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Review

Electroplating for Decorative Applications: Recent Trends in Research and Development

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Abstract: Electroplating processes are widely employed in industrial environments for a large variety of metallic coatings, ranging from technological to decorative applications. Even if the galvanic electrodeposition is certainly a mature technology, new concepts, novel applications, environmental legislation and the new material requirements for next-generation devices make the scientific research in this field still very active. This review focuses mostly at the decorative and wearable applications, and aims to create a bridge between the past knowledge and the future direction that this process, i.e., electrodeposition, is taking. Both the theoretical fundamentals as well as some of the most widespread practical applications—limited to metallic and alloy coatings—are explored. As an integral part of the industrial process, we take a look at the main techniques thought which the quality control of deposits and surfaces is carried out. Finally, global industrial performance and research directions towards sustainable solutions are highlighted.

Keywords: galvanic electrodeposition; electroplating; alloy deposition; galvanic industry research and development; metallic film characterization

1. Introduction

With the advent of the Fourth Industrial Revolution research and development within metal finishing sectors is rising [1,2]. The demand for durable metals and adaptable manufacturing processes are needed across a wide range of applications, from automotive and aerospace to jewelry and machinery [3,4]. An essential step in all manufacturing process is the surface engineering of metals, as this determines the final appearance and functionality of a product. Depending on the desired properties of the surface, base material, and geometry of components, a variety of procedures and technologies are available, classified as additive or subtractive.

Additive processes include deposition methods, such as physical vapor deposition [5–7], laser technology [8], thermal spray [9,10] and electrochemical deposition [11–13], to name a few. Among them, galvanic electrodeposition is scientifically recognized as a mature technology and one

of the most effective, as well as low-cost, in industrial sectors worldwide. The essential feature of electroplating is the diffusion process of ions, resulting in the production of well-defined, high-quality surfaces with a conformal thickness profile. Exact layer thickness control, high quality morphology, and well-controlled composition and uniformity, low thermal load of the work-piece, and low production costs per factory piece are among the main strengths of electroplating. The production of metallic coatings involves electrochemical reactions at the electrode/electrolyte interface, which lead to the deposition of ions from the solution to the electrodic surface with the electron transfer.

The art and science of modern electroplating dates back to the beginning of the 18th century [14,15]. In 1805 an Italian University professor, Luigi V. Brugnatelli, performed the first documented electrodeposition of gold metal from a saturated gold solution on the surface of two large silver medals by means of connection to the voltaic Zn/AgO pile invented in 1796 by Alessandro Volta. However, his work was rebuffed by the emperor Napoleon Bonaparte and suppressed by the French Academy of Sciences. Thirty years later scientists from Russia and England independently devised a process similar to Brugnatelli's work for electroplating copper on metal plates. In 1836 Prof. J. F. Daniell from the King's College described the constant voltage battery consisting of a zinc electrode immersed in sulfuric acid and a copper pot filled with a solution of copper sulfate, thus rediscovering electroplating and the deposition of thin uniform coatings [16]. The work of Daniell was reproduced in 1837 by B. S. Jacobi, who deposited a metal onto an engraved copper plate through a process called electroforming [17].

Electroplating gained interest starting in 1840, when Henry and George Elkington from Birmingham, England, were awarded the first patent for adapting this technology to gold and silver deposition using potassium cyanide as an electrolyte [18]. This led to the establishment of Birmingham as the industrial center for electroplating, where the first large-scale plant was constructed on 1876. Later, Jacobi reported another significant industrial development on the use of more stable ferrocyanides in gold plating, thus providing the capability of depositing gold alloys containing silver and copper. From then on, electroplating quickly spread throughout the rest of the world and became a common process for depositing precious and non-precious metals, including copper, gold, nickel, brass, tin, and zinc. Apart from the advent of electrical power generation and hard chromium plating, few significant scientific improvements were made within the late 19th and early 20th centuries. Rediscovery of electroplating occurred after the Second World War with the discovery of transistors and the growth of the electronics' industry. In 1946 Abner Brenner and Grace E. Riddell discovered the first autocatalytic metal deposition (also known as "electroless" deposition) by adding sodium hypophosphite to a nickel bath [19]. Later research on electroless deposition benefited a very large range of industrial sectors, in particular the metallization of printed wiring boards. Parallel to the discovery of electroless deposition was the production of multi-layered deposits from a single solution. Significant improvements on alloyed and pure multi-layers were outlined by Tench [20] and Yahalom [21] in the 1980s, thus producing deposits with unique mechanical, electrical, optical, and magnetic properties. In addition to advances in plating, more "*user friendly*" and sustainable baths were implemented since the early 1950s by replacing cyanide baths with acidic solutions [22]. Today, a deeper knowledge of the electrochemical aspects underlying electrodeposition as well as research on new materials and emerging technologies are driving the traditional manufacturing process towards a more reliable, flexible and interconnected production [23].

As of 2015 electroplating represented around 37% of the total market share within the metal finishing sectors. The most commonly used galvanically-deposited metals are zinc and zinc alloys (about 15%), followed by nickel, copper, chromium, tin, and precious metals (together approximately 22%) [24]. According to a recent study published by Future Market Insights the global electroplating market is expected to increase at a compound annual growth rate (CAGR) of 3.7% over the forecast period of 2016–2026, projecting revenues of over US $21 billion by the end of 2026 [25]. Significant expansion will occur in the Asia-Pacific, excluding the Japan (APEJ) region, registering a CAGR of 4.6% over the foreseen period. The market for mature electroplating industries in North

America and Western Europe will maintain the leadership. However, large-scale industrialization of electroplating techniques will continue to be limited by strict environmental regulations. Due to adverse ecological impacts, the adoption of plating processes involving toxic metals, such as lead or cadmium, is prohibited by global legislation. Another issue facing industrial development is the price volatility of highly on-demand electroplated materials, i.e., gold, copper, and nickel. In particular, the request for copper, nickel, and its alloys is expected to impact the global market value share for more than 60% by 2026. According to the "Resource Efficient Europe" initiative launched by the European Commission, promoting resource efficiency, a greener and more competitive economy is the priority theme for small and medium-sized enterprises [26]. Although significant technological and processing advancements occurred in the past forty years, industrial firms are still struggling to provide viable solutions to energy conservation, reduction of costs and toxic wastes, as well as strategic challenges such as product durability and corrosion protection [27].

In this respect, alloy plating offers better answers in terms of economic impact and environmental sustainability due to fine tuning the composition, morphology, crystallinity, as well as tailored properties [28–30]. As of today, zinc metals are proved to be commercially successful in automotive, aerospace, and construction industry, while tin and precious metal alloys find applications in fashion jewelry and electronics [31,32].

In recent years new electrochemical processes have emerged, specifically the electrodeposition in ionic liquids (IL) and electropolymerization [33–36]. Although both of these techniques are very promising and are strongly pursued in laboratories worldwide, their use on a large scale is still limited. Ionic liquids are mainly used to deposit metals with a Nernst potential below that of water decomposition and, therefore, cannot be electroplated from aqueous baths [37–39]. The most common example is the electrodeposition of aluminum. The electrolyte is composed of anionic and cationic organic species (also called "deep eutectic solvents"), which are in the liquid phase at low temperature (generally below 100 °C); this allows the salts of the metal precursor to solubilize for the electroreduction process. The need for the complete absence of water is also one of the main drawbacks of this process; in fact ionic liquids are very sensitive to moisture and therefore they must be employed in a special closed environment with a controlled atmosphere. The electropolymerization process involves the reaction of organic monomeric precursors driven by an external electric potential [40–44]. Differently from the aqueous-based electrodeposition, the organic molecules not only occur in a redox reaction, but they also form a network leading to the formation of a polymer. The resulting coatings are generally well-adhered and softer than the metal ones with fewer cracking issues. The final polymer could be either conducting or insulating. The main applications of this process are as electrochemical sensors, anticorrosion coatings, and colored deposits for aesthetical purposes. Being organic-based coatings, the main drawbacks are their degradation over time and the environmental toxicity in the production process due to their precursors.

This review outlines the current research on new materials and process innovation for metal alloy electrodeposition. The state of the art of the science and technology, future directions and open challenges are highlighted from an industrial perspective.

2. Fundamentals of Electrodeposition: Pure Metals and Alloys

2.1. Fundamentals of Electrodeposition: Mass and Charge Balance, Thermodynamics, Kinetics and Growth

An experimental setup for electrodeposition simply requires a suitable vessel and two conducting electrodes (a working electrode (WE) where the film is deposited, and a counter electrode (CE) used to close the circuit) immersed in an electrolyte containing the metal ions to be deposited.

In some cases, a third electrode (the reference electrode) is introduced to measure more precisely the potential at the electrodes (Figure 1), thus providing information on the processes occurring at both the WE and CE. The three-electrode setup is used almost exclusively in research and development, since it is extremely difficult to maintain the required conditions in industrial-sized vessels. The process

is run by an external power source, under potential or current control. Either control methods can be used, with the choice being made based on the knowledge gained from three-electrode experiments. For example, a steep current change can be better-controlled potentiostatically, and vice versa. Various waveforms under potential or current control can also be used to tailor the composition and microstructure; multilayers, for example, can be grown by alternately switching the current or potential between two values, and composition at grain boundaries may be tailored by a short anodic pulse. Pulse plating, by using square, triangular, sinusoidal, or tailored waveforms, is a versatile method to tailor the composition gradients, morphology and, therefore, also properties, as discussed in various monographs [45–47]. Metal coatings can be formed by adding only one elemental species (i.e., Cu or Ni) as metallic salts, while alloy coatings can be produced, under well-defined conditions, by having more than one elemental species in the solution.
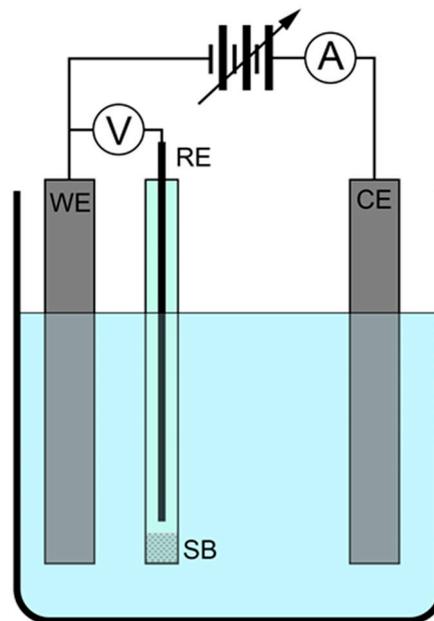

Figure 1. Schematic of an electrochemical cell. WE: working electrode; RE: reference electrode; CE: counter electrode; SB: salt bridge.

In electrodeposition the rate of reduction of metal ions determines the current that flows through the cell and the total charge passed yields to overall coating mass and thickness.

$$Me^{z+} + ze^- \rightarrow Me \tag{1}$$

A formula that relates mass deposited to the charge passed for the reduction process in Equation (1) is derived from the Faraday's law. If M is the mass of the coating, A_{mol} is the molar mass of the element, Q is the total charge, z is the number of electrons exchanged, and F is the Faraday constant, corresponding to the charge of one mole of electrons, $F = 96{,}485$ C/mol $= 26.8$ A·h/mol, the formula is:

$$M = \frac{A_{mol}Q}{zF} \tag{2}$$

For conformal coatings the knowledge of the thickness vs. the charge passed is important; in this case the Faraday expression can be modified to give:

$$D = \frac{A_{mol}jt}{zF\rho} \tag{3}$$

where D is the film thickness, j is the current density (current per unit area), t is the time of deposition, and ρ is the density of the film. Note that the density of an electroplated coating may be different from that of a bulk metal due to the possible presence of vacancies and micro-voids. It should also be noted that Equations (1)–(3) are valid only if no other processes besides Equation (1) is occurring.

Equation (1) is at equilibrium when the rate of metal reduction in the electrolyte equals that of metal dissolution. Under such conditions the electrode potential E_{eq} is determined by the Nernst equation, which reads:

$$E_{eq} = E^{\circ} + \frac{RT}{zF} \ln C_{Me^{z+}} \qquad (4)$$

where E° is the equilibrium potential under standard conditions, R is the gas constant, T is the absolute temperature, ln stands for the natural logarithm, and $C_{Me^{z+}}$ is the concentration of the metal ions in moles per liter.

In order for electrodeposition to occur, the applied potential must be more negative than the equilibrium potential, thus resulting in the reduction/deposition process being faster than the opposite dissolution process. The driving force for metal deposition is, therefore, the difference between the applied potential V_{app} and E_{eq}. This quantity is referred to as the overvoltage:

$$\eta = V_{app} - E_{eq} \qquad (5)$$

The electrodeposition process consists of several elementary consecutive steps: at equilibrium the ions are bound to water molecules or to other molecular species that bind the metal ion, decreasing its effective ability to be reduced. Metal ions are transported initially in the bulk electrolyte by fluid convection (Figure 2). When these ions are at a distance of 0.05–3 mm from the electrode (the hydrodynamic layer) the convection process slows down and the ions start to move only due to diffusion (the diffusion layer, 1–100 µm) under a gradient of concentration generated by the ongoing reduction of metal ions. These ions are first adsorbed at the electrode surface and are reduced by electrons from the electrode. Note that the electrode/electrolyte interface forms a double layer of charges that generates a large electric field ($\sim 10^9$ V/m). The process of metal reduction is strongly affected by the presence of this electric field.
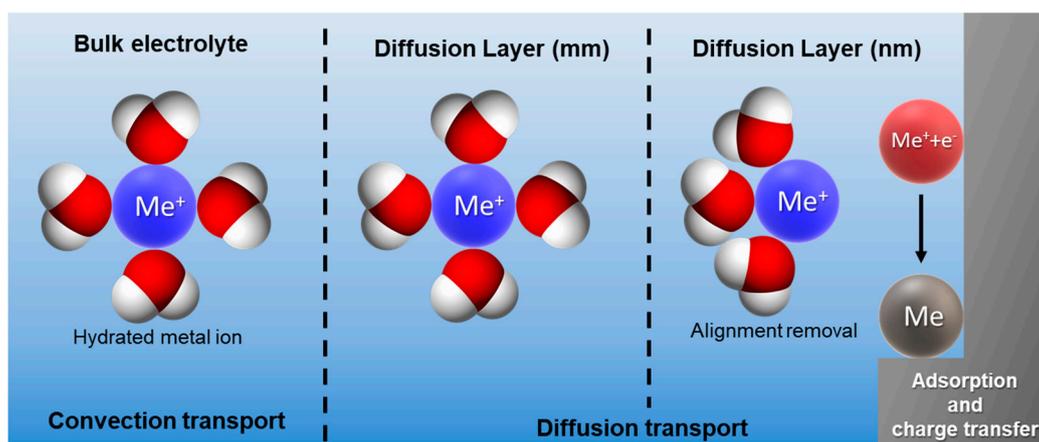

Figure 2. Scheme of transport regimes as a function of the distance from the electrode.

The rate of metal reduction sufficiently far from the equilibrium condition is described by the following expression:

$$J_{kin} = j_0 e^{-\frac{z\alpha F(V_{app} - E_{eq})}{RT}} \qquad (6)$$

where j_0 describes the dynamics of the deposition/dissolution processes at equilibrium, and α ($0 < \alpha < 1$) relates to the symmetry of the energy barrier encountered during electron transfer and is

often approximated to 0.5. Note that the deposition current density increases exponentially with the overvoltage, and at a certain point the deposition rate becomes limited by the arrival of the ions at the electrode surface, which depends from the hydrodynamic conditions imposed in the cell. It is also important to consider that in aqueous solution it is always possible to induce water reduction when the applied voltage is more negative than the redox potential for water reduction to hydrogen.

Under these conditions the process of interest may not occur with 100% efficiency, and some hydrogen may be evolved or incorporated in the coating, resulting in possible changes in properties, in particular embrittlement; this phenomenon depends strongly on the nature of the metal being studied. A typical behavior of the current density as a function of applied potential is shown in Figure 3. The overvoltage determines to a large extent the morphology of the deposits. Electrodeposition in Region 1 (Figure 3) occurs at low deposition rates, resulting in the possibility for the adsorbed atoms to sit at low energy sites, thus forming, in most cases, a smooth, layered film. In Region 2 the deposition rate increases, leading to the formation of more nuclei of an approximately hemispherical shape. Finally, in Regions 3 and most importantly 4, the current approaches the diffusion-limiting current, resulting in the possible formation of dendritic films showing incomplete coverage of the substrate. In order to form a continuous film, it is most practical to deposit in Region 2, where the spread of the existing nuclei results in a continuous coating at a relatively low thickness. Film morphology, however, depends also on two more features:

- The nature of the element being deposited, due mainly to the differences in j_0 generated by the electronic structure and the extent of interaction with water.
- The effect of additives adsorbing at the growing interface; specifically, adsorbing species inhibit growth, resulting in smaller grains and properties changes due to the possibility for the molecules to be incorporated in the growing film.
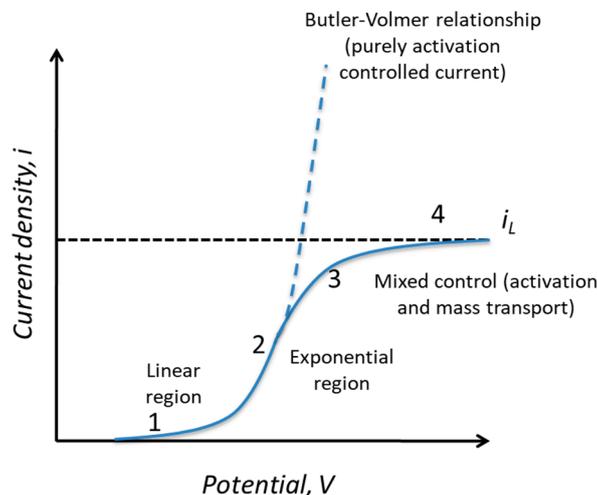

Figure 3. Deposition region dependency from applied potential.

2.2. Electrodeposition of Alloys

The term "alloy" refers to a metallic material containing more than one element. These materials may form a random mixture of the elements, spatially separated regions when the elements are incompatible, or ordered structures where the position of each element is predetermined. These distinct microstructures are determined by the interactions among the elements. From the technological standpoint, alloys are important because their properties (mechanical, magnetic, optical) are usually enhanced, and they can also be tailored for the target function by rationally varying the composition.

The first approach to alloy electrodeposition involves the assumption that the current used for the reduction of metal A remains the same even in the presence of a reduction process for metal B in the

same vessel. This hypothesis requires that no interaction occurs between the two processes. Therefore, it is possible to write the following equations:

$$
\begin{aligned}
J_A &= j_0 e^{-\frac{p\alpha_A F(V_{app}-E_{eq,A})}{RT}} \\
J_B &= j_0 e^{-\frac{q\alpha_B F(V_{app}-E_{eq,B})}{RT}}
\end{aligned}
\tag{7}
$$

Note that the parameters in the above equations are different; in particular, E_{eq} depends on the metal (A or B), resulting in different onset potential for reduction. From these partial currents, it is possible to determine the potential-dependent composition of the alloy:

$$
x_A = \frac{n_A}{n_A + n_B} = \frac{\frac{j_A}{p}}{\frac{j_A}{p} + \frac{j_B}{q}}
\tag{8}
$$

and the overall growth rate:

$$
v_{growth} = \frac{A_{mol,A} j_A}{p} + \frac{A_{mol,B} j_B}{q}
\tag{9}
$$

Similarly to elemental deposition, if the applied potential is more negative than the onset of hydrogen evolution, the process of alloy growth occurs with an efficiency less than 100%, with the consequence that some impurities may be incorporated in the film.

The superposition of the partial currents in alloy deposition, as hypothesized in the equations above, was assumed in the early days of electrodeposition to be the conventional behavior.

In contrast, investigations on various alloys, especially those containing transition metals, have shown that co-deposition of two or more elements results in interactions among the various processes, leading in general to a breakdown of the hypothesis of superposition. Various steps in electrodeposition are responsible for the breakdown of the superposition assumption, including the following:

- Adding ions N^{q+} in an electrolyte containing ions M^{p+} that are complexed by a complexing agent results in a variation of the speciation, giving rise to variations in the partial currents.
- If the deposition of M and N occurs via a multi-step process, intermediates of the two species may compete for adsorption sites at the substrate, and the rate of deposition of each element may vary based on the solubility of such intermediates. This is, for example, the case of Fe-Ni deposition, or of other mutual alloys of the iron group alloys.
- Association of adsorbed species at the electrode may result in the formation of multi-metallic complexes, inducing the deposition of metals that cannot be deposited by themselves. This is the case of the induced deposition of W or Mo in parallel with the deposition of Fe, Ni, or Co.

2.3. UPD and Underpotential Co-Deposition

Electrodeposition processes are characterized among others by (i) diffusional transport processes; (ii) the occurrence of electron transfer to reduce a metal ion into an atom in the growing crystal; and (iii) the low energy of the deposition precursors. The latter feature is very important since the free energy of ions in solution at room temperature is of the order of $3/2 k_B T \approx 0.075$ eV, quite similar to the interaction among atoms in the crystal lattice. This means that, while metal A is deposited on a substrate of the same element at the redox potential predicted by the Nernst equation, the same metal A deposited on a substrate B, where the interaction A-B is stronger than A-A, is deposited at a potential more positive than the value predicted by the Nernst equation. This underpotential deposition (UPD) can be estimated by considering that the shift in the redox potential is given by $\Delta E = -\frac{\Delta G}{zF}$ where ΔG is the difference in the adsorption energy of A onto A and the adsorption energy of A onto B. This process enables the formation of sub-monolayers or a full atomic monolayer on A onto B. A second layer cannot be deposited at the same underpotential since the first layer is now A,

where the deposition potential would be more negative, thus leading to a surface-limited reaction (SLR) that spontaneously generates a single atomic layer.

This behavior is exceedingly useful from a technological point of view and, therefore, widely studied by the scientific community. The deposition process itself is called electrochemical atomic layer deposition (E-ALD or ECALD) [5,48,49]. In some cases, if the substrate is single crystalline or shows a strong crystallographic orientation, it is possible also to obtain an epitaxial deposition of the coating; this technique is called ECALE [50,51].

The bonding strength in alloys can be similarly exploited to shift the potential at which an element in a given alloy can be deposited. The Nernst equation for the deposition of a metal A into an alloy A-B is modified and given by the formula:

$$E_{\text{eq}}(\text{A})_{\text{alloy}} = E°_{\text{A}} + \frac{RT}{zF} \ln\left(\frac{C_{\text{A}^{z+}}}{a_{\text{A,alloy}}}\right) \tag{10}$$

where $a_{\text{A,alloy}}$ is a measure of the extent of interaction of metal A with the alloy. In a solid solution $a_{\text{A,alloy}} < 1$ (i.e., the free energy of A is lower due to the stronger alloy bonding), raising the redox potential above that calculated in the case of a pure metal. This shows that metal A can be deposited at a potential more positive than the redox potential of A, that is, it can be deposited by underpotential processes, while the metal B continues to be deposited at overpotential [52].

A rigorous calculation using the regular solution approximation allows to predict the conditions (the applied potential) to obtain the target composition, under the assumption that deposition occurs under thermodynamic (equilibrium) conditions.

It is important to mention that A and B could also be a metal and a nonmetal; in these instances electrodeposition under potential control may form films of semiconductor compounds [53]; at a finer scale on the other hand, exploiting the E-ALD process it is, thus, possible to alternately deposit one element over the other to artificially synthesize semiconductors [48,54,55].

Furthermore, the selective electro-desorption on a multilayer sample, prepared with the E-ALD method, opens the possibility to obtain a rearranged surface with morphological properties not obtainable with the traditional bulk deposition of the same material. We refer to this process as the selective electrodesorption-based atomic layer deposition (SEBALD) [56–58].

In the last few years, new insights in surface phenomena at the solid/electrolyte interface and the availability of new technologies have promoted a renaissance in the field, forecasting a bright future. For example, the self-terminating electrodeposition observed for several 4d and 3d transition metals allows the growth of a single (or few) metallic monoatomic layer(s) on a substrate, mimicking the atomic layer deposition process. Monolayers of Pt can be grown sequentially simply by pulsing the potential [59], through inhibition of the hydrogen adsorption, while Ni, Fe, and Co can be grown up to ~2 nm, owing to precipitation of hydroxides [60,61]. Another novel electrodeposition process mimics the vapor–liquid–solid method adopted to grow single crystal semiconductor nanowires. In the electrochemical version, called electrochemical liquid–liquid solid (ELLS) growth [62], the metal ions to be reduced (Si, Ge) are dissolved in a liquid metal and reduced at an electrode. The electrodeposition of Si, Ge in aqueous solutions results in poor crystallinity. In contrast, the ELLS method results in good crystallinity due to the high mobility. This method has the potential to revolutionize the formation of semiconductors for solar cells. On the technological front, advances in motion control at the submicron scale allow electrodeposition at a liquid meniscus to form nanowires directly [63], and free-form microprinting of metals has been achieved by modifying atomic force microscope (AFM) tips to inject the electrolyte at a predetermined location, forming overhangs, spirals, and walls [64]. Many advances should be expected through our improved knowledge of electrochemical surface processes and further technological advances.

3. Chemistries for Metal and Alloy Deposition

Before the actual electrodeposition, the base metal needs a pretreatment in order to clean, degrease, and activate the electrodic surface [65]; only afterwards is the galvanic deposition is performed. The substrate is rarely coated with only one metal, but more commonly follows multilayer depositions (Figure 4). This approach is preferred because directly depositing the final alloy on the substrate results most of the time in adhesion problems due to internal stresses and then peeling. In the metal finishing sector there are several galvanic processes [66,67], but traditionally (brass, bronze, and ZAMA base metals) a thick layer (5–20 μm) of nickel or copper is deposited at first. This interlayer allows a good leveling and provides a smooth, shining surface. However, these metals are rarely the final coating and, usually, additional layers are deposited until the desired color is set. An important aspect to keep in mind is also the inter-diffusion of the metals between the different layers that lead to a progressive change in the properties of the product. The phenomenon of diffusion is largely present in the case of gold coating over gold [68], with resulting reddening and grade loss of the precious finish; for this reason, one or more barrier layers are generally inserted between these two deposits. Historically, the most common barrier layer was a nickel deposit of 1–5 μm, but due to allergenic and environmental problems it was gradually replaced with bronze, deposits of 2–5 μm, followed by 0.5–1 μm of palladium. Aluminum substrates follow the same procedure described for brass, but a zinc electroless coating must be performed before the actual galvanic process to avoid adhesion problems due to the passivation layers that form on this metal.

Silver substrates follow a different process; a first deposition of galvanic silver metal is performed to eliminate the typical porosity that comes from the lost-wax casting products; this is followed by a rhodium plating, interspersed with a layer of palladium, which prevents the oxidation and blackening of the metal, leaving the silvery appearance.

In some cases, after the precious layer (typically 0.5–1 μm), a flash deposition is added (0.05–0.02 μm) to give a special color to the surface and therefore we talk about yellow gold, light gold, rose gold, black gold, etc. To obtain a particular effect, this flash deposit could also be partially removed by mechanical action, revealing the underlying layer.
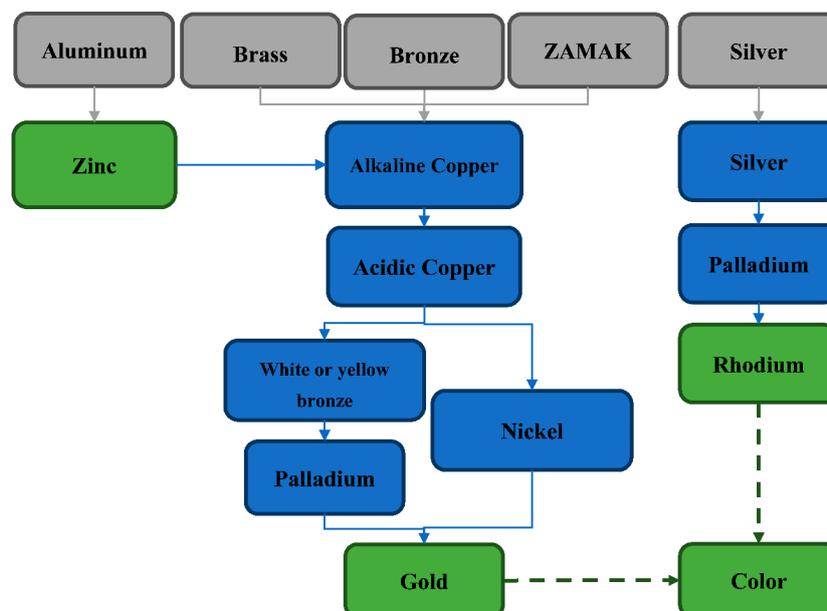

Figure 4. General scheme of the most common electrodeposition processes. The boxes' color differentiates between the base metals (gray), intermediate depositions (blue), and the finishing layers (green).

3.1. Copper

The main copper deposition baths are alkaline cyanide-based or acidic solutions based on sulfuric acid, often used one after the other. Historically, the cyano-alkaline baths have been used as first but these are going into disuse because of their danger in operation and toxicity, due to the use of cyanide and disposal costs. They are still utilized to deposit a first layer of copper on non-precious metals that would be attacked by strong acids or which would be affected by an uncontrolled chemical deposition. The main components of these baths [69] are copper (I) cyanide, potassium cyanide, and potassium hydroxide, in addition to organic additives that improve the appearance of the deposit. Previously, sodium-based baths were also widespread, but potassium is gradually replacing them with better performance. Copper cyanide is an insoluble salt and because of this an excess of cyanide is added to facilitate the formation of a soluble complex. The operating temperature is between 25 and 60 °C, and higher temperatures allow to increase the current density, which is generally 0.5–4 A/dm^2. The deposits from this bath have a thickness of 0.5–2 μm for a deposition time of 1–5 min. In these baths the anodes are made of very pure electrolytic copper which gradually dissolves, decreasing the need to add it as a salt; if the copper content in solution becomes excessive the anodes can be replaced with steel plates or mixed oxides. These baths have the advantage of being very penetrating and easy to control. The main disadvantages, in addition to the presence of cyanide, are the low efficiency (30%–60%: little metal is deposited with respect to the quantity of current supplied) and a low gloss and leveling (the ability to cover surface defects).

Due to strict environmental regulations, industrial firms are starting to implement low-impact baths for copper deposition. Good alternatives to cyano-alkaline baths are solutions based on copper and potassium pyrophosphates [70]. However, because of the hydrolysis and decomposition processes from which this bath suffers, the temperature should be in the range 22–30 °C and pH between 8.0 and 8.5. These conditions limit the operating current density, which is generally 0.6–1.5 A/dm^2. Compared to the cyano-alkaline baths, the pyrophosphate solutions have a higher penetrating power, however, they are subject to organic contaminations and are less stable.

Acidic-copper baths [71], created to obtain a very shiny and leveling deposit, are now used in many sectors, from printed circuits, to electroforming and plastics metallization. These baths are typically simple to manage and inexpensive to maintain. The conductivity of the bath is very high and the current yield is close to 100%. The components of the bath are simply copper sulfate (II) and sulfuric acid, in addition to organic additives. Strong stirring is required in this bath using insufflated air. The typical operating temperature is low (20–25 °C), the current density is 1.5–3 A/dm^2 and it is possible to obtain very shiny deposits even tens of microns thick during a deposition of 15–30 min. In this case the anodes are made of highly pure, oxygen free, copper with a content of phosphorous of 0.02%–0.08% and they must be coated with Meraklon bags (textile polypropylene) to prevent the detachment of black films from them if the process works at excessively high current densities.

3.2. Zinc

Zinc is the metal most widely used for electrodeposition. Historically, it is the element dedicated to the protection of ferrous materials from corrosion. This characteristic is due to two protection mechanisms: the first is physical; indeed, this metal oxidizes easily in contact with the air but, unlike iron, it passivates, forming a layer of compact and insoluble oxide, such that the atmospheric agents do not reach the underlying material. However, in the case of the presence of scratches or porosity, there is also an electrochemical protection. Indeed, zinc metal has an electrochemical standard potential that is very negative, and in particular more negative than iron, therefore, if rust is formed, a galvanic cell is activated in which the zinc is sacrificed by acting as an anode, restoring the metallic iron. In recent times, iron has been replaced by aluminum in many fields, but similar galvanizing processes are still used even on this metal. Furthermore, in order to provide aluminum with a different metallic finish, zinc must be used as an intermediate layer to promote adhesion. In analogy to copper baths there are alkaline and acidic zinc solutions [72]; the first one was also the first employed with the use of cyanide.

They were economically favorable and they required simple management, but due to environmental and health restriction laws the acidic bath is currently the only one present on the market. The zinc deposits are typically 5–15 μm thick, grown at a current density of 2–3 A/dm^2 and the solutions are based on sulfate and chloride compounds. Recently, new formulations for the co-deposition of zinc alloys have been studied to improve the mechanical properties and corrosion resistance of pure zinc coatings [73,74].

3.3. Nickel

Nickel plating is another very common galvanic process. Being a very glossy deposit, it is often used for decorative purposes, accessorizing and jewelry, as a finishing or intermediate layer; but also has good technical characteristics of weldability, adhesion, magnetic properties and corrosion resistance [66,67], which makes it perfect also for the automotive and electronic industries. Depending on the applications, baths could be used that provide glossy or opaque deposits. Many formulations are available, but the best known, from which many are inspired, is without a doubt Watt's baths. Even if this metal is still widely used, health regulations have restricted its use, particularly with regard to wearable items [75,76]. Still used for accessories such as shoes, belts, and bags, it has been practically banned for products that directly contact the skin. Following this, two new denominations are used: nickel-free and hypoallergenic-nickel, or simply hypoallergenic. The nickel-free appellation refers to the fact that all products are completely free of the metal both on the surface and in the underlying layers, alone or in alloy with other metals. The term hypoallergenic, on the other hand, refers to an object that has an internal layer of nickel or an external nickel alloy, but which, if subjected to conditions of strong corrosion, does not release this metal [77,78].

3.4. Bronzes

The electrodeposition of bronzes is a relatively recent technique born from the need to replace nickel in decorative applications in contact with the skin for hypoallergenic purposes [79,80]. Like nickel, bronze acts as a barrier layer, preventing, or limiting, the diffusion of the underlying copper towards the outside. The bronze baths are basically divided into two categories: the yellow bronzes and the white bronzes. As can be deduced from the name, the former has a more yellowish appearance while the latter exhibits a silver hue; this characteristic is attributable to the percentage of copper present in the alloy compared to tin (and to the minimum part to zinc). Despite the difference in the deposit, it is not mandatory that the ratio of metals in the composition of the bath be the same: indeed, the yellow and white bronze baths can have almost the same amount of metals but, varying the amount of cyanide and potash, it varies the deposition of the components. Even the maintenance that these baths need is the same. As mentioned, these are alkaline cyanurate baths in which there are two main metals (copper and tin) supported by at least a third (zinc), but there may also be other metals (palladium, indium, etc.) to confer particular chemical-physical characteristics to the coating. This type of bath requires continuous maintenance in order not to unbalance the alloy and keep unchanged the amount of cyanide (which slows down the deposition of copper favoring the tin) and potassium hydroxide (which slows down the deposition of tin favoring the copper). Furthermore, the pH must be kept strongly alkaline (>12) to avoid the precipitation of the tin (amphoteric) in the form of hydroxide. The operating temperature is high (55–70 °C) and anodes with mixed oxides are used. The required current density is approximately 1 A/dm^2 and deposits of 2–7 μm are obtained for deposition times of 10–20 min. Even if the electroplating of bronzes is a process studied from more than twenty years, the research in this field is still very active and it is focused to increase both the bath stability of both the bath and the wear resistance of the final coating. New formulations varying the ratio among Cu, Zn, Sn, and other noble metals are under investigation [81]. In these alkaline solutions, the tin is generally in present the stable form of Sn(IV) and copper as the monovalent ion Cu(I). New types of baths without cyanide have been studied, exploiting Cu(II) and Sn(II), stable in acidic electrolyte, also providing improvements in the electric efficiency.

3.5. Palladium

The electrodeposition of palladium metal has been known since the nineteenth century [82], but its use became common only in the 1980s, when new legislative measures banished nickel from objects intended for use in prolonged contact with the skin. Palladium is used both as a final coating and as an intermediate layer to improve corrosion resistance, increase the adhesion of subsequent precious deposits, and to act as a diffusion barrier layer [83]. Palladium deposition typically takes place in two steps of a first pre-palladium "strike" followed by the thick deposit of 0.5–1.5 μm. There are both acid and alkaline baths. The acidic formulations are easier to prepare, but have some disadvantages, including stability, metal pollution, and aggressiveness towards the substrate. For this reason, the most common commercially available baths have a pH higher than 9, in which the metal is stabilized in the form of an ammonia complex. The most widespread compound is PdNi alloy [84], which is employed in industry to limit the use of gold in connectors or as a substitute for lead-based solder alloys. In recent years, electrodeposition has also spread to palladium-iron alloys [85], especially for wearable objects. The main limitation of this deposit is the presence of microcracks due to the co-deposition of hydrogen. In recent times doubts have emerged also on the allergenic power of this metal; specific studies are still underway although legislative measures are already being evaluated [86,87].

3.6. Gold

The electrodeposition of gold is a very broad subject because, being the final layer, many variations are required to optimize both the appearance and the composition [88,89]. The gold finishing is employed in a large number of fields due both to its electrical and anti-corrosion properties, as well as its aesthetical properties. The gold alloys range from 12 kt up to 24 kt: low grade alloys (12–18 kt) have applications in electronics as electric contacts, while high grade alloys (18–24 kt) are mostly used for decorative purposes. There are gold deposition baths of both acidic, neutral, and alkaline baths, which use cyanurate salts of gold with valence I or III, with numerous secondary metals: Fe, Cu, Ni, Co, Ru, and Ag, etc. The main distinction that is made between these baths is based on the maximum thickness that they are able to deposit, thus distinguishing "thick" baths and "color" baths. The former has a higher concentration of gold (1–3 g/L) and allows to obtain typical deposits up to 3 μm; in these baths gold is usually alloyed with iron, obtaining a yellow deposit, or nickel, for a lighter coating, also called 1 N. If the color of these deposits is the one required, the object is considered finished, otherwise it goes to the color bath. They are characterized by thicknesses less than 0.2 μm and precious metal concentrations lower than one gram per liter. There are yellow [90], light and white [91], pink [92], and blue [93] golds. Moreover, the so-called black golds, containing Co and Ru in the alloy, are also on the market [94]. They can act as a final color or, thanks to their remarkable softness, can be partially uncovered to give the object an "antique" look.

Typically, the gold baths do not require much maintenance and have a very long life. The necessary corrections are only carried out to adjust the color, acting on the ratios of the various metals. Nowadays the majority of gold electroplating baths use cyanide electrolytes or cyanide gold salts. These compounds are very dangerous for human health; major research efforts are now focused on finding valid alternatives by using non-cyanide formulations [95].

3.7. Other Metals

In addition to the metals and alloys which have already been discussed, there are numerous electrodeposition processes for various applications. Silvering is used both for decorative purposes and in electrical engineering for electrical contacts (since this metal is cheaper than gold), but also in optical applications due to its high reflectivity. Silver is also deposited on objects of the same metal, obtained through casting, to reduce its porosity. Silver baths are characterized by very high concentrations of cyanide (up to 200 g/L), and silver metal bars are used for the anodes [96].

A commonly used finishing on silver is rhodium. Rhodium does not darken, and is hardly attacked and corroded. It has high hardness, and is also an extremely light and reflective metal. These features lead to its use in both the technical and decorative sectors. Rhodium is generally deposited from acidic solutions based on sulphates or phosphates [97]. Platinum usually competes with rhodium for use in applications, as these two share many features of resistance to corrosion and gloss. Moreover, platinum is even more inert, even if it is not as hard. Rhodium baths have been preferred for a long time to those of platinum because of their simpler formulation, but platinum is the most effective for particular electronic applications and high temperature (aeronautics) applications. Moreover, the deposition of platinum on less-noble metals (e.g., titanium and tantalum), makes it excellent for the production of inert electrodes, anodes for the electrodeposition of noble metals, and cathodic protection. After the formulation of new simpler baths, this metal has also been incorporated in decorative finishes [98].

Compared to other metals, ruthenium has a relatively recent history of electrodeposition. The main interest lies in the economic convenience of the metal compared to rhodium and platinum, despite the fact that they share many chemical and mechanical characteristics. The most-used salts of ruthenium are sulfamates, chlorides, and the corresponding nitrosilic compounds [99]. The metal is generally used in the trivalent form, but it can partly and spontaneously form the tetravalent ion, making the calculation of the cathodic efficiency complex. The metallic ruthenium deposit is grayish-white in color, similar to rhodium and platinum, but the "black ruthenium" formulation can also be found on the market, in which specific additives are incorporated into the deposit to obtain a dark color [67].

Chromium is another metal used both for decorative purposes (thin layers) and for technical-mechanical purposes (thick layers) [100–102]. It is among the hardest and most glossy deposits. Historically, its deposition has been substantially different from all the others (until now), because the metal cation is not used, but instead the anion (chromium and dichromate) in which the metal is contained. However, due to the toxicity of hexavalent chromium and related legislative restrictions, solutions based on trivalent chromium chlorides and sulphates are also taking hold [103]. There are still many other metals that can be electrodeposited and which are used for several applications (e.g., iridium, iron, cobalt, manganese, indium, thallium, bismuth, etc.). However, these metals are generally used in alloys with other metals to improve both their decorative and technical characteristics, rather than being used individually [13].

4. Industrial Trends and Environmental Impact

With the increasing requirements on performance, quality, functionality, and reproducibility of the plated piece the metal finishing sector is changing considerably. Improvements in plating technology and increased variability in customer preferences have meant shifts in the traditional share of markets in order to comply with the strict requests on new coating qualities and performance. Several official statistics reveals electroplating now dominates the global metal finishing profits with almost 40% of the market share and it is expected to be over US $21 billion by 2026 [25]. The process is uniformly distributed among the different national sectors following the plating trend Ni ≈ Zn > Cr > anodizing > Au ≈ Ag > electroless [1]. For each plating process variable procedures are available depending on the particular industry and operators' skills. Some of them are complicated or unprofitable and they might pose industries at risk due to high personnel and energy costs. The trend towards globalization is forcing small and medium-sized enterprises to increase their level of automation and resource efficiency by implementing new electrolyte design and galvanic layer identification. Through automatic plants both physical and chemical parameters can be controlled, thus leading to more reproducible results. The integration of a statistical experimental design and the evaluation of the galvanic layers' performance is now a status quo in many sectors [104]. The real challenge for the industry of the future is the sustainable control of the effluent water and the final disposal of chemicals at low investment costs. Plating operations are headed by ultrasonic cleaning, stripping of metal surfaces by alkali, and surface activation with acids. Rinsing with water is performed after

each step of the electrodeposition. Rinsing, cleaning, and stripping are the main sources of wastewater, which has to be collected and treated for reuse in the production line and for external discharge. Wastewater generated by the electroplating processes are highly toxic due to the presence of cyanurate compounds, and heavy metals such as Cu, Zn, As, Be, Cd, Pb, Cr(VI), and Ni [105,106]. Specifically for wearing and decorative applications, another aspect to be considered is the degree of metal release in a particular object. The prolonged contact with nickel, cadmium, lead, cobalt, and beryllium are cited by toxicological studies as dangerous [107] and regular authorities are limiting the exposure to alloys containing these metals.

4.1. Nickel

Among heavy metals, nickel has been listed as a major source of concern for the human health. The subjects majorly exposed to nickel and its alloys are workers of the electroplating industry. Examples of nickel containing alloys are nickel copper, nickel silver, and white gold. The release of nickel into the atmosphere during the manufacturing process may lead to respiratory diseases in human and increase the risk of carcinogenicity by inhalation of dust and fumes [108–110]. In addition, skin contacts with nickel during cutting and welding operations may lead to dermatitis in allergenic subjects [111,112]. Similar effects have been also observed in people wearing inexpensive jewelry or using stainless steel accessories [113]. The sweat present on the skin's surface might cause metal dissolution and subsequent tissue absorption, with potentially harmful local and systemic effects [114].

According to the REACH (Registration, Evaluation, Authorisation, and Restriction of Chemicals) regulations, the nickel content in alloys is limited to 500 ppm (0.05%). The reference standard for coated accessories is the leaching test under EN 12472:2009 [115] followed by the determination of nickel release under EN 1811:2015 [116], which sets the limit at 0.5 $\mu g/cm^2/week$. Articles that do not pass these tests shall not be placed on the market. The released nickel amount is generally measured through electrochemical methods or inductively coupled plasma (ICP) after dissolution in an artificial sweat solution for different periods of time (1 h, 24 h, 1 week, and 1 month). Several studies have been published on the influence of sweat components on the degree of nickel release from copper-nickel [117] and white gold alloys [118]. The results demonstrated the relevance of pH and compounds such as lactic acid and urea on metal corrosion, and provided in vitro data on the bioaccessibility of the metal at simulated skin contact. To prevent metal release from alloys, several authors have recommended the use of topcoats over bright nickel coatings [119,120]. Conventional chromium deposition from hexavalent electrolytes is the best low-cost commercial coating. However, due to strict legislative limitations, nickel baths are now replaced with different galvanic depositions, such as white bronzes, palladium, or palladium-iron systems. Moreover, a good alternative to nickel in PdNi and ZnNi deposits is indium, at a percentage varying between 10% and 20% [121].

In addition to restrictions on wearable items, nickel is also subject to environmental pollution limitations, due to its nature as a heavy metal [122,123] that has been widely used in the automotive industry, for corrosion resistance, and for electronic applications as an intermediate layer between copper contacts and gold coating.

4.2. Lead

Lead was a metal vastly used in jewelry to brighten colors, anti-corrosion agent and make the accessories heavier, today the main application is in lead accumulators, in which copper or aluminum substrate in contact with sulfuric acid is plated with lead [124]. However, its use in alloy is restricted to less than 0.05% in weight due to high toxicity. Toxic effects of lead have been known for a long time [107]; if present in the environment it accumulates in the human body, damaging tissues and the nervous system. Restrictions on its use is especially important in jewelry and toys due to children's vulnerability to lead poisoning [125,126]. The reference standards for the determination of total lead in a sample are ISO 105-E04:2013 [127] and EPA 6010C:2014 [128].

4.3. Cadmium

Cadmium is another banned substance due to its carcinogenicity for ingestion or inhalation. Long-term exposure to this metal leads to renal dysfunction, lung disease, and bone problems. Cadmium is present as an alloy in jewelry [125,129], gold deposits for electroforming or as a stabilizer in non-metal components. It is usually added to alloys to impart specific technical and functional properties to the metals. The REACH 1907/2006 European regulations set the limit to 0.01% (100 mg/kg) by weight of metal. In Au/Cu/Cd alloys cadmium is replaced by indium due to similar anticorrosion properties [130]. As in the case of lead, the reference standards for the determination of total cadmium in a sample are ISO 105-E04:2013 [127] and EPA 6010C:2007 [128].

5. Quality Control of Electroplated Products

One of the main aspects of a manufacturing company is to manage the quality of their product and take action to improve their performance to be competitive in the market. From an industrial perspective quality is seen as being the fraction of products that are made right the first time in each of the various stages of the production line. Establishing a quality assurance program by planning resources dedicated to screening is therefore of crucial importance for operation managers. Especially in the electroplating industry a proper balance between expenses, functionality, and quality should be considered. Today, the cost growth of raw materials and the even more rigid consumer requests drive the quality control process towards a "zero defect manufacturing", forcing companies to move their business from inspection- to diagnosis-oriented strategies [131].

Although there are no definite regulations regarding technical specifications for the final performance of an object, every industrial firm must demonstrate that a product will pass several tests in order to be accepted by the customer. Specific to galvanic deposition, standard analysis includes: hardness and wear resistance, color assessment, and general surface quality of the end products. Moreover, depending on the artifacts' use and the surrounding environment in which they are introduced, resistance to corrosion and adhesion are measured. In the following sections the state of the art of industrial quality control is discussed highlighting the future research trends.

5.1. Real Thickness Determination

A fundamental parameter in quality control is the precise determination of the electrodeposited thickness. Depending on the type of alloy system and/or layer numbers the end products might have different mechanical properties. For example, a thick deposit can be under very tensile stress and possibly not adherent, and especially if it is made of precious metal, it turns out to be a significant profit loss. On the other hand, if the layer is too thin, gloss, diffusion, color, and corrosion problems might occur.

The most common methods for measuring the thickness are through scanning electron microscopy (SEM) of metallographic cross-sections or using X-ray fluorescence (XRF). Cross-sectional analysis allows acquiring a direct image of the layers' sequence and then measure the thickness, so quantification is very simple even if the operator needs some foresight in the case of ill-defined edges. The main disadvantages of this approach are the high cost of the instrument (€60,000–200,000) and the sample preparation, which is slow and destructive. On the other hand, XRF allows for non-destructive and fast measurements, keeping the cost low.

The price for a benchtop instrument is around €40,000–60,000. The analysis is based on illuminating the sample with X-rays and measuring the fluorescence. Using an appropriate calibration curve, the thickness of all the layers can be measured, with a typical 10% standard deviation. The main drawbacks of this method are the need to know the exact sequence and composition of all the layers, in order to measure the thickness, and the impossibility of measuring layers in which a certain element is repeated: for example, in a typical deposition bronze/copper/brass, the copper layer cannot be

measured because it is present in both the deposits and brass, while bronze can be measured by analyzing the tin and correcting the result based on its percentage in the alloy.

In 2018, Giurlani et al. [132] developed a new methodology based on X-ray microanalysis for the determination of the thickness and the composition of electrodeposited thin films. The proposed method employed a combination of energy dispersive microanalysis spectra acquisition and Monte Carlo simulation. This method has better lateral resolution than the XRF technique currently used in the galvanic industry and allows reliable measurement on thin (less than 500 nm) precious metal films with the capability to determine metals in the 1% concentration range. The approach was validated by the analysis of electrodeposited plates with known metal thickness using various approaches and custom-made software. The results were compared with other techniques showing an uncertainty of 9%, which is consistent with the literature data obtained using real standards [133]. The method has been validated on copper-based substrates covered by a layer of gold-nickel alloy.

5.2. Color Assessment

The exact determination of the color has a central role in the quality control of electroplated deposits. At a first sight the task may seem trivial, since color measurements are easily accessible even to untrained personnel. However, environmental factors, as well as intrinsic properties of the objects might generate inconsistent data [134], thus causing communication problems between the producer and customer.

The formalism commonly used for color assessment is the *Lab* color space (also named CIELAB and CIE1976 [135]) in which the three coordinates L^*, a^*, and b^* are taken into account. L^* identifies the brightness with values from 0 to 100, a^* the red-green component ($a^* > 0$ red, $a^* < 0$ green), and b^* the yellow-blue component ($b^* > 0$ yellow, $b^* < 0$ blue). The coordinates a^* and b^* do not have fixed limits but are generally in the range of ± 100. The color coordinates $a^* = b^* = 0$ represent grays. When discussing perceptual differences between target and sample colors, several metrics have been proposed in the past [136]. The first historical approach, which is also the simplest and consequently the most commonly used, defines color perception as the Euclidean distance between the coordinates of two different colors [135]:

$$\Delta E = \sqrt{\left(L_1^* - L_2^*\right)^2 + \left(a_1^* - a_2^*\right)^2 + \left(b_1^* - b_2^*\right)^2} \tag{11}$$

Generally, the just notable difference (JND) to distinguish the color difference between two samples placed one next to the other is for $\Delta E^* < 1$; however later studies evaluated the proper threshold as low as $\Delta E^* = 2.3$ [137].

In practice, companies generally tend to give an acceptable range for the colorimetric coordinates ($L^* \pm dL$; $a^* \pm da$; $b^* \pm db$), whose values are defined by the customer.

Colorimetric coordinates are obtained from the mathematical combination of illuminant and sample reflectance spectra and the tristimulus color matching functions, which determines how the eye perceives the chromaticity [138].

Aside from improvements in the prediction of subjective visual alterations from instrumental measurements, precise color assessment is still a matter of discussion among scientists and a strategic challenge for private companies [139]. For example, color matching and harmony between metallic parts in automotive applications demand specialized skills and efforts in process control [140]. Moreover, the tiny dimensions and irregular patterns of fashion accessories require the use of colorimeters with very small apertures and/or expensive analytical methods. In 2017, Giurlani et al. [141] discussed the implications of surface finish, texture, and instrumental settings on color tolerance of electrodeposited surfaces. The authors compared the color output operated by colorimeters generally used in manufacturing with a UV-Vis spectrophotometer and discussed the reproducibility among various fashion companies. They found industrial differences are significantly perceptible compared to exact data with a tolerance $1 < \Delta E^* < 3$.

5.3. Surface Inspection and Mechanical Properties

The ability to discriminate features from normal and defective regions of artifacts is of primary importance. Galvanic industries have to guarantee surface integrity and product performance over a defined time period. Defects generally occurring during the electroplating process include dull or burnt deposits, poor coverage, and tarnishing. Moreover, non-precious alloys, such as brass, bronze, and ZAMAK (zinc, aluminum, magnesium, and copper alloy) are exposed to oxidation and corrosion. Especially for decorative sectors the generation of a thin film patina affects the value of the article.

Surface inspection has been, for a long time, a human task generating high workload and misinterpretations. Today, the integration of automatic visual systems in the production line is actually improving product quality control, thus reducing costs and increasing the production rate. Although literature on machine vision systems is vast, works focused on the surface examination of electroplated product is scarce. Most studies are related to phenomena occurring prior to the deposition process, such as scratches and holes by polishing and grinding [142,143].

The first comprehensive paper on automated electroplating defects inspection appeared in 2005 [144,145] where a comparative analysis of vision systems has been presented. Byrne and Sheahan from the UK built a solution consisting of a high-speed color camera using a constant white light source and an image acquisition system with real-time feedback. The previous approach resulted in the inline traceability and detection of a wide range of defects with a tolerance of about 14%. Using the differential design of experiments analysis, the authors demonstrated a 30% reduction on the defective parts per million in a selected manufacturing company.

Later works by Poroch and Kumar in 2011 [146] used statistical methods in the quality evaluation of electroplating deposits by considering process, equipment, and materials properties. Their comprehensive studies opened new directions to achieve defect free products in any electroplating industry.

Other essential parameters for the quality control of decorative and protective coatings are hardness and adhesive wear. Thin metal films exposed to external stresses and temperature changes are subjected to mechanical deformations, which could affect the quality and therefore acceptance of the delivered goods. The adhesion between two metal layers is determined by the force needed for the detachment of the coating from the base, and it is the resultant of several factors such as the porosity of the base surface, the methods of surface activation, bath composition, and differences in plasticity and thermal expansion between metal base and top coats.

The methods for examining the coatings' adhesion are classified as qualitative and quantitative, and are described in detail in several scientific papers and in reference standards. These mechanical tests play an important role in the evaluation of product durability. The earliest tests are fast and easy to perform; however, they do not provide information on the bonding forces between the metal base and the coatings. International standards describing qualitative examinations are thermal shock under ASTM B571-97:2008 [147], the network of cuts method under ISO 2819:2017 [148] and ISO 11644:2009 [149], and the tape test under ISO 11644:2009 [149]. The generation of blisters or exfoliations during a product's examinations indicates weak adhesion and therefore acceptance failure.

Though difficult, the quantitative assessment of coating adhesion allows measurement of the binding force between the base metal and the topcoats. A typical standard is the tensile testing under ISO 105-E03:2010 [150], which permits quantification of the tendency of hard thin top layers to cracking and delamination. Specifically, tensile tests and biaxial stress measurements are extremely important to assess adhesion failures on aluminum and electrodeposited copper alloys [151,152]. Research on the mechanical behavior of nanolaminated composites and alloys is a relatively new field, and the development of interfacial adhesion models to predict experimental observations is still challenging [153].

5.4. Corrosion Resistance Tests

Product durability is a fundamental aspect which a producer must deal with. Mechanical tests were presented in the previous sections, but the chemical corrosion must also be evaluated. Contrary to the other properties to be characterized, the effects of time and environment on a sample are not quantities that can be measured a priori, since we are obliged to wait for their occurrence. However, there are many official methods to simulate accelerated aging. Industries sometimes carry out corrosion tests after mechanical tests in order to obtain a more pronounced effect, as in the internal quality control of the products.

The most common international corrosion tests are: the effects of exposure to damp heat with or without leather (ISO 4611:2010 [154] and ISO 17228:2015 [155]), resistance to synthetic sweat (ISO 3160-2:2015 [156]), salt spray test (ISO 9227:2017 [157]), and tests with chemicals derived from atmospheric pollution, such as thioacetamide (ISO 4538:1978 [158]), sulfur dioxide, and nitric acid ISO 4524:2000 [159].

6. Conclusions

In this review, we provided an overview of the electrodeposition of metals and metal alloys with particular attention paid to industrial applications. The theoretical part was explored to understand the phenomena that lead to the deposition of one or more metals. Then, baths used to obtain the most common deposits were specifically analyzed. Several application sectors were considered, from decorative purposes to wearable ones, but also technical, electronics, automotive, urban planning applications, etc.

In this work, while underlining the strong connection of the main topic with the scientific and academic world, we also wanted to give a review of applications in the industrial sector because these two worlds, which are gradually moving in separate directions, can work together to share a reciprocal benefit. Keeping this in mind, we extended the discussion to legislative regulations and characterization methods for the deposits in order to get a complete overview on the topic.

Although timidly present at the academic level, research in this sector is very active and, above all, necessary at the industrial level in order to overcome the current limits, to anticipate legislative restrictions, and to progress technologically with new materials. The hottest topics currently in the research are the reduction of precious metal content from deposits (e.g., from 24 kt gold to 18 kt gold) [160,161] while maintaining good corrosion characteristics, mainly acting on the porosity and compactness of deposits, as well as the use of new alloy materials; the replacement of cyanide from many baths with non-toxic compounds [162]; the elimination of heavy metals which are more or less harmful, such as cadmium, nickel, and palladium [106]; new methods of the management and control of waste and waste water, alternative engineering [163–165] processes, and the synthesis of new alloys.

For some of these topics, research is ahead of others, as we have shown in this work, but further improvements and innovations are needed everywhere.

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References

1.   Larson, C. Global comparisons of metal finishing sectors: Part 2, some technology and operational variations. *Trans. IMF* **2012**, *90*, 232–236. [CrossRef]

2. Veinthal, R.; Kulu, P.; Žikin, A.; Sarjas, H.; Antonov, M.; Podgurski, V.; Adoberg, E. Coatings and surface engineering. Industry oriented research. *Est. J. Eng.* **2012**, *18*, 176–184. [CrossRef]

3. Presuel-Moreno, F.; Jakab, M.A.; Tailleart, N.; Goldman, M.; Scully, J.R. Corrosion-resistant metallic coatings. *Mater. Today* **2008**, *11*, 14–23. [CrossRef]

4. Nuss, P.; Eckelman, M.J. Life cycle assessment of metals: A scientific synthesis. *PLoS ONE* **2014**, *9*, e101298. [CrossRef] [PubMed]

5. Sharan, T.T.; Maarit, K. Atomic layer deposition of p-type semiconducting thin films: A review. *Adv. Mater. Interfaces* **2017**, *4*, 1700300. [CrossRef]

6. Choy, K.L. Chemical vapour deposition of coatings. *Prog. Mater. Sci.* **2003**, *48*, 57–170. [CrossRef]

7. Aubert, A.; Danroc, J.; Gaucher, A.; Terrat, J.P. Hard chrome and molybdenum coatings produced by physical vapour deposition. *Thin Solid Films* **1985**, *126*, 61–67. [CrossRef]

8. Tassin, C.; Laroudie, F.; Pons, M.; Lelait, L. Improvement of the wear resistance of 316L stainless steel by laser surface alloying. *Surf. Coat. Technol.* **1996**, *80*, 207–210. [CrossRef]

9. Vardelle, A.; Moreau, C.; Akedo, J.; Ashrafizadeh, H.; Berndt, C.C.; Berghaus, J.O.; Boulos, M.; Brogan, J.; Bourtsalas, A.C.; Dolatabadi, A.; et al. The 2016 Thermal Spray Roadmap. *J. Therm. Spray Technol.* **2016**, *25*, 1376–1440. [CrossRef]

10. Liu, T.; Yao, S.-W.; Wang, L.-S.; Yang, G.-J.; Li, C.-X.; Li, C.-J. Plasma-sprayed thermal barrier coatings with enhanced splat bonding for CMAS and corrosion protection. *J. Therm. Spray Technol.* **2016**, *25*, 213–221. [CrossRef]

11. Sudagar, J.; Lian, J.; Sha, W. Electroless nickel, alloy, composite and nano coatings—A critical review. *J. Alloys Compd.* **2013**, *571*, 183–204. [CrossRef]

12. Innocenti, M.; Di Benedetto, F.; Giaccherini, A.; Salvietti, E.; Gambinossi, F.; Passaponti, M.; Foresti, M.L. E-ALD: Tailoring the optoeletronic properties of metal chalcogenides on Ag single crystals. In *Semiconductors*; Inguanta, R., Ed.; InTech: Rijeka, Croatia, 2018.

13. Zangari, G. Electrodeposition of alloys and compounds in the era of microelectronics and energy conversion technology. *Coatings* **2015**, *5*, 195–218. [CrossRef]

14. Greene, J.E. Tracing the 5000-year recorded history of inorganic thin films from ~3000 BC to the early 1900s AD. *Appl. Phys. Rev.* **2014**, *1*, 41302. [CrossRef]

15. Hunt, L.B. The early history of gold plating. *Gold Bull.* **1973**, *6*, 16–27. [CrossRef]

16. Daniell, J.F. *On Voltaic Combinations*; Richard Taylor: London, UK, 1840.

17. Jacobi, M.H. *Die Galvanoplastik, Oder das Verfahren coharentes Kupfer in Flatten Oder nach sonst gegebenen Formen unmittelbar aus Kupferauflosungen auf galvanischem Wege zu produciren*; Eggers und Co.: St. Petersburg, Russia, 1840.

18. Elkington, G.; Elkington, H. Improvements in Coating, Covering, or Plating certain Metals. British Patent 8447, 25 March 1840.

19. Abner, B.; Riddell, G.E. Nickel Plating by Chemical Reduction. U.S. Patent 2532283a, 5 May 1947.

20. Tench, D.; White, J. Enhanced tensile strength for electrodeposited nickel-copper multilayer composites. *Metall. Trans. A* **1984**, *15*, 2039–2040. [CrossRef]

21. Yahalom, J.; Zadok, O. Formation of composition-modulated alloys by electrodeposition. *J. Mater. Sci.* **1987**, *22*, 499–503. [CrossRef]

22. Landolt, D. Electrodeposition science and technology in the last quarter of the twentieth century. *J. Electrochem. Soc.* **2002**, *149*, S9–S20. [CrossRef]

23. Kang, H.S.; Lee, J.Y.; Choi, S.; Kim, H.; Park, J.H.; Son, J.Y.; Kim, B.H.; Noh, S. Do Smart manufacturing: Past research, present findings, and future directions. *Int. J. Precis. Eng. Manuf. Technol.* **2016**, *3*, 111–128. [CrossRef]

24. Lampke, T.; Steger, H.; Zacher, M.; Steinhäuser, S.; Wielage, B. Status quo und Trends der Galvanotechnik. *Materialwissenschaft und Werkstofftechnik* **2008**, *39*, 52–57. [CrossRef]

25. Future Market Insights Electroplating Market: Global Industry Analysis and Opportunity Assessment, 2016–2026. Available online: https://www.futuremarketinsights.com/reports/electroplating-market (accessed on 18 July 2018).

26. Alkaya, E.; Demirer, G.N. Improving resource efficiency in surface coating/painting industry: Practical experiences from a small-sized enterprise. *Clean Technol. Environ. Policy* **2014**, *16*, 1565–1575. [CrossRef]

27. Valdez, B.; Schorr, M.; Zlatev, R.; Garrillo, M.; Stoytcheva, M.; Alvarez, L.; Eliezer, A.; Rosas, N. Corrosion Control in Industry. In *Environmental and Industrial Corrosion*; Schorr, M., Ed.; InTech: Rijeka, Croatia, 2012; pp. 19–54.

28. Landolt, D. Electrochemical and materials science aspects of alloy deposition. *Electrochim. Acta* **1994**, *39*, 1075–1090. [CrossRef]

29. Bicelli, L.P.; Bozzini, B.; Mele, C.; D'Urzo, L. A review of nanostructural aspects of metal electrodeposition. *Int. J. Electrochem. Sci.* **2008**, *3*, 356–408.

30. Brenner, A. Electrodeposition of Alloys Containing Sulfur. In *Electrodeposition of Alloys: Principles and Practice*; Academic Press: London, UK, 1963; pp. 607–615, ISBN 9781483223117.

31. Pushpavana, M. Critical review on alloy plating: A viable alternative to conventional plating. *Bull. Electrochem.* **2000**, *16*, 559–566.

32. Raykhtsaum, G. PGM Highlights: Platinum alloys: A selective review of the available literature. *Johns. Matthey Technol. Rev.* **2013**, *57*, 202–213.

33. Darmanin, T.; De Givenchy, E.T.; Amigoni, S.; Guittard, F. Superhydrophobic surfaces by electrochemical processes. *Adv. Mater.* **2013**, *25*, 1378–1394. [CrossRef] [PubMed]

34. Brett, C.M.A. Deep eutectic solvents and applications in electrochemical sensing. *Curr. Opin. Electrochem.* **2018**, in press. [CrossRef]

35. Hosu, O.; Bârsan, M.M.; Cristea, C.; Săndulescu, R.; Brett, C.M.A. Nanostructured electropolymerized poly(methylene blue) films from deep eutectic solvents. Optimization and characterization. *Electrochim. Acta* **2017**, *232*, 285–295. [CrossRef]

36. Hosu, O.; Barsan, M.M.; Cristea, C.; Săndulescu, R.; Brett, C.M.A. Nanocomposites based on carbon nanotubes and redox-active polymers synthesized in a deep eutectic solvent as a new electrochemical sensing platform. *Microchim. Acta* **2017**, *184*, 3919–3927. [CrossRef]

37. Armand, M.; Endres, F.; MacFarlane, D.R.; Ohno, H.; Scrosati, B. Ionic-liquid materials for the electrochemical challenges of the future. *Nat. Mater.* **2009**, *8*, 621–629. [CrossRef] [PubMed]

38. Abbott, A.P.; Dalrymple, I.; Endres, F.; Macfarlane, D.R. Why use Ionic Liquids for Electrodeposition. In *Electrodeposition from Ionic Liquids*; Wiley-VCH: Weinheim, Germany, 2008; pp. 1–13.

39. Zhang, Q.; Wang, Q.; Zhang, S.; Lu, X.; Zhang, X. Electrodeposition in ionic liquids. *ChemPhysChem* **2016**, *17*, 335–351. [CrossRef] [PubMed]

40. Horwitz, C.P.; Suhu, N.Y.; Dailey, G.C. Synthesis, characterization and electropolymerization of ferrocene monomers with aniline and phenol substituents. *J. Electroanal. Chem.* **1992**, *324*, 79–91. [CrossRef]

41. Sharma, P.S.; Pietrzyk-Le, A.; D'Souza, F.; Kutner, W. Electrochemically synthesized polymers in molecular imprinting for chemical sensing. *Anal. Bioanal. Chem.* **2012**, *402*, 3177–3204. [CrossRef] [PubMed]

42. Antuña-Jiménez, D.; Díaz-Díaz, G.; Blanco-López, M.C.; Lobo-Castañón, M.J.; Miranda-Ordieres, A.J.; Tuñón-Blanco, P. Chapter 1—Molecularly Imprinted Electrochemical Sensors: Past, Present, and Future. In *Molecularly Imprinted Sensors*; Elsevier Science & Technology: Amsterdam, The Netherlands, 2012; pp. 1–34.

43. Selvolini, G.; Băjan, I.; Hosu, O.; Marrazza, G. DNA-based sensor for the detection of an organophosphorus pesticide: Profenofos. *Sensors* **2018**, *18*, 2035. [CrossRef] [PubMed]

44. Yoshida, T.; Zhang, J.; Komatsu, D.; Sawatani, S.; Minoura, H.; Pauporté, T.; Lincot, D.; Oekermann, T.; Schlettwein, D.; Tada, H.; et al. Electrodeposition of inorganic/organic hybrid thin films. *Adv. Funct. Mater.* **2009**, *19*, 17–43. [CrossRef]

45. Puippe, J.C. Qualitative Approach to Pulse Plating. In *Theory and Practice of Pulse Plating*; Puippe, J.C., Leaman, F., Eds.; American Electroplaters' Society: Orlando, FL, USA, 1986; ISBN 0936569026.

46. Zanella, C.; Leisner, P. 6th European pulse plating seminar. *Trans. Inst. Met. Finish.* **2014**, *92*, 178–179. [CrossRef]

47. Chandrasekar, M.S.; Pushpavanam, M. Pulse and pulse reverse plating-Conceptual, advantages and applications. *Electrochim. Acta* **2008**, *53*, 3313–3322. [CrossRef]

48. Innocenti, M.; Bencistà, I.; Bellandi, S.; Bianchini, C.; Di Benedetto, F.; Lavacchi, A.; Vizza, F.; Foresti, M.L. Electrochemical layer by layer growth and characterization of copper sulfur thin films on Ag(111). *Electrochim. Acta* **2011**, *58*, 599–605. [CrossRef]

49. Bencista, I.; Di Benedetto, F.; Innocenti, M.; De Luca, A.; Fornaciai, G.; Lavacchi, A.; Montegrossi, G.; Oberhauser, W.; Pardi, L.A.; Romanelli, M.; et al. Phase composition of Cu_xS thin films: Spectroscopic evidence of covellite formation. *Eur. J. Mineral.* **2012**, *24*, 879–884. [CrossRef]

50. Gregory, B.W.; Stickney, J.L. Electrochemical atomic layer epitaxy (ECALE). *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *300*, 543–561. [CrossRef]

51. Innocenti, M.; Forni, F.; Pezzatini, G.; Raiteri, R.; Loglio, F.; Foresti, M.L. Electrochemical behavior of As on silver single crystals and experimental conditions for InAs growth by ECALE. *J. Electroanal. Chem.* **2001**, *514*, 75–82. [CrossRef]

52. Stanko, B.; Zangari, G. Electrochemical Surface Processes and Opportunities for Material Synthesis. In *Advances in Electrochemical Science and Engineering*; Alkire, R.C., Bartlett, P.N., Lipkowski, J., Eds.; Wiley-Blackwell: Hoboken, NJ, USA, 2015; pp. 59–106.

53. Lincot, D. Electrodeposition of semiconductors. *Thin Solid Films* **2005**, *487*, 40–48. [CrossRef]

54. Pezzatini, G.; Loglio, F.; Innocenti, M.; Foresti, M.L. Selenium(IV) electrochemistry on silver: A combined electrochemical quartz-crystal microbalance and cyclic voltammetric investigation. *Collect. Czechoslov. Chem. Commun.* **2003**, *68*, 1579–1595. [CrossRef]

55. Innocenti, M.; Bencista, I.; Di Benedetto, F.; Cinotti, S.; De Luca, A.; Bellandi, S.; Lavacchi, A.; Muniz Miranda, M.; Vizza, F.; Marinelli, F.; et al. Underpotential deposition of Sn on S-covered Ag(111). *ECS Trans.* **2013**, *50*, 1–7. [CrossRef]

56. Innocenti, M.; Bellandi, S.; Lastraioli, E.; Loglio, F.; Foresti, M.L. Selective electrodesorption based atomic layer deposition (SEBALD): A novel electrochemical route to deposit metal clusters on Ag(111). *Langmuir* **2011**, *27*, 11704–11709. [CrossRef] [PubMed]

57. Innocenti, M.; Zangari, G.; Zafferoni, C.; Bencistà, I.; Becucci, L.; Lavacchi, A. Selective electrodesorption based atomic layer deposition (SEBALD) modifications of silver surfaces for enhancing oxygen reduction reaction activity. *J. Power Sources* **2013**, *241*, 80–86. [CrossRef]

58. Giurlani, W.; Giaccherini, A.; Salvietti, E.; Passaponti, M.; Comparini, A.; Morandi, V.; Liscio, F.; Cavallini, M.; Innocenti, M. Selective electrodesorption based atomic layer deposition (SEBALD) of bismuth under morphological control. *Electrochem. Soc. Interface* **2018**, *27*, 77–81.

59. Liu, Y.; Gokcen, D.; Bertocci, U.; Moffat, T.P. Self-terminating growth of platinum films by electrochemical deposition. *Science* **2012**, *338*, 1327–1330. [CrossRef] [PubMed]

60. Vanpaemel, J.; Sugiura, M.; Cuypers, D.; Van Der Veen, M.H.; De Gendt, S.; Vereecken, P.M. Electrochemical deposition of subnanometer Ni films on TiN. *Langmuir* **2014**, *30*, 2047–2053. [CrossRef] [PubMed]

61. Wang, R.; Bertocci, U.; Tan, H.; Bendersky, L.A.; Moffat, T.P. Self-terminated electrodeposition of Ni, Co, and Fe ultrathin films. *J. Phys. Chem. C* **2016**, *120*, 16228–16237. [CrossRef]

62. Fahrenkrug, E.; Maldonado, S. Electrochemical liquid-liquid-solid (ec-LLS) crystal growth: A low-temperature strategy for covalent semiconductor crystal growth. *Acc. Chem. Res.* **2015**, *48*, 1881–1890. [CrossRef] [PubMed]

63. Hu, J.; Yu, M.F. Meniscus-confined three-dimensional electrodeposition for direct writing of wire bonds. *Science* **2010**, *329*, 313–316. [CrossRef] [PubMed]

64. Hirt, L.; Ihle, S.; Pan, Z.; Dorwling-Carter, L.; Reiser, A.; Wheeler, J.M.; Spolenak, R.; Vörös, J.; Zambelli, T. Template-free 3D microprinting of metals using a force-controlled nanopipette for layer-by-layer electrodeposition. *Adv. Mater.* **2016**, *28*, 2311–2315. [CrossRef] [PubMed]

65. Offredi, P. *Il Manuale del Lavaggio Industriale. Solventi, Detergenti, Impianti Legislazione e Impatto Ambientale*; HB PI.ERRE Editrice: Milano, Italy, 1999.

66. Bertorelle, E. *Trattato di Galvanotecnica*; Metallurgia e siderurgia; Hoepli: Milano, Italy, 2016; ISBN 9788820374983.

67. Thecniche Nuove. *Manuale di Trattamenti e Finiture*; Tecniche Nuove: Milano, Italy, 2003; ISBN 9788848164054.

68. Siu, C.; Man, H.; Yeung, C. Electrodeposition of Co-Mo-P barrier coatings for Cu/Au coated systems. *Surf. Coat. Technol.* **2005**, *200*, 2223–2227. [CrossRef]

69. Benner, H.L.; Wernlund, C.J. The high efficiency cyanide copper bath. *J. Electrochem. Soc.* **1941**, *80*, 355–365. [CrossRef]

70. Stareck, J.E. Electrodeposition of Copper and Bath Therefore. U.S. Patent 2,250,556, 29 July 1941.

71. Willis, W.J. Electrodeposition of copper, Acidic Copper Electroplating Baths and Additives Therefor. U.S. Patent 4,347,108, 31 August 1982.

72. Grossblatt, G.H. Zinc Plating Baths. U.S. Patent 3,883,405, 13 May 1975.

73. Grill, C.D.; Kollender, J.P.; Hassel, A.W. Preparation and investigation of combinatorially electrodeposited zinc-nickel, zinc-cobalt, and zinc-nickel-cobalt material libraries. *Phys. Status Solidi Appl. Mater. Sci.* **2017**, *214*, 1600706. [CrossRef]

74. Hegde, A.C.; Venkatakrishna, K.; Eliaz, N. Electrodeposition of Zn-Ni, Zn-Fe and Zn-Ni-Fe alloys. *Surf. Coat. Technol.* **2010**, *205*, 2031–2041. [CrossRef]

75. Cavallotti, P.L. Nickel allergy. *AIFM Galvano Tec. e Nuove Finiture (Italy)* **2001**, *11*, 42–43.

76. Ngan, V. Jewelry Allergy. Available online: https://www.dermnetnz.org/topics/jewelry-allergy/ (accessed on 18 July 2018).

77. Torabinejad, V.; Aliofkhazraei, M.; Assareh, S.; Allahyarzadeh, M.H.; Rouhaghdam, A.S. Electrodeposition of Ni-Fe alloys, composites, and nano coatings—A review. *J. Alloys Compd.* **2017**, *691*, 841–859. [CrossRef]

78. Oriňáková, R.; Turoňová, A.; Kladeková, D.; Gálová, M.; Smith, R.M. Recent developments in the electrodeposition of nickel and some nickel-based alloys. *J. Appl. Electrochem.* **2006**, *36*, 957–972. [CrossRef]

79. Hovestad, A.; Tacken, R.A.; Mannetje, H.H. Electrodeposited nanocrystalline bronze alloys as replacement for Ni. *Phys. Status Solidi C* **2008**, *5*, 3506–3509. [CrossRef]

80. Dos Santos, W.A.T.; Dos Santos, W.I.A.; De Assis, S.L.; Terada, M.; Costa, I. Bronze as alternative for replacement of nickel in intermediate layers underneath gold coatings. *Electrochim. Acta* **2013**, *114*, 799–804. [CrossRef]

81. Walsh, F.C.; Low, C.T.J. A review of developments in the electrodeposition of tin-copper alloys. *Surf. Coat. Technol.* **2016**, *304*, 246–262. [CrossRef]

82. Atkinson, R.H.; Raper, A.R. The Electrodeposition of Palladium. *Trans. IMF* **1932**, *8*, 10.1–10.24. [CrossRef]

83. Vilaplana, J.; Romaguera, C. New developments in jewellery and dental materials. *Contact Dermat.* **2007**, *39*, 55–57. [CrossRef]

84. Pushpavanam, M.; Natarajan, S.R.; Balakrishnan, K.; Sharma, L.R. Electrodeposition of palladium-nickel alloy. *Bull. Electrochem.* **1990**, *6*, 761–764.

85. Baumgärtner, M.E.; Gabe, D.R. Palladium-iron alloy electrodeposition. Part I single metal systems. *Trans. IMF* **2000**, *78*, 11–16. [CrossRef]

86. Augthun, M.; Lichtenstein, M.; Kammerer, G. Studies on the allergenic potential of palladium alloys. *Dtsch. Zahnarztl. Z.* **1990**, *45*, 480–482. [PubMed]

87. Muris, J.; Goossens, A.; Gonçalo, M.; Bircher, A.J.; Giménez-Arnau, A.; Foti, C.; Rustemeyer, T.; Feilzer, A.J.; Kleverlaan, C.J. Sensitization to palladium and nickel in Europe and the relationship with oral disease and dental alloys. *Contact Dermat.* **2015**, *72*, 286–296. [CrossRef] [PubMed]

88. Renner, H.; Schlamp, G.; Hollmann, D.; Lüschow, H.M.; Tews, P.; Rothaut, J.; Dermann, K.; Knödler, A.; Hecht, C.; Schlott, M.; et al. Gold, Gold Alloys, and Gold Compounds. Available online: https://onlinelibrary. wiley.com/doi/abs/10.1002/14356007.a12_499 (accessed on 25 May 2018).

89. Drost, E.; Haußelt, J. Uses of gold in jewellery. *Interdiscip. Sci. Rev.* **1992**, *17*, 271–280. [CrossRef]

90. Klotz, U.E.; Tiberto, D.; Held, F. Optimization of 18-karat yellow gold alloys for the additive manufacturing of jewelry and watch parts. *Gold Bull.* **2017**, *50*, 111–121. [CrossRef]

91. MacCormack, I.B.; Bowers, J.E. New white gold alloys—Their development on the basis of quantitative colour assessment. *Gold Bull.* **1981**, *14*, 19–24. [CrossRef]

92. Cretu, C.; Van Der Lingen, E. Coloured gold alloys. *Gold Bull.* **1999**, *32*, 115–126. [CrossRef]

93. Fier-Bühner, J.; Basso, A.; Poliero, M. Metallurgy and processing of coloured gold intermetallics—Part II: Investment casting and related alloy design. *Gold Bull.* **2010**, *43*, 11–20. [CrossRef]

94. Corti, C.W. Blue, black and purple! The special colours of gold. In Proceedings of the International Jewellery Symposium, St. Petersburg, Russia, 3–7 July 2006.

95. Dtrijević, S.; Rajčić-Vujasinović, M.; Trujić, V. Non-cyanide electrolytes for gold plating—A review. *Int. J. Electrochem. Sci.* **2013**, *8*, 6620–6646.

96. Missey, R.J. Gold and silver plating basics. *Prod. Finish.* **2010**, *75*, 142–147.

97. Wberg, A.M. Rhodium plating. *Met. Finish.* **1995**, *93*, 283–288. [CrossRef]

98. Missey, R.J. Platinum plating. *Met. Finish.* **1995**, *93*, 282. [CrossRef]

99. Wberg, A.M. Ruthenium plating. *Met. Finish.* **1995**, *93*, 289. [CrossRef]

100. Snyder, D.L. Decorative chromium plating. *Met. Finish.* **1999**, *97*, 219–226. [CrossRef]

101. Dennis, J.K.; Such, T.E. *Nickel and Chromium Plating*; Woodhead Publishing: Cambridge, UK, 1986.

102. Henning, H.F. Chromium plating. *Ann. Occup. Hyg.* **1972**, *15*, 93–97. [CrossRef] [PubMed]

103. Gardner, A. Decorative trivalent chromium plating. *Met. Finish.* **2006**, *104*, 41–45. [CrossRef]

104. Lilian, F.S.; Aderval, S.L. Experimental Design and Response Surface Analysis as Available Tools for Statistical Modeling and Optimization of Electrodeposition Processes. In *Electroplating*; Sebayang, D., Ed.; InTech: Rijeka, Croatia, 2012; pp. 147–166.

105. Vasudevan, S.; Oturan, M.A. Electrochemistry: as cause and cure in water pollution—An overview. *Environ. Chem. Lett.* **2014**, *12*, 97–108. [CrossRef]

106. Salles, F.J.; Sato, A.P.S.; Luz, M.S.; Fávaro, D.I.T.; Ferreira, F.J.; da Silva Paganini, W.; Olympio, K.P.K. The environmental impact of informal and home productive arrangement in the jewelry and fashion jewelry chain on sanitary sewer system. *Environ. Sci. Pollut. Res.* **2018**, *25*, 10701–10713. [CrossRef] [PubMed]

107. Kanwal, R.; Fiza, F.; Iqra, W.; Hamid, A.M.S. Prevalence of exposure of heavy metals and their impact on health consequences. *J. Cell. Biochem.* **2018**, *119*, 157–184. [CrossRef]

108. Jin, R.; Zhu, Y.; Qian, H. Quantum-sized gold nanoclusters: Bridging the gap between organometallics and nanocrystals. *Chem. A Eur. J.* **2011**, *17*, 6584–6593. [CrossRef] [PubMed]

109. Bencko, V. Nickel: A review of its occupational and environmental toxicology. *J. Hyg. Epidemiol. Microbiol. Immunol.* **1983**, *27*, 237–247. [PubMed]

110. Denkhaus, E.; Salnikow, K. Nickel essentiality, toxicity, and carcinogenicity. *Crit. Rev. Oncol. Hematol.* **2002**, *42*, 35–56. [CrossRef]

111. Kasprzak, K.S.; Sunderman, F.W.; Salnikow, K. Nickel carcinogenesis. *Mutat. Res. Mol. Mech. Mutagen.* **2003**, *533*, 67–97. [CrossRef]

112. Seilkop, S.K.; Oller, A.R. Respiratory cancer risks associated with low-level nickel exposure: An integrated assessment based on animal, epidemiological, and mechanistic data. *Regul. Toxicol. Pharmacol.* **2003**, *37*, 173–190. [CrossRef]

113. Yang, K.; Ren, Y. Nickel-free austenitic stainless steels for medical applications. *Sci. Technol. Adv. Mater.* **2010**, *11*, 14105. [CrossRef] [PubMed]

114. Franken, A.; Eloff, F.C.; Du Plessis, J.; Du Plessis, J.L. In vitro permeation of metals through human skin: A review and recommendations. *Chem. Res. Toxicol.* **2015**, *28*, 2237–2249. [CrossRef] [PubMed]

115. *EN 12472:2005+A1:2009 Method for the Simulation of Wear and Corrosion for the Detection of Nickel Release from Coated Item*; European Committee for Standardisation: Brussels, Belgium, 2009.

116. *EN 1811:2011+A1:2015 Reference Test Method for Release of Nickel from All Post Assemblies Which Are Inserted into Pierced Parts of the Human Body and Articles Intended to Come into Direct and Prolonged Contact with the Skin*; European Committee for Standardisation: Brussels, Belgium, 2015.

117. Brugnoni, C.; Bianchi, R.; Bianchini, A.; Stroosnijder, M.F. Influence of Experimental Test Conditions on the Ni Release of a Cu-Ni Alloy in Artificial Sweat. In *Materials for Medical Engineering*; Wiley-Blackwell: Hoboken, NJ, USA, 2005; pp. 243–248.

118. Midander, K.; Julander, A.; Kettelarij, J.; Lidén, C. Testing in artificial sweat—Is less more? Comparison of metal release in two different artificial sweat solutions. *Regul. Toxicol. Pharmacol.* **2016**, *81*, 381–386. [CrossRef] [PubMed]

119. Whittington, C.M.; Lo, W.Y. Prevention of nickel release from electroplated articles in the context of allergic contact dermatitis: further outcomes. *Trans. IMF* **2018**, *96*, 63–70. [CrossRef]

120. Whittington, C.M.; Lo, W.Y.; Yau, M.Y. Prevention of nickel release from decorative nickel-chromium electroplated articles in the context of allergic contact dermatitis. *Trans. IMF* **2015**, *93*, 176–179. [CrossRef]

121. Hebing, Z.; Man, L.; Dongsheng, L.; Mengqing, X.; Weishan, L. Electrochemical behaviors of zinc-indium alloy electroplating in alkaline solutions. *Acta Metall. Sin.* **2011**, *47*, 1055–1060. [CrossRef]

122. Alam, N.; Corbett, S.J.; Ptolemy, H.C. Environmental health risk assessment of nickel contamination of drinking water in a country town in NSW. *Public Health Bull.* **2008**, *19*, 170–173. [CrossRef]

123. Kisku, G.C.; Markandeya; Kushwaha, H.; Arora, S. Environmental health risk estimation of heavy metals accumulated in soil and cultivated plants irrigated with industrial effluents. *Adv. Recycl. Waste Manag.* **2016**, *1*, 1000108. [CrossRef]

124. Schlesinger, M.; Paunovic, M. *Modern Electroplating*, 5th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2011; ISBN 9780470167786.

125. Guney, M.; Zagury, G.J. Heavy metals in toys and low-cost jewelry: Critical review of U.S. and Canadian legislations and recommendations for testing. *Environ. Sci. Technol.* **2012**, *46*, 4265–4274. [CrossRef] [PubMed]

126. Canfield, R.L.; Henderson, C.R.; Cory-Slechta, D.A.; Cox, C.; Jusko, T.A.; Lanphear, B.P. Intellectual impairment in children with blood lead concentrations below 10 μg per deciliter. *N. Engl. J. Med.* **2003**, *348*, 1517–1526. [CrossRef] [PubMed]

127. *ISO 105-E04:2013 Textiles—Tests for Colour Fastness—Part E04: Colour Fastness to Perspiration*; International Organization for Standardization: Geneva, Switzerland, 2013.

128. *EPA Method 6010D (SW-846): Inductively Coupled Plasma—Atomic Emission Spectrometry*; United States Environmental Protection Agency: Washington, DC, USA, 2014.

129. Pouzar, M.; Zvolská, M.; Jarolím, O.; Vavrušová, L.A. The health risk of cd released from low-cost jewelry. *Int. J. Environ. Res. Public Health* **2017**, *14*, 520. [CrossRef] [PubMed]

130. Wojczykowski, K. New Developments in Corrosion Testing: Theory, Methods and Standards. Available online: https://www.pfonline.com/articles/new-developments-in-corrosion-testing-theory-methods-and-standards (accessed on 18 July 2018).

131. Eleftheriadis, R.J.; Myklebust, O. A guideline of quality steps towards zero defect manufacturing in industry. *Proc. Int. Conf. Ind. Eng. Oper. Manag.* **2016**, 332–340.

132. Giurlani, W.; Innocenti, M.; Lavacchi, A. X-ray Microanalysis of precious metal thin films: Thickness and composition determination. *Coatings* **2018**, *8*, 84. [CrossRef]

133. Zhuang, L.; Bao, S.; Wang, R.; Li, S.; Ma, L.; Lv, D. Thin film thickness measurement using electron probe microanalyzer. In Proceedings of the IEEE 2009 International Conference on Applied Superconductivity & Electromagnetic Devices (ASEMD '09), Chengdu, China, 25–27 September 2009; pp. 142–144.

134. *Colorimetry*, 3rd ed.; CIE: Vienna, Austria, 2004; ISBN 3-901-906-33-9.

135. *Colorimetry—Part 4: CIE 1976 L*a*b* Colour Space*; CIE: Vienna, Austria, 2007.

136. Ronnier, L.M. The quality of light sources. *Color. Technol.* **2011**, *127*, 75–87. [CrossRef]

137. Mahy, M.; Van Eycken, L.; Oosterlinck, A. Evaluation of uniform color spaces developed after the adoption of CIELAB and CIELUV. *Color Res. Appl.* **1994**, *19*, 105–121. [CrossRef]

138. Capitán-Vallvey, L.F.; López-Ruiz, N.; Martínez-Olmos, A.; Erenas, M.M.; Palma, A.J. Recent developments in computer vision-based analytical chemistry: A tutorial review. *Anal. Chim. Acta* **2015**, *899*, 23–56. [CrossRef] [PubMed]

139. Melgosa, M.; Gómez-Robledo, L.; García, P.A.; Morillas, S.; Fernández-Maloigne, C.; Richard, N.; Huang, M.; Li, C.; Cui, G. Color-quality control using color-difference formulas: Progress and problems. In Proceedings of the Third International Conference on Applications of Optics and Photonics, Faro, Portugal, 8–12 May 2017; p. 104530U7.

140. Medina, J.M.; Díaz, J.A. Fluctuation scaling of color variability in automotive metallic add-on parts. *Prog. Org. Coat.* **2017**, *104*, 118–124. [CrossRef]

141. Giurlani, W.; Gambinossi, F.; Salvietti, E.; Passaponti, M.; Innocenti, M. Color measurements in electroplating industry: implications for product quality control. *ECS Trans.* **2017**, *80*, 757–766. [CrossRef]

142. Madrigal, A.C.; Branch, W.J.; Restrepo, A.; Mery, D. A method for automatic surface inspection using a model-based 3D descriptor. *Sensors* **2017**, *17*, 2262. [CrossRef] [PubMed]

143. Malamas, E.N.; Petrakis, E.G.M.; Zervakis, M.; Petit, L.; Legat, J.-D. A survey on industrial vision systems, applications and tools. *Image Vis. Comput.* **2003**, *21*, 171–188. [CrossRef]

144. Byrne, G.; Sheahan, C. Comparative analysis of vision systems for electroplating surface quality inspection. *Int. J. Prod. Res.* **2005**, *43*, 3787–3801. [CrossRef]

145. Byrne, G.; Sheahan, C. Inline color vision for specific electroplating defect identification. *J. Manuf. Process.* **2006**, *8*, 133–143. [CrossRef]

146. Kumar, A.; Clement, S.; Agrawal, V.P. Quality modelling and analysis of electroplating system using graph theory matrix approach. *Int. J. Prod. Qual. Manag.* **2011**, *8*, 85–112. [CrossRef]

147. *ASTM B571-97(2008)e1 Standard Practice for Qualitative Adhesion Testing of Metallic Coatings*; American Society for Testing and Materials International: West Conshohocken, PA, USA, 2008.

148. *ISO 2819:2017 Metallic Coatings on Metallic Substrates—Electrodeposited and Chemically Deposited Coatings—Review of Methods Available for Testing Adhesion*; International Organization for Standardization: Geneva, Switzerland, 2017.

149. *ISO 11644:2009 (IULTCS/IUF 470) Leather—Test for Adhesion of Finish*; International Organization for Standardization: Geneva, Switzerland, 2009.

150. *ISO 105-E03:2010 Textiles—Tests for Colour Fastness—Part E03: Colour Fastness to Chlorinated Water (Swimming-Pool Water)*; International Organization for Standardization: Geneva, Switzerland, 2010.

151. Ono, Y.; Morito, S.; Li, C. Stress measurement using EBSD analysis of grains in copper foil. *Exp. Mech.* **2012**, *52*, 493–502. [CrossRef]

152. Sharma, T.; Shaver, P.; Brown, D.A.; Brüning, R.; Peldzinski, V.; Ferro, A. Time evolution of stress and microstructure in electroplated copper films. *Electrochim. Acta* **2016**, *196*, 479–486. [CrossRef]

153. Wang, J.; Zhou, Q.; Shao, S.; Misra, A. Strength and plasticity of nanolaminated materials. *Mater. Res. Lett.* **2017**, *5*, 1–19. [CrossRef]

154. *ISO 4611:2010 Plastics—Determination of the Effects of Exposure to Damp Heat, Water Spray and Salt Mist*; International Organization for Standardization: Geneva, Switzerland, 2010.

155. *ISO 17228:2015 (IULTCS/IUF 412) Leather—Tests for Colour Fastness—Change in Colour with Accelerated Ageing*; International Organization for Standardization: Geneva, Switzerland, 2015.

156. *ISO 3160-2:2015 Watch-Cases and Accessories—Gold Alloy Coverings—Part 2: Determination of Fineness, Thickness, Corrosion Resistance and Adhesion*; International Organization for Standardization: Geneva, Switzerland, 2015.

157. *ISO 9227:2017 Corrosion Tests in Artificial Atmospheres—Salt Spray Tests*; International Organization for Standardization: Geneva, Switzerland, 2017.

158. *ISO 4538:1978 Metallic Coatings—Thioacetamide Corrosion Test (TAA Test)*; International Organization for Standardization: Geneva, Switzerland, 1978.

159. *ISO 4524-2:2000 Metallic Coatings—Test Methods for Electrodeposited Gold and Gold Alloy Coatings—Part 2: Mixed Flowing Gas (MFG) Environmental Tests*; International Organization for Standardization: Geneva, Switzerland, 2000.

160. Gross, O.; Eisenbart, M.; Schmitt, L.Y.; Neuber, N.; Ciftci, L.; Klotz, U.E.; Busch, R.; Gallino, I. Development of novel 18-karat, premium-white gold bulk metallic glasses with improved tarnishing resistance. *Mater. Des.* **2018**, *140*, 495–504. [CrossRef]

161. Pezzato, L.; Magnabosco, G.; Brunelli, K.; Breda, M.; Dabalà, M. Microstructure and mechanical properties of a 18 kt 5 N gold alloy after different heat treatments. *Metallogr. Microstruct. Anal.* **2016**, *5*, 116–123. [CrossRef]

162. Jaszczak, E.; Polkowska, Ż.; Narkowicz, S.; Namieśnik, J. Cyanides in the environment—Analysis—Problems and challenges. *Environ. Sci. Pollut. Res.* **2017**, *24*, 15929–15948. [CrossRef] [PubMed]

163. Marcus, M.I.; Vlad, M.; Mitiu, M.A.; Anghel, A.M.; Marinescu, F.; Laslo, L.; Ilie, M.; Szep, R.; Ghita, G.; Matei, M.; Holban, E.; Dumitru, F.D. Recovery of galvanic sludge by physicochemical mechanisms. *J. Environ. Prot. Ecol.* **2017**, *18*, 1117–1126.

164. Sulimova, M.A.; Litvinova, T.E. Metallurgical production waste treatment efficiency increase. In Proceedings of the 16th International Multidisciplinary Scientific GeoConference & EXPO SGEM2016, Albena, Bulgaria, 28 June–7 July 2016; pp. 569–576.

165. Sofińska-Chmiel, W.; Kołodyńska, D. Application of ion exchangers for the purification of galvanic wastewater from heavy metals. *Sep. Sci. Technol.* **2018**, *53*, 1097–1106. [CrossRef]