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# Sustainable Coatings on Metallic Alloys as a Nowadays Challenge

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**Abstract:** Starting with a description of the meaning of sustainable coating nowadays, this review presents a selection of methods for sustainable coatings manufacture using raw materials, saving energy and costs. This selection creates an introduction for the coatings performances of intensively investigated coated alloys and their multifunctionality. There are many examples and EU recommendations to be discussed, and we especially chose to introduce sustainable coatings with both industrial and medical functions, such as bioinspired films and coatings on high-entropy alloys, biodegradable metallic alloys, etc. A special focus is on nanotechnology and nanomaterials in green procedures, enhancing coatings' multifunctionality, introducing green corrosion inhibitors, smart additives, and coatings based on superhydrophobicity. The conclusions and future perspectives of sustainable and multifunctional coatings, as expressions of sustainable advanced materials, are based on important motivations of such studies.

**Keywords:** sustainable coatings; metallic alloys; green procedures

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## 1. Introduction

At the end of the last century and the beginning of the new one, the concept of enhancing materials properties only at the surface, as an economic way of increasing quality, was leading to a large number of procedures for surface modifications, including all kinds of coatings at the micro- and nano-level [1–6].

In the last decade, the dynamic development in industrial [7] and biomedical fields has been very aggressive, looking for more and more speed and performance of materials behavior in their service life. In this context, it is mandatory to keep in mind the future of our planet. Avoiding the depletion of natural resources, finding greener industrial processes, and maintaining an ecological balance became a challenge for all of us. All researchers also have a duty to share the knowledge in this domain, as a part of the sustainability of their strategy. As is well known, article 3 of the Treaty of European Union is a commitment to a 'high level of protection and improvement of the quality of the environment' [8].

In general, any sustainable product design is based on multiple inter-connected principles [9], as shown in Figure 1.

Sustainable materials refer to materials with a relatively positive impact on the environment, and they are used for product fabrication and service delivery [3]. The selection of sustainable materials depends both on objective and subjective factors, and several models have been proposed for their design [10]. The research in this field, with the help of nanotechnology [11], has been intensively extended in the last years, and a great part, such as in the building construction domain [12], has been transferred successfully into economic production quickly. Sustainable coatings have the general characteristics of sustainable materials that have a reduced negative impact on the environment, providing a chance for recycling and reduced elaboration costs, while maintaining the performances. An expression of this commitment in the field of coatings is of interest for bioinspired protections [13,14], green corrosion inhibitors [15,16], smart additives [17,18], etc.

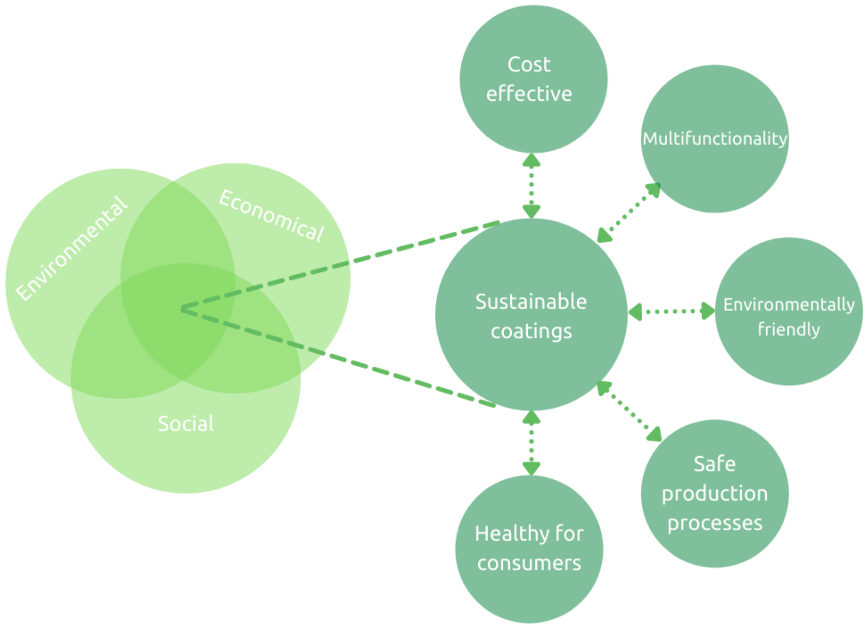


**Figure 1.** Schematic depiction of sustainable coatings based on the three pillars of sustainability.

The sustainability of coatings is characterized by the use of materials with multiple functionalities, while employing methods that minimize the waste, have low prices, pose little threat to humans, and save energy and resources [19]. Considering these highly complex factors, it is clear that a line between sustainable and non-sustainable processes cannot be drawn, but the principle aspects have been discussed and outlined, and therefore everyone must assess and improve. The latest regulations imposed by the governmental policies are forcing industries, as well as consumers, to find more sustainable, environmentally friendly approaches [20]. The multifunctional coatings sustain the materials and energy savings, serving different applications [21–23], for example, interesting research that addresses the current waste of millions of tons of fruits and vegetables, caused by decay, promotes an edible coating consisting of non-toxic zinc oxide nanoparticles with diameters between 10 and 40 nm, chitosan, and Arabic gum [24]. Another sustainable coating consisting of a thin layer of yttrium-doped zinc oxide–cadmium oxide on a glass substrate was proposed for the detection of $CO_2$. The sol-gel spin method used is a low-cost method that does not require much energy consumption or high amounts of chemicals [25].

The aim of this manuscript, and its novelty, is to present the challenges in sustainable coatings on metallic alloys research, regarding the trends in enhancing multifunctionality and performances using more environmentally friendly procedures [14,26].

In the present conditions of aggressive climate change [27], a narrative review with identified objectives about sustainable coatings, for more protection and future perspectives, is necessary. Although it is impossible to say which coating is better, we hope that through our review research, we may identify multiple sustainable methods that can be employed simultaneously to create a sustainable coating that may be further escalated in the industry, and ultimately improve the quality of life.

## 2. Methods

The safe-by-design (SbD) concept implementation aims at obtaining safer materials and products, safer use of products and safer industrial production. Compared to the older approach, which focused on measures applied retroactively, this approach would ideally be employed in the first steps of development, rather than once the process is started. However, improvements in reducing the risk for humans and the environment can still be achieved even in the later stages [28–30].

As an example, in a company that used pure silicon nanoparticles to increase the performance of batteries, the SbD concept implementation helped in lowering the toxicity threat for the workers, as well as lowering the risk of explosion, while achieving higher stability and performance. To do so, the nanoparticles' size was increased from 40 nm to 75 nm to reduce the alveolar deposition and the nanoparticles were coated with amorphous carbon, which led to increased performance and lower risk of explosion [29,31].

### 2.1. Methods in the Present Narrative Review Elaboration

We aim to present, through this review, important trends and challenges in sustainable coatings development, in the present conditions. We also try to objectively analyze the current research conducted in the area of functional coatings on metallic alloys and highlight the practices that promote sustainability.

The selection of the discussed articles is based on the current trends, their novelty and relevance to this review. It is important to mention that over 150 records were identified through multiple searches and screened for this summary.

### 2.2. Methods for the Development of Sustainable Coatings

The traditional manufacturing techniques, machining and casting, are generating a large amount of waste materials. Therefore, to achieve environmental sustainability researchers have begun to pay more attention to other methods, such as laser cladding, producing functional coatings with improved properties, while reducing the waste material and improving the costs associated [32–37]. The cold spray process has also been proposed as a sustainable, versatile method that can be used with various substrates for multiple applications. Although copper and aluminum were mostly used as coating materials, ceramic coatings, cobalt, nickel, iron or organic coatings can also be achieved [38].

A topic that is becoming more frequently discussed and studied is that of superhydrophobic surfaces. This is mainly due to the possible extensive applications, such as anti-icing, anti-corrosion, anti-fogging and self-cleaning coatings. This interesting property has been firstly observed in nature, in lotus leaves, rice leaves and butterfly wings. Although the fluorinated compounds are useful in creating this type of coating and have been used, they may be harmful to the environment, having bioaccumulative and toxic effects. Therefore, researchers moved towards non-fluorinated compounds that can manifest the same characteristics. These surfaces can be fabricated through multiple sustainable methods, such as spray coating, spin coating, dip coating, grafting method and vapor deposition method [39,40].

In many industrial processes, an important step is the purification of organic solvents from mixtures with water. Coatings may help as well in the case of azeotropic or near azeotropic mixtures, where the conventional separation methods require high energy consumption, besides having low efficiency. Considering the sustainability principles, a zeolite-based membrane, highly water-selective was constructed on an aluminum oxide support through wet gel conversion, using small quantities of gel and no organic matrix [41]. Another coating, based on the antifouling properties of zwitterions, has been used on stainless steel mesh by immersing the substrate in a copolymer solution. The copolymer used was a combination between dopamine methacrylamide (DMA) and a zwitterionic monomer, 2-methacryloyloxyethylphosphocholine (MPC). The coating has proved to be very efficient, separating the water from a mixture with n-hexane with an efficiency above 97% [42].

## 3. Trends in Enhancing Coatings Performances on CoCr Alloys and Other Metallic Alloys (Including High-Entropy Alloys)

There are several alloys with low density, resistance to corrosion, and reduced ion release in a large number of environments, as well as good mechanical behavior for a large temperature domain. These properties recommend alloys such as stainless steel, CoCr, aluminum, magnesium, and titanium alloys, also depending on other factors, namely, thermal and electrical properties, wear, stability, and processing costs, to be used in various industrial applications and the medical field [43–48].

Of course, for a specific application, each alloy has a different performance and the struggle for more efficiency in advanced technologies has introduced surface modifications, including coatings for more safety and more functionality in the service life. In Table 1, we present a summary of some alloys with different applications, before and after being coated, to highlight the improvements that a coating can bring. Some of the values reported here were approximated, as they were read on the figures available.

**Table 1.** Comparison between the properties of some uncoated and coated alloys.

| Alloy | Coating | Parameter | Uncoated Alloy | Coated Alloy | Ref. |
|---|---|---|---|---|---|
| 45 steel | FeNiCoCrTi0.5Nb0.5 | Hardness (HV) | 852 | 294 | [49] |
| Q235 steel | $CoCr_{2.5}FeNi_2Ti$ | $I_{corr}$ in simulated saturated salty water solution ($\mu A\ m^{-2}$) | $4.531 \times 10^{-4}$ | $1.386 \times 10^{-4}$ | [35] |
| | | Microhardness (HV) | 192 | 450 | |
| | | Wear weight loss (mg) | 5.8 | 3.2 | |
| Ti64 | Ti64+CoCr | Porosity (%) | 0.9 | 3.2 | [50] |
| | | Hardness (HV) | 360 | 430 | |
| | | Friction coefficient $\mu$ | 0.56 | 0.8 | |
| | | Wear rate ($\times 10^{-4}\ mm^3/Nm$) | 7.9 | 1.7 | |
| Zircaloy-4 | $ZrSi_2$ | Pool boiling ($kW/m^2$) | 858 | 813 | [51] |
| | | Leidenfrost temperature (°C) | 300 | 345 | |
| Ti-6Al-4V | Ti | Microhardness (HV) | 332.7 | 433.8 | [52] |
| | | Wear volume ($mm^3$) | 0.08 | 0.02 | |
| | | Wear width (µm) | 1.96 | 1.52 | |
| TiNbZr | Pectin/polypyrrole loaded with gentamicin | $I_{corr}$ in simulated body fluid (SBF) ($\mu A\ cm^{-2}$) | $1.715 \times 10^{-2}$ | $0.032 \times 10^{-2}$ | [53] |
| | | Growth inhibition (%)—*S. Aureus* | No antibacterial activity | 86.82 | |
| | | Growth inhibition (%)—*P. Aeruginosa* | No antibacterial activity | 80.00 | |
| | | Cell density (a.u.) | 0.55 | 0.75 | |
| Ti-5Cu | $TiO_2/Cu_2O$ | Contact angle (°) | 61 | 18 | [54] |
| | | Surface roughness (µm) | 0.221 | 0.427 | |
| | | $I_{corr}$ in 0.9% NaCl ($\mu A\ cm^{-2}$) | $1.85 \times 10^{-7}$ | $0.47 \times 10^{-7}$ | |
| | | Corrosion resistance of the inner layer ($M\Omega\ cm^2$) | 3.52 | 4.86 | |
| | | Antibacterial rate on *S. aureus* (%) | 83.4% | >99% | |
| CoCr | $TiO_2$–Ag | Wear (µm) | 20 | 5 | [55] |
| | | Wear loss (mg) | 0.3 | 0.1 | |
| | | Frictional force (N) | 1.85 | 0.94 | |

**Table 1.** *Cont.*

| Alloy | Coating | Parameter | Uncoated Alloy | Coated Alloy | Ref. |
|---|---|---|---|---|---|
| CoCr | Nb-Ta | Surface roughness (µm) | 1.16 | 3.49 | [56] |
| | | Contact angle (°) | 90 | 120 | |
| | | Microhardness (HV) | 500 | 800 | |
| | | $I_{corr}$ in Ringer's solution (µA $cm^{-2}$) | 3.03 | 0.369 | |
| | | MTS cell proliferation (absorbance) | 0.23 | 0.39 | |
| | | Hemolysis ratio (%) | 4.8 | 3.11 | |
| CoCr | TiSiON | Friction coefficient µ | 0.34 | 0.06 | [57] |
| | | Wear rate K ($\times 10^{-5}$ $mm^3$/Nm) | 3.5 | 0.6 | |
| CoCr | HA+12%Sr | Surface roughness (µm) | 1.2 | 4.6 | [58] |
| | | Microhardness (HV) | 480 | 310 | |
| | | Contact angle (°) | 93.81 | 56.12 | |
| | | $I_{corr}$ in Ringer's solution (µA $cm^{-2}$) | 2.59 | 0.08 | |
| CoCrNbMoZr | Diamond-like carbon–Ag | Contact angle (°) | 77 | 66 | [6] |
| | | $I_{corr}$ in simulated body fluid (SBF) (µA $cm^{-2}$) | 2.268 | 0.498 | |
| | | $I_{corr}$ in artificial saliva (µA $cm^{-2}$) | 1.127 | 0.390 | |
| | | Corrosion resistance due to the surface oxide layer in SBF (Ω) | 715.1 | 1185 | |
| | | Corrosion resistance due to the surface oxide layer in artificial saliva (Ω) | 3055 | 4509 | |
| | | Growth inhibition index (I%)—*S. Aureus* | No antibacterial activity | 61.75 | |
| | | Growth inhibition index (I%)—*P. Aeruginosa* | No antibacterial activity | 56.4 | |

This paper presents examples and the reasons why, during the last fifteen years, the industry and the biomedical field moved from conventional materials to micro- and nano-level materials, as more technically, environmentally, or economical solutions. As can be observed in Table 1, in the last years, the selection of alloys and the development of their processing are also strongly influenced by the safe use and the behavior in the environment.

CoCr alloys were firstly introduced at the beginning of the last century, in the aerospace industry, for the remarkable corrosion resistance of these alloys is similar to stainless steel, which is based on the formation of a passivation thin layer of $Cr_2O_3$. The molybdenum addition produces finer grains, which induces higher strengths after the majority of processing. The chromium enhances corrosion resistance, as well as solid solution strengthening of the alloy. Being biocompatible, CoCr alloys have been used successfully as implant materials, both coated and uncoated. Despite the advantages, due to the toxicity of cobalt and the allergic reactions caused by Ni [59], the discussion to eliminate CoCr and NiCr from dentistry has arisen [60]. The prevalence of nickel allergy has been estimated years ago in around 28.5% of the general population, and cannot be considered anymore as having a low potential risk [61,62].

The cobalt chromium alloys are widely used in metal on metal, or metal on plastic bearing, due to their great wear and corrosion resistance [57,63]. This alloy is also used in coronary stents, due to its elasticity and plasticity [64]. As a part of the new EU Medical Devices Regulation (MDR) (2017/745), toxicological risks of the cobalt–chromium alloys used in dentistry have been proposed to be applied in 2021 [65], cataloging Co as carcinogenic, mutagenic, and detrimental for reproduction [66]. It is important to mention that the trend to eliminate the use of CoCr and NiCr, due to toxicological risks evidenced in the EU regulations, has a relatively slow rate, and nowadays, more evaluations of their ion release are taking place [67]. Simultaneously with alternative strategies to reduce the risk of heavy metals for dental health, improving the quality of the CoCr alloys by changing their surface composition using coatings [68], new advanced technologies in obtaining CoCr for alloys have been tested [69,70].

Regarding their use as biomaterials, besides the possible metal ion release, the difference in modulus between the alloy and the bone, and the resistance to wear are also problems that need to be addressed [63]. The problems related to wear are not limited to biomaterials, they are related to all mechanical parts of automobiles, aircraft engines, and various equipment [71].

Coatings can help in overcoming these issues, and further improved the alloys properties. A successful coating deposition was achieved on a CoCr alloy via laser-engineered net shaping, using premixed powders of CoCrMo and tricalcium phosphate, and CoCrMo, tricalcium phosphate, and $Al_2O_3$. The hardness was increased by 40.2% and 60.7%, while the wear rate decreased by 82.3% and 71.6%, respectively [63]. Other surface coatings aim at improving the biological interaction. A biofunctionalization of a CoCr alloy was performed with genetically modified elastin-like recombinamers, to selectively promote the endothelial cell adhesion and multiplication [64]. Another simple, effective method used to prepare a biomimetic coating on a CoCr substrate has proven to be the immersion of the pretreated substrate in PBS solution, obtaining a uniform layer of hydroxyapatite [72].

Although CoCr alloys may exhibit superior mechanical properties compared to stainless steels and Ti alloys, the ions released upon corrosion can induce hypersensitivity and induce inflammatory reactions. In an attempt to mitigate these issues, several coatings were developed over time. Hydroxyapatite-reinforced Sr powder was used to create a layer through plasma spray, obtaining increased mechanical properties and biocompatibility [58]. Other approaches considered creating a metallic coating composed of more biocompatible metals, Nb and Ta. The coating was successful, obtaining improved corrosion resistance and increased hemocompatibility [56]. More-recent research describes the formation of a Ti nanolayer by thermal evaporation and posterior plasma nitriding processes, improving the tribological behavior of the uncoated alloy [73]. Also based on Ti, a nanostructure $TiO_2$–Ag coating was proposed to obtain an antimicrobial, bioactive surface [55].

Innovative strategies with both new advanced technologies and new coatings in obtaining new CoCr alloys have been introduced [6,70]. Regarding new compositions or alloys with new structures and properties, the trend is to involve more elements that are capable of inducing more functionality, even with the addition of small quantities. Frequently, such elements are rare elements, such as cerium, yttrium, or lanthanide, which are inducing remarkable mechanical properties and stability at elevated temperatures [74–76].

In the last decade, the strategy to design high-entropy alloys (HEAs) for structural service in the transportation and energy industries has significantly enlarged [77]. HEAs were designed for low ($\leq$150 °C), medium ($\leq$450 °C), and high ($\geq$1100 °C) service temperatures. The intermetallic phases were proposed as consistent with HEA definitions, and the strategy developed includes both single-phase, solid solution HEAs and HEAs with intentional addition of a second phase for particulate hardening [78].

The thermodynamic evaluation was helping to systematically screen and evaluate a large number of HEAs, by integrating high-throughput computations and experiments. The HEAs had attracted attention, due to their high strength/hardness, high wear resistance, high fracture toughness, excellent low- and high-temperature performance and structural stability, good corrosion, and oxidation resistance [79,80].

The initial approach of HEA manufacturing was to increase the element number and, simultaneously, the mixing entropy of the material, to establish a stable solid solution for alloy formation. It is an idea for multi-principal element alloys (MPEAs) or complex alloys (CCAs) to provide better performance through composition adjustment and by controlling the phase composition, including transitions from a single-phase solid solution towards a variety of complex phase compositions [81]. In such a way, a vast number of HEAs were divided into two main categories, after analyzing their deformation mechanisms [82]. The first category is based on the crystallographic structure of the phase, and it includes FCC-based, BCC-based, HCP-based, amorphous, and intermetallic HEAs. The second category, based on the type of phase, includes single-phase, dual-phase, eutectic, and multi-phase HEAs [83].

The most used techniques to prepare HEAs in bulk are ingot metallurgy, powder metallurgy, and selective laser melting [84], while laser cladding and magnetron sputtering methods are commonly used to prepare HEA coatings [49,85]. The selective laser melting technology (SLM) was investigated with Ar and $N_2$ as protective gases, on the alloy $CoCr_{2.5}FeNi_2TiW_{0.5}$. It was observed that the use of Ar led to the formation of a single-phase solid solution, while the use of $N_2$ led to the formation of a second phase (TiN). Although some studies suggest that a single-phase solid solution is preferred, the average yield strength, ultimate tensile strength, and average elongation showed higher values in the case of $N_2$ [86].

One of the downsides of preparing HEA is the cost associated with the production of such an alloy, due to the large percentage of rare metals. Methods for improving the problems associated with this are already starting to emerge. Therefore, to benefit from the properties of these materials, but also consider the sustainability principles, HEA coatings can be created on simpler substrates. To investigate this, a $CoCr_2FeNiMo_x$ coating was created through the laser cladding method, on a carbon steel substrate. It was observed that the coating provided improved mechanical properties and increased corrosion resistance [34]. A similar coating, also created by laser cladding, consisting of $CoCr_{2.5}FeNi_2Tix$, was created on a stainless steel substrate, obtaining increased corrosion resistance and improved hardness [35].

The zirconium alloys, namely, zircaloys, are widely researched as accident-tolerant fuels, especially after the Fukushima accident. Their mechanical properties, as well as their corrosion resistance and neutron irradiation resistance, make them a good fuel cladding material. One of the biggest challenges is that, in contact with high-temperature, large levels of hydrogen are released. Several coatings have been proposed to help with this issue, FeCrAl, CrAlN, CrAlSiN, SiC, CN, Cr [87–92]. Moreover, zirconium and zirconium alloys are used as implant materials, having great biocompatibility [93–95].

Titanium and titanium alloys are also intensively used in a large number of applications, due to their outstanding corrosion resistance, great mechanical properties, and good biocompatibility [54,96]. A problem with these alloys as biomaterials is that they may be a cause of thrombosis when they come into contact with blood, as in the case of coronary stents, and anticoagulation medication is usually prescribed to prevent this from happening. Coatings that encapsulate drugs, such as aspirin, have been proposed to further improve the biocompatibility [97]. Other coatings aim at improving the biocompatibility by obtaining bacteriostatic [98,99] and bactericidal [100] properties. In other applications, such as the aerospace industry, the mechanical properties of titanium alloys need further improvement, and multiple hard coatings were developed as a solution [100].

Furthermore, creating different oxide nanocomposites from oxides such as, $ZrO_2$, $ZnO_2$, and $TiO_2$ is also of great interest nowadays, due to their potential multifunctional properties, such as antibacterial, antireflecting, self-cleaning, etc. [101]. Additionally, for the synthesis of $TiO_2$ nanoparticles, a large number of green methods have already been proposed, based on extracts from plants, fungi, and even bacteria [102].

## 4. New Challenges in Coatings on Biodegradable Mg Alloys

The biodegradable Mg alloys show great potential as biomaterials, due to their density and elastic modulus, which are very close to those of the human bone. However, their high degradation rate may not be suitable in all cases [103–106]. They are also investigated for other fields, such as electronics, aerospace, automotive, etc. [107,108]. It is clear that not all Mg alloys behave in the same way, and that choosing the alloying elements is the first step in developing a successful material. Different elements, and their influence on the microstructure and the corrosion resistance, were presented by Fattah-alhosseini and Chaharmahali in a review study [109].

Magnesium alloys react easily in the physiological environment, considering a neutral pH, the following reaction takes place:

$$Mg + 2H_2O \rightarrow Mg^{2+} + 2OH^- + H_2 \uparrow \quad (1)$$

Due to the hydrogen gas resulted in the reaction, which is only tolerated in a very low dose (0.01 mL/cm$^2$/day), a gas pocket may form, leading to implant failure. Moreover, both the hydrogen and the hydroxyl anion can disrupt cellular functions. Additionally, the local alkalization leads to the formation and precipitation of hydroxides on the alloy surface, which can react with the chloride anions, causing pitting corrosion [110–112].

Creating surface coatings may help in overcoming this limitation. Moreover, functional coatings can further improve the biocompatibility of such alloys [113–117]. Several novels, multifunctional coatings are presented in Table 2, and some of these, along with others, are discussed in more detail below.

**Table 2.** Multifunctional coatings on Mg alloys.

| Substrate | Coating | Coating's Characteristic | Method Used | Results | Ref. |
|---|---|---|---|---|---|
| MgAlZn (AZ31) | Nanocontainers of 2-mercaptobenzothiazole loaded with mesoporous silica nanoparticles and layered double hydroxide nanosheets shell | Nanocontainers with uniform spherical shape with an approximate diameter of 90 nm after loading and encapsulation | Dip coating | -highly improved corrosion resistance | [118] |
| MgAlZn (AZ31) | Micro-arc oxidation/ciprofloxacin-polymethyltrimethoxysilane | Bird-like structure, approximate thickness of 35 µm | Micro-arc oxidation and dipping | -increased corrosion resistance<br>-long-term drug release<br>-efficient inhibition on *S. aureus* and *E. Coli* | [119] |
| MgAlZn (AZ31) | MgO and polytetrafluoroethylene nanoparticles | Polymer-like, porous multilayer with rough surface texture | Plasma-induced thermal-filed assisted crosslink deposition | -superhydrophobic<br>-improved mechanical properties<br>-high-temperature resistance<br>-self-cleaning<br>-low friction coefficient | [116] |
| MgAlZn (AZ31) | 2-methylene-1,3-dioxepane,vinyl acetate, 7-(2-methacryloyloxyethoxy)-4-methylcoumarin, and dopamine methacrylamide | Biodegradable copolymer coating | Electrophoretic deposition and UV irradiation treatment | -increased corrosion resistance<br>-good cytocompatibility | [120] |
| MgZnYNd | hyaluronic acid/polyethyleneimine nanoparticles after fluorination/poly-dopamine treatment | Hydrophilic surface with different roughness depending on the size of the nanoparticles | Dip coating | -improved corrosion resistance<br>-better biocompatibility | [121] |
| MgYNdZr (WE43) | poly(etherimide) and sirolimus loaded poly(lactic-co-glycolic acid) | Polymer asymmetric coating, consisting of an inner single layer and an outside/side sirolimus loaded double layer | Sequential spray coating | -great substrate adhesion<br>-improved cytocompatibility and corrosion resistance<br>-slow release rate of sirolimus | [122] |

**Table 2.** *Cont.*

| Substrate | Coating | Coating's Characteristic | Method Used | Results | Ref. |
|---|---|---|---|---|---|
| MgZnMn | nano-hydroxyapatite (nHA) | Cubical nanoparticles with interconnected surface porosities of 5–10 µm. Coating thickness between 12 and 22 µm depending on the nHA concentration | Electric discharge machining | -very reduced degradation rate -increased microhardness -improved cytocompatibility | [113] |
| MgCaZn | $Ta_2O_5$ and poly (ε-caprolactone)/MgO-Ag | Dense film of $Ta_2O_5$, with no cracks or pores covered with nanofibers (200–360 nm diameter) with porous structure | Magnetron sputtering and electrospinning coating | -improved corrosion resistance -antibacterial activity | [123] |
| MgZnCa | Silk fibroin/sodium alginate | Uniform coating, without cracks, with an average thickness of 5 µm | Micro-drop deposition | -improved mechanical properties and corrosion resistance | [104] |
| MgZnYNd | poly-dopamine/hyaluronic acid (HA) | Surface with particles of several micrometers and various roughness depending on the molecular weight of the HA used | Dip coating | -improved corrosion resistance -pro-endothelialization ability | [106] |

In the case of biomaterials, most coatings focus on calcium phosphate, as it is the main component of the bone tissue and has excellent biocompatibility. Multiple physical and chemical methods have been developed with time, which can create such coatings. One of these methods, which can be performed at room temperature and does not require high cost, is the electrodeposition method [124]. Plasma electrolytic oxidation (PEO), also known as micro-arc oxidation (MAO), is another promising technique that is capable of creating coatings based on the species that originate from the substrate, and the species from the electrolyte used [125]. The method was successfully used on a Mg–5Zn–0.4Ca alloy in a phosphate solution, creating a porous, three-layer coating. The electrochemical data showed a decrease in the corrosion current and an increase in the corrosion resistance, compared to the Mg substrate [126].

Three different coatings were created on a Mg alloy (Mg–2Zn–1Gd–0.5Zr), to decrease the degradation rate and improve the resistance to wear. One coating was achieved through MAO, using KF, $(NaPO_3)_6$ and $Ca(OH)_2$, while the other two coatings were performed through immersion of the sample. For the coating named Ca-P, the samples were immersed in KF for 24 h, after which they were placed in a solution that contained $NaNO_3$, $Ca(H_2PO_4)_2$, and $H_2O_2$ for another 24 h, and for the coating named Sr-P, the samples were immersed in a solution containing $Sr(NO_3)_2$ and $NH_4H_2PO_4$ at 80 °C for 12 min. It was observed that through MAO and Sr-P coatings, the degradation resistance of the alloy was improved, while the Ca-P coating increased the wear resistance [103].

In another study on a Mg-Ca alloy, the coating formed through MAO was further improved by creating another coating on top of poly (lactic acid) (PLA), through a simple dip-coating process. This second layer has effectively sealed the porosities of the first layer, improving the corrosion resistance even more [127].

Graphene and graphene oxide were also used with PEO to create a thicker coating layer that improves the corrosion resistance and the resistance to wear [109].

While some coatings may help in solving the problems related to this type of alloy, researchers must avoid introducing possible additional problems, as in the case of non-degradable coatings. With this idea in mind, several degradable coatings have been studied, poly-L-lactide (PLLA), poly(3-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and poly(lactic-co-glycolic) acid (PLGA). These coatings were prepared through spin-coating, giving uniform, non-porous coatings. From this, PLLA, PHB, and PHBV had successfully suppressed the corrosion of the substrate, due to the lower water permeability, and also improved cell proliferation [110].

Another approach that showed positive results and must be considered is related to the treatment of the substrate before coating. In a research conducted by Li et al., it was shown that by changing the microstructure through equal channel angular pressing (ECAP) before MAO coating, the degradation rate can be further improved and so can the mechanical properties of the alloy. By refining the grain size, it was possible to obtain a denser coating, compared to the alloy as-cast; therefore, the corrosion resistance was improved [128].

Aiming at saving time and improving the costs, one of the techniques used for cutting and shaping biomaterials (electric discharge machining—EDM) was also used to create a coating of nano-hydroxyapatite on a Mg–Zn–Mn alloy. The coating helped in reducing the degradation rate by 90.85%, while improving cell attachment and proliferation [113,129].

More recently, researchers are starting to create a path for multifunctional coatings that could extend the use of this type of alloy in challenging environments [118,119,130]. One such method was developed to create a multilayer with both organic and inorganic components, through plasma-induced thermal-field-assisted crosslinking deposition (PTCD). The method is an eco-friendly method, allowing hierarchical textures to be created, in which the inorganic layer and the organic layer grow simultaneously, in one step [116].

Another issue with biodegradable Mg alloys, besides their fast degradation rate, is the poor antibacterial performance. The use of nanoparticles, nanofibers, or multilayer coatings to inhibit bacterial infections or to provide a suitable substrate for drug-loading is gaining more and more attention. Following the idea of inducing antibacterial properties, a type of surface coating was proposed, using silver-doped hydroxyapatite nano-powder (Ag-HA) by micro-arc oxidation. The coating clearly provided antibacterial properties, but decreased the corrosion resistance [131].

Research on a Mg–Ca–Zn alloy that was aiming at tackling both these issues, while considering the sustainability principles, has proposed a surface coating with a layer of tantalum oxide ($Ta_2O_5$), through physical vapor deposition (PVD), to reduce the degradation rate, followed by a layer of poly(ε-caprolactone)/magnesium oxide–silver (PCL/MgO–Ag) through electrospinning, to induce antibacterial properties [123].

## 5. Nanofabrication Aspects of Green Procedures in Enhancing Coatings Multifunctionality (Green Corrosion Inhibitors, Biomimetic Coatings, Bioinspired Coating Based on Superhydrophilic and Superhydrophobic Coatings, Smart Additives)

In the initial time of their applications, nanotechnology and nanostructures were regarded as having only positive effects in many fields, but after the initial period, when more knowledge had been accumulated, especially regarding the impact on health, the merits and demerits were better understood [132,133]. In the coatings world, the nanostructures benefits were exploited successfully, enhancing performance and functionality in many domains, introducing more stability and corrosion resistance in various aggressive environments, including bioliquids. A better cell response, as well as more adhesion and better mechanical properties [134–136] were obtained via more green coating fabrication methods. Some multifunctional coatings that are discussed in more detail below are presented in Figure 2.

Various procedures are practically used to control metals corrosion, and coatings are the most widely performed for this purpose [137–139]. Generally, coatings to retard corrosion act by one or a combination of the following mechanisms: (1) cathodic protection, with a more electropositive material serving as sacrificial anode [140]; (2) anodic passivation by the formation of a passive layer that acts as a barrier against corrosion [141]; (3) electrolytic inhibition, which impedes the corrosion, blocking the transport of ions between the anode and cathode using a diffusion barrier [142]; and (4) active corrosion inhibition, which bind ligands to the metal surface, stopping corrosion development [139]. Active corrosion inhibition based on barrier building involves the coating failure and the incorporation of components selectively released upon coating damage, into the newly formed protective barrier on the metal surface [138,143].

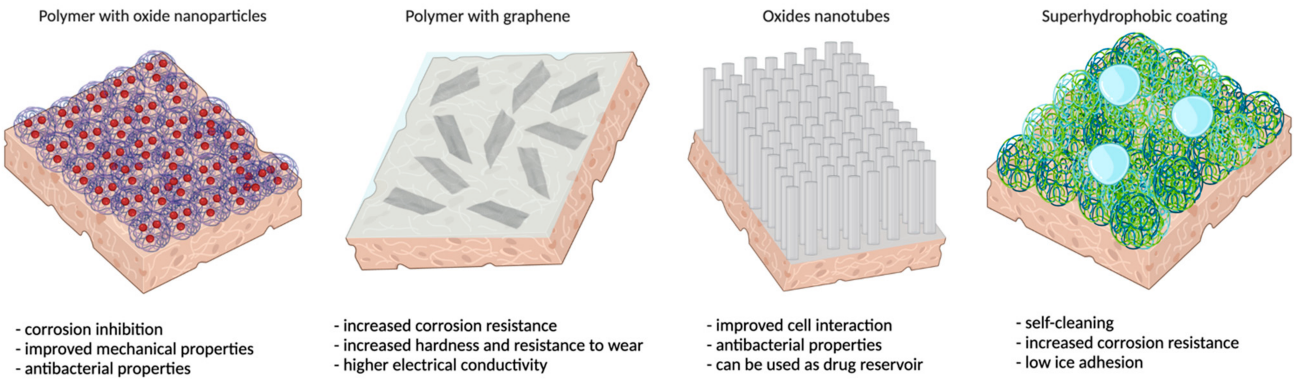


**Figure 2.** Schematic representation of some multifunctional coatings on metallic alloys and their properties/applications.

The polymers used for coating [144] have weak resistance to the penetration of corrosive solution at the metal/coating interface, and introducing nanoparticles in polymer coating is improving the protection of the surface [145]. Depending on the nanoparticle type and dimensions, the new hybrid coating could induce other properties, such as antibacterial inhibition, wear resistance, etc. We mention the recent investigation related to the incorporation of ZnO nanoparticles into nanosilica-containing epoxy formulations, leading to not only better corrosion resistance, but enhanced mechanical properties as well [146]. Nanocomposites in which the nanoparticles of one phase are dispersed within a continuous polymeric matrix phase represent a topical design approach to multifunctional coatings, resolving problems such as dispersion and compatibility [140].

The incorporation of metallic, porous metal oxide, graphene, and carbon nanotubes within polymeric matrices are explored and explained as active corrosion inhibition [147,148]. Such an active corrosion retard mechanism is based on the electroactive properties of metals, graphene, carbon nanotubes, or on their ability to serve as reservoirs for active corrosion inhibitors such as porous silicon oxide, layered double hydroxides, and halloysite [149,150]. Both ways of action provide multifunctional opportunities for novel coatings [140], developing a systematic design approach for corrosion inhibition when other properties are induced as well.

Smart coatings based on the polymer matrix doped with carbon nanomaterials, such as carbon nanotubes or graphene, enhance their performance, increasing their barrier properties, corrosion resistance, hardness, and wear strength [151–155]. This is a new generation of protective organic coatings, capable to respond intelligently to damage or external stimuli. Carbon nanostructures induce new functionalities to coatings [156], related to the higher electrical conductivity [142] of nanocomposites, due to the percolation network formation. Having electrical resistance, such coatings can be used as sensors and gauges, and act as self-heaters. When an electrical voltage is applied, it can be used in defogging and deicing.

The design of graphene nanocomposite coatings for aluminum alloy protection is also an important aspect of sustainable and green procedure for aircraft industry development. Aluminum itself, as structural aircraft material, has an excellent passive layer, but the need to stabilize high-strength alloys involves the addition of other components, leading to a complex microstructure with various intermetallic inclusions that render the resulting material more vulnerable to local corrosion. Chromium-based conversion coating is a remarkable protection of aluminum, but it is well known that hexavalent chromium effluents released at various points in production, as a byproduct, have a highly toxic and carcinogenic effect [142]. The ecological toxicity and human health impact of hexavalent chrome have led to the strict regulation of its use in products [140,157], and no chromate pretreatment being imposed [158].

With the increasing use of aluminum alloys for vehicular applications, the development of sustainable chrome-free coatings has emerged as imperative. Zinc and trivalent chrome are used frequently to protect steel substrates, but are ineffective in providing sacrificial cathodic protection to aluminum alloys, due to the value of aluminum redox potential. Magnesium-based nanocomposite coatings have been developed, but, due to the high reactivity of Mg particles, the safe preparation of a surface-passivated Mg surface is difficult, especially in some environments [159]. The graphene nanocomposite coating with sub-30 µm thickness is a successful alternative when it is dispersed in a matrix such as a polyetherimide matrix, showing very good corrosion inhibition of Al 7075 substrates, even when exposed to saline environments for a long time [160].

Biomimetic coatings are another type of coatings, inspired from nature, as nature has already solved many complex problems through natural selection. Therefore, these coatings have been investigated in different areas, such as solutions for marine biofouling [161], building construction materials [162], and medicine [163].

The synthesis of biomimetic coatings is showing very promising results in medicine, creating materials with improved biocompatibility [164–166], while, in other areas, the morphology of these bioinspired coatings generates versatile properties, such as a hair-like composite coating, consisting of $Fe_3O_4$ particles, resin, and perfluorodecyltriethoxysilane, which has water-collecting and superamphiphobic properties [167], or a flower-like coating, composed of $CeO_2$ and polydopamine, creating a superhydrophobic surface that can be used to prevent hydrate plugging [168].

An important characteristic of modern coatings, which can define future applications, is the value of contact angle. A coating with a contact angle value greater than 150° in water is a superhydrophobic surface, and presents not only deicing ability, but also stimuli-chromism, antibacterial activity, flame retardant, and lubricating properties. Coatings with contact angle values less than 90° are hydrophilic, and when the values are under 10°, the surface is superhydrophilic [169–171]. A large number of coating components can increase or decrease the contact angle, leading to a biomimetic structure that is able to induce special properties and multifunctionality. An example of a contact angle decrease leading to better performance is anodic oxidation on the surface of the ZrTi substrate. The anodizing process of the ZrTi substrate is a simple and low-cost method, and depending on the chosen anodizing parameters (duration of anodizing, electrolyte, etc.), the structure and the morphology vary, leading to different types of nanostructures, such as pores, tubes, or channels [172–175]. After annealing, the nanopores and nanotubes oxides ($Zr_3O$, $ZrO_2$), along with TiZr mixed oxides ($Ti_2ZrO_6$, $Ti_2ZrO$, $ZrTiO_4$), have contact angle values between 2° and 6°, and present an antibacterial effect. An interesting correlation between contact angles, roughness values, their stability in bioliquids, and biological aspects was obtained for investigations performed on the hybrid complex coating on the same alloy substrate, covered with a biomimetic composition of hydroxyapatite (HA) and chitosan (CS) in various ratios. Compared with the noncoated alloy, and depending on the chitosan content, this bioinspired coating presents better properties; the most hydrophilic one, with the ratio HA:CS = 1:2, has the lowest reactive oxygen species (ROS) level and the best organized actin cytoskeleton, which promotes the most remarkable cell proliferation rate [176,177].

Another superhydrophilic surface with many more multifunctional applications, such as self-cleaning, oil/water separation, antifogging, etc., was elaborated in a one-step coating method [178] that is suitable for a variety of substrates, both inorganic and organic, using the coordination complexes of natural phytic acid (PA) and Fe(III) ions. The final coatings are very thin and transparent, elaborated in a fast process that is cost-effective and environmentally friendly. The high density of phosphonic acid groups was proposed to be responsible for the superhydrophilicity in such a procedure [178]. A plant-inspired, layer-by-layer, self-assembly, superhydrophobic modification of various highly hydrophilic polymer materials, based on a molecular building block of the PA–Fe(III) complex to anchor the substrate and the hydrophobic thiol groups (HT), was proposed initially, to separate the oil–water mixture and oil spill clean-up [179]. It is a green modification method that can be applied to a variety of substrates.

According to the Cassie–Baxter model [180], the hydrophobic behavior of the material surface is a synergic effect of the chemical properties and the roughness of the material surface. Although silicon/fluorine materials are known as very low surface energy materials, with remarkable properties, such as weather and corrosion resistance, and refractory and oxidation stability [181], the high price of silicon/fluorine-modified coatings, and their difficult elaboration process, limits their applications. A more economical method to fabricate a formulation based on fluorine resins and $SiO_2$ nanoparticles yielded performance comparable to other commercially available systems. This was applied for the conservation of the monuments allowing graffiti removal, and decreasing damages [182], with fewer costs and environmental impacts. Other methods based on the increase in contact angles were developed, introducing various polymeric sponges with superhydrophobic properties [183].

Smart additives, such as self-sealing and self-healing, based on graphene penetrated the plastic industry, being used in greenhouse, food packaging, and self-curing concrete applications. Multifunctional graphene-based nano-additives and high-performance polymer nanocomposites have enhanced mechanical, thermal, flame retardancy, and smoke-suppressive properties [17], being another example of nano-aspects for sustainable methods, increasing the life of materials.

To summarize the important achievements in the field of nanocoatings, it is important to have a look at the development of nanocontainer-based self-healing coatings that are able to release anticorrosion inhibitor agents or other active components. The concept of such coatings combines the classic passive component of the coating matrix (layer) with an active agent that is responsive for both internal and external events in different environments [184].

In the last years, the role of green attributes in production processes of sustainable coatings was established, and their impact on operational, commercial, and economic benefits was understood, contributing to a better coatings selection [185].

## 6. Conclusions

In the last decades, we have become significantly more aware of the impact that we have on the environment, and have gathered a better understanding of the processes happening at the sub-micrometer level. Through a combination of this knowledge, we observe a rapid increase in the research areas towards designing materials at the nanometric scale, while evaluating the sustainability of the processes involved. Researchers are continuously evaluating methods and materials to find the right combinations between materials properties, and safe, economical, and environmentally friendly methods.

The coatings developed nowadays are more complex, regarding both composition and design. Regardless of the alloy used as the substrate, there is increased research on polymeric coatings that include nanoparticles or active pharmaceutical substances, and sometimes even both. Other coatings, consisting of metallic oxide nanostructures and graphene-based nanostructures, are also of great interest, due to the multifunctional nature of these coatings. High-entropy alloy coatings must also be mentioned, as they represent a relatively new area that we are just beginning to explore, but are already showing great results.

Although things are evolving at a very fast pace, we observe that research is keeping up and finds sustainable solutions. The difficult part may be implementing these solutions in the industry sector, and the real challenge is to make these changes fast enough, so that the environmental damage will not become irreversible. We can say that greener coatings in all kinds of fields, including biomedical, electronic, automotive, and construction applications, are the right response to the current challenges.

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