponds to a high nucleation density and low growth rate, as shown in Fig. 1.2c. Since the growth of particles is restricted by the impingement of the nuclei with each other, it is easy to

\[ \text{Mg}^{2+} + 2 \text{OH}^- \rightarrow \text{Mg(OH)}_2 \]  

(1.4)
facilitate the formation of phosphate conversion coating with refined particles (Fig. 1.2c and d) (Zhang et al., 2019). Therefore, determining the appropriate pH range of the solution is crucial for coating formation.

In addition, due to the active nature of Mg, galvanic corrosion caused by the second phases, i.e., \( \beta \) or \( \text{Mg}_{17}\text{Al}_{12} \), in the Mg alloy always plays a dominant role in the corrosion rate. At the cathodic site (i.e., \( \beta \)), the cathodic reaction takes place and consumes the electrons generated from the anodic site (\( \alpha \)-Mg matrix phase). At the same time, on the anodic sites, Mg dissolves to form free Mg\(^{2+} \) ions, which provide electrons to the cathodic sites.

However, there exist some AlMnSi particles instead of \( \beta \) phase in the AZ31 Mg alloy. Therefore, the AlMnSi particles with a higher potential act as the cathode, and the \( \alpha \)-Mg matrix with a lower potential becomes the anode (Zeng et al., 2011a). In other words, the negative standard corrosion potential of Mg makes it prone to galvanic corrosion (Cai et al., 2018) by externally coupled with any dissimilar metals or by internally with secondary phases/impurities (Liu et al., 2019b; Saji, 2019; Coy et al., 2010). These issues must be tackled to address the high corrosion rate of Mg alloys.

### 1.2 Conversion Coatings

Conversion coatings have been employed on the surfaces of metals and alloys for more than a century. Generally speaking, conversion coatings refer to the coatings produced by chemical or electrochemical treatment of the metallic surface using coating solutions. Meanwhile, this coating can function as a stand-alone corrosion protection coating and/or as an adhesion promoting layer for the succeeding organic coating. Besides, conversion coatings involve (but are not limited to) molybdenum, chromium, vanadium, phosphate, cerium, and zinc-rich layers to increase the polarization resistance of the surface and hence decrease corrosion rates. Currently, there are a number of ways to classify conversion coatings. However, one of the most useful classifications is dividing them into chemical conversion coatings, electrochemical conversion coatings, and others. Among them, chemical conversion coatings are one of the most cost-effective methods of surface modification of Mg alloy substrates.

### 1.3 Chemical Conversion Coatings

Chemical conversion coatings are highly adherent due to the presence of chemical bonds and serve as an intermediate layer (i.e., Mg(OH)\(_2\)) between the coating and its underlying metal (Hornberger et al., 2012). Most importantly, short processing duration, easy operation, and cost-effective raw chemicals used for bath solutions are very favorable for industrial manufacturing. Currently, chromate, phosphate,
rare-earth salt, carbonate, phytate, and other solutions are commonly used in the chemical conversion process of Mg alloys (Fig. 1.3) (see Sect. 1.4). This chapter provides a brief summary of important chemical conversion coatings for Mg alloys. More details of these coatings could be found in subsequent chapters.

Chemical conversion coating is by far the most common method used in surface modification of Mg alloy. Placing a metallic substrate in a chemical conversion solution causes the following reaction at the interface:

$$m \ A + n \ B^{x-} \rightarrow A_m B_n + x n \ e^-$$  \hspace{1cm} (1.5)

where A refers to the metal that reacts with the medium, B refers to the anion of the medium, and $x$ refers to electron valence.

Chemical conversion coatings consist of thin layers of one or more materials that have been deposited onto or grown from the surface of Mg alloy substrates, which range in thickness from less than 100 nm to hundreds of microns (Song et al., 2020).
The chemical conversion coatings are applied to Mg alloys either to enhance corrosion resistance or to improve the coating adhesion or, ideally, to do both. This wet-coating technology, in general, generates a layer uniformly covering the surface of Mg alloy. The protective properties of chemical conversion coatings depend on the type of Mg alloy substrate and its surface conditions as well as the thickness and integrity of the coatings. Consequently, many factors affect the quality of the final coating, including the composition of the Mg alloy substrates, chemical pretreatments, composition of the conversion formulations, post-treatments, and operating parameters, such as pH, temperature, and immersion time (Abatti et al., 2018). All these factors influence the structure, composition, and performance of chemical conversion coatings. In addition, the characteristics of chemical conversion coatings have been extensively investigated including composition, structure, physical, and mechanical properties, solubility in ambient systems, porosity, hardness, abrasion resistance, adhesion, as well as corrosion resistance of Mg alloy substrates. Presently, chemical conversion coating of Mg alloy seeks continuous development to fulfill the growing demands of new properties that coatings are expected to bring while keeping the coating process economical but exhibiting the best corrosion protection based on greener formulations.

1.4 Major Types of Chemical Conversion Coatings

1.4.1 Chromate Conversion Coatings

Formation of chromate conversion coatings has been one of the most successful corrosion protection methods for light alloys. The major reasons for the widespread use of chromate conversion coatings are the high efficiency, high electric conductivity, ease of application, and self-healing capability; furthermore, they provide the greatest level of under-film corrosion resistance and facilitate the application of further finishing treatment. These advantages have made them a standard method of corrosion protection. In chromate conversion coatings, chromium exists in two different states: hexavalent chromium (Cr (VI)) and trivalent chromium (Cr (III)); the latter is the more stable form. The formation of chromate conversion coatings is accomplished by a series of dissolution, oxidation, reduction, and precipitation reactions. Once the Mg alloy substrate is immersed in the conversion bath, instant dissolution of the alloy occurs at the initial stage, followed by the interaction between the substrate and the solution at the interface. Moreover, Cr$^{6+}$ (Cr (VI)) reduces to Cr$^{3+}$ (Qi et al., 2021). When pH >6, Cr$^{6+}$ mainly exists in the form of CrO$_4^{2-}$ (Eq. 1.6). In this process, metallic Mg reacts with the solution to generate Mg and hydroxide ions, which significantly increases the interfacial pH, which in turn promotes the reactions (Eqs. 1.6–1.9). The dissolution and formation of the coating occur at the same time, and the reaction reaches an equilibrium state.
$$3 \text{Mg} + \text{Cr}_2\text{O}_7^{2-} + 8 \text{H}^+ \rightarrow 2 \text{Cr}^{3+} + 3 \text{MgO} + 4 \text{H}_2\text{O} \quad (1.6)$$

$$\text{Cr}^{3+} + 3 \text{OH}^- \rightarrow \text{Cr(OH)}_3 \quad (1.7)$$

$$\text{Cr(OH)}_3 + \text{OH}^- \rightarrow \text{CrO}_2^- + 2 \text{H}_2\text{O} \quad (1.8)$$

$$\text{Mg}^{2+} + 2 \text{CrO}_2^- \rightarrow \text{Mg(CrO}_2)_2 \quad (1.9)$$

However, Cr (VI) has been listed as one of the most toxic substances due to its carcinogenic effect and its harmfulness to the environment as a waste product due to current environmental legislation (Qi et al., 2020). Along with increasing calls for a total ban on toxic Cr (VI) in chemical conversion coating processes, many attempts have been made to develop eco-friendly alternatives (Liao et al., 2021b). Subsequently, Cr (III) was proposed as a possible alternative but proved to be less effective than Cr (VI). Consequently, there exists a need to identify new chemical conversion coating processes that can meet the requirements of recent environmental legislation and the desire for increased performance and multi-functionality.

### 1.4.2 Phosphate Conversion Coatings

Phosphate conversion coatings are made up of thin crystalline layers of phosphate compounds that adhere to the surface of the Mg alloy substrate. As we know, phosphate is the major component of bone tissue and is also an important part of implant (e.g., bone scaffolds), surface coatings, and commercial bone substitute materials (Song et al., 2019). Moreover, with excellent corrosion resistance and protection, phosphate conversion coatings make an obvious candidate as an alternative to chromate conversion coatings (Duan et al., 2018). Needless to say, the development of high-quality phosphate conversion coatings is gaining unprecedented attention. Nevertheless, micro-galvanic corrosion-induced dissolution at the substrate-coating interface is the predominant cause of alloy coating failure. Therefore, mitigating the micro-galvanic corrosion of Mg alloys will not only suppress the corrosion rate of the alloy but simultaneously improve the protectiveness or service life of the coatings. Liao et al. used pretreatment to remove the Alₓ(Mn,Fe)ᵧ phase to enhance the corrosion resistance of the phosphate conversion coating (Liao et al., 2021a). Generally speaking, a wide variety of phosphating compositions are available, but the best choice should be made in consideration of the nature of the Mg alloys and their end-use. Phosphate conversion coatings are generally insoluble in an aqueous solution at neutral pH, but soluble in acidic solutions (Chen et al., 2013b). Figure 1.4 illustrates how the predominance of Mg, Mn, Ca, and Zn in the presence of phosphate varies with pH and metal ion concentrations. For each of the metals presented, there is a boundary between an insoluble phosphate and soluble metal ions that extends diagonally from low pH, high metal ion concentration to high pH, low metal ion concentration. The location of this boundary varies according to metal ion species.
The popular phosphate conversion coatings systems (Table 1.1.) for Mg alloys include Ba-P (Chen et al., 2012), Ca-P (Cui et al., 2020), Ce-P (Zeng et al., 2016), Fe-P (Zai et al., 2019), Mn-P (Mosialek et al., 2011), Mo-P (Ishizaki et al., 2013), Sr-P (Han et al., 2016; Ke et al., 2019), and Zn-P (Yao et al., 2020). Combining the coating performance and Mg alloy nature, phosphate conversion coatings for biomedical usage have covered mainly Zn-P, Ca-P, and Zn-Ca-P coatings (Zeng et al., 2013, 2016) (Fig. 1.5). For example, the schematic diagram (Fig. 1.6) illustrates the formation mechanism of Zn-Ca-Ce-P coating. Once the Mg alloys are immersed in an acidic phosphating bath, the formation of coating promotes the compactness of Zn-Ca-Ce-P coating. Biologically relevant calcium phosphate belongs to the orthophosphate group and naturally occurs in several biological structures, including teeth and bone (Li et al., 2016). Consequently, calcium phosphate (Ca-P) coatings possess...
<table>
<thead>
<tr>
<th>Coatings</th>
<th>Composition</th>
<th>pH</th>
<th>Temp. (°C)</th>
<th>Duration (min)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-P</td>
<td>30 g/L Mn(NO3)2</td>
<td>2.0</td>
<td>60–85</td>
<td>30–40</td>
<td>Zhou et al. (2008)</td>
</tr>
<tr>
<td></td>
<td>40 g/L NaH2PO4</td>
<td></td>
<td></td>
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<tr>
<td>Ba-P</td>
<td>25 g/L Ba(NO3)2</td>
<td>2.35–3.0</td>
<td>50–70</td>
<td>5–30</td>
<td>Liu et al. (2008)</td>
</tr>
<tr>
<td></td>
<td>15 mL/L Mn(NO3)2</td>
<td></td>
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<tr>
<td></td>
<td>25 g/L NH4H2PO4</td>
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<tr>
<td>Mo-P</td>
<td>0.1~0.5 M Na2MoO4·2H2O</td>
<td>2.0</td>
<td>50</td>
<td>1–20</td>
<td>Ishizaki et al. (2013)</td>
</tr>
<tr>
<td></td>
<td>0.2 M H3PO4</td>
<td></td>
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<tr>
<td></td>
<td>0~0.2 M KF</td>
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<tr>
<td></td>
<td>0.18 M H2SO4</td>
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<tr>
<td>Ce-P</td>
<td>5 g/L Ce(NO3)3·6H2O</td>
<td>--</td>
<td>Room temp</td>
<td>120</td>
<td>Wang et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>1 g/L citric acid</td>
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<tr>
<td>Zn-P</td>
<td>10.0 g/L NaH2PO4</td>
<td>2.5</td>
<td>50</td>
<td>20</td>
<td>Zai et al. (2020)</td>
</tr>
<tr>
<td></td>
<td>6.0 g/L Zn(NO3)2</td>
<td></td>
<td></td>
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<tr>
<td>Ca-P</td>
<td>25 g/L Ca(NO3)2</td>
<td>3.0</td>
<td>40</td>
<td>5</td>
<td>Song et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>25 g/L NH4H2PO4</td>
<td></td>
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<tr>
<td>Mg-P</td>
<td>0.24 M H3PO4</td>
<td>4.27</td>
<td>25</td>
<td>30</td>
<td>Yin et al. (2020)</td>
</tr>
<tr>
<td></td>
<td>0.1 M Mg(OH)2</td>
<td></td>
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<tr>
<td>Sr-P</td>
<td>0.1 M Sr(NO3)2</td>
<td>3.0</td>
<td>65</td>
<td>2</td>
<td>Zeng et al. (2016)</td>
</tr>
<tr>
<td></td>
<td>0.06 M NH4H2PO4</td>
<td></td>
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<tr>
<td>Fe-P</td>
<td>100 mmol/L Na3PO4·12H2O</td>
<td>4.27</td>
<td>25</td>
<td>30</td>
<td>Yin et al. (2020)</td>
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<tr>
<td></td>
<td>8.43 mmol/L FeSO4·7H2O</td>
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<tr>
<td>Zn-Ca-P</td>
<td>10.0 g/L Na2HPO4</td>
<td>2.5</td>
<td>50</td>
<td>10–20</td>
<td>Zeng et al. (2011a)</td>
</tr>
<tr>
<td></td>
<td>4.0 g/L NaNO2</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>6.0 g/L Zn(NO3)2</td>
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<td></td>
<td>2.0 g/L NaF</td>
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</table>

**Fig. 1.5** Classification diagram of phosphate conversion coatings on Mg alloys
excellent biocompatibility, osteoconductivity, and nontoxicity which have attracted wide attention in bone replacement and biomedical application in orthopedics.

### 1.4.3 Rare-Earth Conversion Coatings

The rare-earth (RE) elements are a group of 17 elements that consists of the 15 lanthanides (La, Ce, Pr, Nd, Pm, Sa, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) and the two transition metals (Sc and Y). In recent years, RE conversion coatings, mostly cerium conversion coatings, have been extensively investigated for light alloys. Major superiorities of RE conversion coatings are modest price, excellent corrosion resistance, acceptable eco-friendliness, and synergism and compatibility with inorganic and organic co-additives. These conversion coatings are found to be mainly composed of oxides and hydroxides of rare-earths along with Mg oxides/hydroxides. Meanwhile, a significant number of works were reported that RE conversion coatings typically have a crack-mud surface morphology with a bi-/tri-layered structure having an inner compact crystalline layer. Most of the RE salts have high solubility in water. It is known that the majority of RE elements (Sm, Eu, and Yb) exist in solution as \([\text{RE(H}_2\text{O)}_n]^{n+}\). However, in addition to the \(\text{RE}^{3+}\) state, cerium is known to exist as \(\text{Ce}^{4+}\) (Saji, 2019).

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**Fig. 1.6** Schematic diagrams of formation of Zn-Ca-Ce-P coating (Zeng et al., 2016). (Reproduced with permission from (Zeng et al., 2016) © 2016 The Nonferrous Metals Society of China. Published by Elsevier Ltd.)
Several studies have reported that RE conversion coatings can provide excellent corrosion resistance to the Mg alloys substrate in aggressive electrolytes, especially for shorter durations. However, for long-term performance, subsequent treatment is essential. Generally, phosphate is used for the post-treatment of RE conversion coatings. Calado et al. showed that the combined effect of cerium and organophosphate makes cerium tri(bis(2-ethylhexyl)phosphate) (Ce(DEHP)₃) as an excellent inhibitor for AZ31 alloys, being able to sense and act upon different local pH environments, both in intact and damaged coatings. Hence, adding a certain amount of Ce(DEHP)₃ to a phosphate coating formulation led to efficient, long-term self-healing protection of the underlying Mg alloy substrate (Calado et al., 2020). In addition, organic co-additives, such as silanes and gelatins, can also observably improve the coating adhesion and corrosion resistance. Song et al. prepared gelatin-chitosan microcapsules containing La(NO₃)₃ via complex coagulation method. In a NaCl solution environment, microcapsules can effectively avoid corrosion by releasing active and restorative materials immediately after the coating integrity changes. The cerium conversion coating with microcapsules exhibits a much higher corrosive resistance than the coating without microcapsules and indicates the achievement of a self-healing performance (Song et al., 2016). Correa et al. reported that cerium ion is introduced in the silane matrix, and it increases coating thickness and hydrophobicity and confers good healing properties on defects formed by aggressive species. The addition of a corrosion inhibitor to silane coatings can modify barrier properties of the layer, increasing its thickness and densification, thus improving anti-corrosive performance (Correa et al., 2011). Saei et al. discovered that the addition of Mn²⁺ and polyvinyl alcohol (PVA) additives to a cerium-containing solution remarkably increases the corrosion protection performance of the deposited film. Furthermore, the cerium conversion coating reduces the number of galvanic couples that exist on the AZ31 Mg alloy surface, thus preventing it from corrosion. Figure 1.7 depicts a schematic of the cerium conversion coating. It can be seen that Mn²⁺ causes Mn (OH)₂ and MnO₂ deposition on the cathodic sites in the early stage of the reaction. PVA includes many oxygen-containing groups, among which the lone pair electrons of the oxygen groups can be shared with the empty orbital of Mg to form a PVA-Mn²⁺ complex in the cerium solution. Eventually, PVA-Mn²⁺ complexes may be converted into PVA-Mg²⁺ and PVA-Ce³⁺ complexes on the anodic sites of the AZ31 Mg alloy surface through a cation exchange reaction (Saei et al., 2017).

1.4.4 Fluoride Conversion Coatings

Studies have shown that fluoride is essential in the daily diet and is considered to be necessary for dental and skeletal growth. It is also one of the few known agents that can be used clinically for the prevention and treatment of osteoporosis. Many researchers studied the design of suitable conversion coatings to provide not only superior protection to the Mg alloy substrate but also biodegradability so that they can be degraded gradually allowing the healing of the damaged tissue. Among the
Fig. 1.7 Schematic presentation of the influence of PVA on the cerium conversion coating formation (Saei et al., 2017). (Reproduced with permission from (Saei et al., 2017) © 2017 Elsevier Ltd.)
conversion coating techniques utilized to match this need, the fluoride conversion pathway has aroused great interest for being one of the simplest and effective methods to improve the corrosion resistance of Mg alloy in corrosive media by the generation of a protective layer with high adhesion. In particular, the chemical conversion treatment of Mg alloys in fluorine solutions has been considered as an effective alternative for improving the corrosion resistance due to the formation of a compact, chemically inert, water-insoluble, biodegradable, and biocompatible MgF₂ layer.

In general, the conventional fluoride conversion coating preparation technique is dipping of the Mg alloy substrate in a hydrofluoric acid (HF) solution to form a protective layer of Mg hydroxide fluorides on the surface. Moreover, the structure, composition, and corrosion performance of those coatings can be affected by the different variables related to the conversion bath. In this regard, Barajas et al. evaluated the influence of the microstructure on the formation-biodegradation mechanism of conversion coatings synthesized on the AZ31 Mg alloy by immersion in HF solutions under different concentrations and treatment times (Fig. 1.8). Firstly, the AZ31 Mg alloy substrate reacts with the conversion solution to generate H₂. Further, AlₓMnᵧ particles are also dissolved in presence of HF solution, while RE-containing particles remain undissolved. Subsequently, Mg²⁺ ions, formed during the process, react simultaneously with OH⁻ to produce magnesium hydroxy fluoride compound on the AZ31 Mg alloy substrate surface (Fig. 1.8a, b). Nevertheless, the instability of Mg(OH)₂ in acidic solutions causes the hydroxide ions to be replaced by fluoride ions within the Mg(OH)₂Fₓ coating (Fig. 1.8c). From the results obtained in the investigation, it is important to highlight that the treatment time and HF concentration have a significant effect on the thickness of the coating. Meanwhile, the presence of cracks is preferentially caused by the presence of intermetallic particles in the Mg alloy substrate (Fig. 1.8d) (Barajas et al., 2019). Yan et al. have reported that the fluoride coating can improve not only the corrosion resistance but also the surface biocompatibility of the AZ31B alloy, and the antibacterial property of the coating was demonstrated in their study as well (Yan et al., 2014). Zhang et al. studied the effect of HF treatment on corrosion behavior and surface composition of Mg-Nd-Zn-Zr alloy. Direct cell adhesion ability is greatly improved due to increased surface energy and a decreased corrosion rate after fluoride treatment. Furthermore, both the Mg-Nd-Zn-Zr alloy substrate and the coating showed no adverse effect on human umbilical vein endothelial cells viability and spread morphology, indicating excellent cytocompatibility (Zhang et al., 2014b). Unfortunately, HF is a highly toxic solution that can cause incurable burns on contact with the skin. Taking into account the above advantages and disadvantages, many researchers developed a new chemical conversion method to replace the HF solution, to better apply it to human body. Currently, in addition to coatings prepared in HF solutions, unconventional fluoride conversion coatings can be prepared by immersing Mg alloys into Na[BF₄] salt melt. The results showed that the coating exhibits higher corrosion potential and lower corrosion current density than those prepared by immersing Mg alloy in HF solutions. Meanwhile, the polarization resistance of the coating with unconventional fluoride conversion