A Review on the Efficacy of Electroplating in Deteriorating Environments

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Abstract. Electroplating is an electrochemical process that involves a chemical response of the constituents in an aqueous mixture, due to galvanic excitation that causes the formation of thin film layers i.e. the coating, on the substrate of the material. Very few surface finishing techniques exist that serve the purposes of various functional applications and aesthetic appeal. Electroplating stands out as one of those surface finishing techniques that impact peculiar properties. This paper presents an overview of the multifunction application and efficacy of electroplating in different corrosive environments.

Keywords: Electroplating, Electrochemical, Coating, Chemical, Environments

1. Introduction

Corrosion is a worldwide phenomenon, a major force in the society without an absolute cure. It is especially of detriment to the engineers, as their work requires the use of materials, especially metals, which seem to be corrosion’s area of focus [1]. In Nigeria, corrosion also affects our most profitable, economy boosting ventures, the oil sector. Using a case study of the OML 124, an onshore oil production platform giving corrosion costs per oil barrel to be $1,216,236 annualized for 5 years [1]. Corrosion occurs at various rates, and a large variety of materials from metals like iron and copper, and non-metals like ceramics and rubber. It is a thermodynamic and electrochemical process that occurs for example; when a metallic surface is exposed to an aqueous electrolyte, this forms an anodic site (oxidation process) that produces electrons in the metal and a cathodic site (reduction process), that make up the corrosion cell [2]. Corrosion is widely studied as there is so much to gain from its prevention, various methods of coating and techniques of substrate inhibition have been invented and innovated into practical applications for various fields, such as in the oil and gas sector in off-shore areas which possess various solutes in the sea water, and the field of transportation where various parts of mechanical devices are lubricated with oils and liquids to enable better movement of parts and reduce wear, still have detrimental effects to the materials themselves are they are subjected to the forces that dissolve and degrade them in these solutions.

1.1 Types of Corrosion

The natural phenomenon comes in many forms such as:

- Crevice corrosion: Crevice corrosion occurs often in situations where liquid seeps into cracks or gaps in metals or other materials, and this opening remains sufficiently narrow for the liquid to remain stagnant [3]. This results in capillary action which forces the fluid into the gap, and the tighter or smaller the gap, the greater the capillary forces. The stagnant zone causes slow/ non-existent transportation of fluid into or out of the gap [4].
Hydrogen embrittlement: This form of corrosion takes place at the cathode, the area which is generally believed to be safe from corrosion, as it is the member that is reinforced. Hydrogen molecules are formed from reduced hydrogen ions at the cathode and these molecules bubble out as hydrogen gas [3].

Stress corrosion cracking: Stress corrosion cracking occurs due to the stresses or fatigue which weakens already weak sections of a metal undergoing forces, which undergo corrosion, thereby undergo cracking in specific solutions, as aluminum alloys crack in the presence of chlorine and mild steel cracks in the presence of various alkali solutions [2].

Intergranular corrosion: The segregation of iron in grain boundaries, when small amounts of iron are available in aluminum as an example, wherein the solubility of iron is low, causing intergranular corrosion [2]. Intergranular attack is hastened by the potential difference between grains and various grain boundaries, this means that the attack is based on the accessibility of the anodic sites at grain boundaries [5].

[2] investigated the growing concern of corrosion on metal and polymer materials. The corrosion costs in India was estimated to Rs 1 Lakh each year – the phenomenon described as a degradation of a material because of its reaction with its environment. This dependence on its environment leaves its prevention and care techniques highly varied as standards must be created based on the prevailing local conditions and climate conditions. India and various other countries have weather varying wildly from site to site based on location and time; the methods used to avert the corrosion of metals in specific parts of India, as a tropical climate, would not be the best fit for places such as Greenland, with its cold and snowy front. The authors argue that without corrosion, our economies would drastically change, which in the direction of this imposed could mean a net positive increase and a betterment in the standards of human life throughout the world. It describes that there is still a long battle against corrosion, as improved technology can only come from research and development through the awareness of individuals, and with only high-scale industries taking most note of corrosion prevention, we are still a long way from optimal corrosion inhibition, as most business, small scale and medium sized enterprises pay no heed to the effects of corrosion at all.

[6], discussed the role of corrosion protection in the oil and gas industries where the various corrosion types and associated agents are thoroughly researched to determine methods of mitigation. Examples such as pitting corrosion are monitored with standards of the oil and gas industry, such as the critical pitting temperature using ASTM G48 and ASTM G-150, using the E method which has been approved to be inherently resistant to pitting corrosion and its effects in fuel piping and high temperature oxidation processes. It was also noted that stresses induced in steel material and equipment are exposed to chlorine induced stress corrosion cracking. All this couples up to high costs and maintenance, as various equipment and materials, featuring the Nalli given in a data table show material composition of these equipment composed mainly of iron, which is subject to corrosion, but is inhibited through the process of alloying and coatings. There are two main types of metal coatings – Metals serving as coatings on various substrates and coatings on metal substrates which is a reversal of the former and counterpart. The former can be named metallizing, while the latter is secularly described as a film/paint type which may include inks or other types of coatings. The application of surface coatings/plating to metal substrates for part finishing is now widespread in the manufacturing industry [7]. These films provide various boosts to the mechanical, physical and sometimes, chemical properties of the metal. The most widespread coating and surface plating technologies include:

- Vapor Deposition;
- Chemical and Electrochemical Deposition;
- Spraying [8].

These various methods have proved effective for a manifold of situations peculiar to that requiring the coating. The most commercially successful coating methods still remain those of chemical and electrochemical depositions: Electroplating and electroless deposition being branches under the plating method. Nickel electroplating has been in study as early as the beginning of the 20th [9], with various forms
of electroplating being studied before this. Electroless deposition meanwhile, began its studies in 1946, which was mid-way into the 20th century, at the 34th annual AES meeting, with Grace Riddle and Abner Brenner bringing to light results on their previous studies concerning electroless nickel baths [10]. These two methods are extremely similar in practical as they both compose majorly of chemical baths of particular compositions, but are differentiated by the occurrence of galvanic action in the electroplating process.

Electroplating comes in through the protection technique of surface coatings, where it known as an electrochemical process that involves a chemical response of the constituents in an aqueous mixture, due to galvanic excitation that causes the formation of thin film layers i.e. the coating, on the substrate of the material. Very few surface finishing techniques exist that serve the purposes of various functional applications and aesthetic appeal; electroplating stands to be one of those surface finishing techniques. Electroplating is an electrochemical plating process that improves visual appearance, and improves both the service life and performance of materials during that period [9]. The electroplating technique involves the application of a metallic coating to a metal substrate, or the surface of a conducting material through an electrochemical reaction. This process of coating exists as both an art and a form of science, as it is a derivation from various lessons of physics and chemistry, but no form of studying will produce an expert electroplater, as in this case, the experience given by this process holds no substitute. In comparison with other techniques, electroplating offers a manifold of advantages such as accuracy in control, low energy requirements, good duplicability, flexibility, high production rate, economy in scaling, even coating, waste reduction and the capability to coat more complex topology and geometry [11]. Specifically, nickel deposits produced by electroplating are usually characterized by low porosity, proficient tribo-corrosion properties and high density, with increase in strength accompanied by reduction in the grain sizes of these deposits.

Considering the application of electroplating of nickel, a study into nickel deposition shows its widespread use, and development into understanding it’s underlying mechanisms; with the properties and microstructure being mainly dependent on electrolyte composition and parameters of the plating process. An example of which shows nickel sulphamate baths being used generally for high speed plating processes due to the fact that the nickel deposits from this formulation display low internal stresses and expansive ductility [9]. These days, electroplating is generally accepted and utilized, as it opens up more opportunity for the study of microsystems providing a means that is much simpler in practice and cost effective [12]. An electroplating process requires standard equipment to work, although more equipment can be brought in to make the job smoother, the general electrolysis cell consists of:

1. The cathodes, which are the negative electrode, representing the material which is used to plate;
2. The anodes, which are the positive electrode, representing the material which is to be plated;
3. The electrolyte plating solution which plater commonly call the “bath”;
4. The components completing the external electrical circuit which include the power supply, current conducting cables and measuring tools [13].

The electrical relationships established as the fundamentals for the occurrence of the electroplating process were propounded by Michael Faraday in 1833, and have remained unchanged since their inception. These laws are important to the understanding and practical application of the process, they are have to do with the examination of the electrical energy and chemical changes resulting from the electrical energy due to its amount, where during electrodeposition, the amount of current passing through the anodes and cathode denotes the rate of the coating and the amount to be deposited, which is a direct indication of the laws of faraday (electrical energy is proportional to chemical change) [14]. Electroplating evolved from these laws to be utilized in these major applications:

1. Improving visual fidelity
2. Protection of materials
3. Special surface properties
4. Improving Physical properties
The electroplating process is generally done for improvements in visual fidelity, resistances, evolution of special surface properties or general improvement of physical properties in engineering disciplines, or a mixture of any. To achieve these required properties, the parameters, or factors, which control the process of plating must be observed and controlled; these factors determine the thickness of the deposition, the appearance, the uniformity and overall outlook of the plated metal. These factors include: The temperature of the bath; current density; the time of deposition; the bath concentration; agitation; material involved (metal ions); Potential of hydrogen (pH) [14].

Possessing the perfect parameters for electroplating and the deposition baths gives process stability at an interval and enables programming for duplicity at various scales. It is therefore imperative – to achieve an efficient coating process – to select materials carefully and give accurate pre-treatment to the cathode and anode, and engage in a careful selection process of bath components, current density and other important factors [15].

2 Electroplating Theory
The process of electroplating is based off the two physical laws of Michael Faraday where it is stated that the chemical power of a current of electricity is directly proportional to the amount of electricity that passes through it and the second law states that electrochemical equivalents coinciding are exactly the same with ordinary chemical equivalents. It is expressed mathematically as:

\[ Q = zmF \]

Where \( z \) = number of electrons
\( m \) = number of moles
\( F \) = Faraday’s constant (=96500 coulombs/mole)

The cathode is usually the piece to be plated while the anode could be sacrificial or inert, and there exists variation of electroplating techniques such as rack, barrel or strip plating. Where barrel plating is performed while rotating barrels and is a general method of application, but for too large a material, rack plating is used, where the samples are held using racks made with heavy gauge copper wire. The last method is strip or reel plating, which is for plating a continuous strip of material.

2.1 Mechanism of Electroplating Using Nickel.
Taking nickel as the metal for deposition, from the survey of various baths, the reaction mechanism and developed kinetics of nickel deposition has been studied [9]. This generally accepted mechanism involves two sequential electron charge transference and the formation of an absorbed complex derived from the inclusion of the presence of an anion. This mechanism is represented in the equations 2.1 to 2.7:

\[ \text{Ni}^{2+} + \text{X}^- = \text{NiX}^+ \]  \hspace{1cm} (2.1)
\[ \text{NiX}^+ + e^- = \text{NiX} \_\text{ads} \]  \hspace{1cm} (2.2)
\[ \text{NiX} \_\text{ads} + e^- = \text{NiX}^- \]  \hspace{1cm} (2.3)

The anion involved (X-) is dependent on the bath applied, so using a watt’s bath which includes NiSO\(_4\) + NaCl + H\(_3\)BO\(_3\) will therefore make X\(^-\) into Cl\(^-\). Research also shows that the ion, NiOH\(^+\), is an important participant in the transference of charge in an unbuffered electrolyte:

\[ \text{Ni}^{2+} + \text{H}_2\text{O} = \text{Ni(OH)}^+ + \text{H}^+ \]  \hspace{1cm} (2.4)
\[ \text{Ni(OH)}^+ + e^- = \text{Ni(OH)} \]  \hspace{1cm} (2.5)
\[ \text{Ni(OH)} \_\text{ads} + \text{Ni}^{2+} + 2e^- = \text{Ni} + \text{Ni(OH)} \_\text{ads} \]  \hspace{1cm} (2.6)
\[ \text{Ni(OH)} \_\text{ads} + e^- = \text{Ni} + \text{OH}^- \]  \hspace{1cm} (2.7)

The Ni(OH)\(_{ads}\) stands for the operating intermediate which can also contain a chloride complex. The electroplating bath is structured methodically to provide the deposition of nickel ions to the surface of the substrate, a typical setup is shown in Figure 1.
A typical electroplating setup can be self-assembled with the proper materials, being a simple process that utilizes electric current to cause a reduction of dissolved metal ions to take position forming a thin layer of film on an electrode. Requirements for electroplating are: A power supply in the form of a D.C. rectifier, an electrolyte solution, a cathode, and an anode. Other components necessary to foster easier use and better coating include: a non-conductive container (glass conical flasks), jumper cables with alligator clips, a stirrer and heater. The sample needed to be coated will be submersed in an electrolyte developed through a proper combination of components to foster the proper coating environment and connected as the cathode to the setup, while electrodes should be placed equidistant from the sample in the electrolyte also in the conical flask, connected as the anode. Electrons flow from anode to cathode, through the electrolyte, and the flow of electrons is dependent on the potential difference between the terminals.

### 3 Electroplating Technique

There is a justifiable reason and ample opportunity for the study of corrosion and its inhibition, various research has been done; will be done, and is currently being done to derive methods to avoid corrosion, thereby preserving lives and properties, and in hopes for a technologically advanced future, the banner lies on researchers, to discover ways and techniques to break the conventional to reach new heights.

[17] investigated the influence of various refractory particles on the characteristics and microstructure of electrodeposited nickel discussed the popularity of composite coatings compared to that of metallic coating due to the enhanced tribo-corrosion properties they develop on substrate materials, therefore, to further the study of this, giving tests of particles of SiC, Si₃N₄ and Al₂O₃. Studies include the wear properties, composition using XRD, and hardness tests which lead to conclusions where Si₃N₄ displayed an increased
hardness due to Hall Petch strengthening and better wear resistance overall compared to the SiC and Al₂O₃ counterparts.

[18] studied the corrosion resistance of electrodeposited Ni-B and Ni-B-Si₃N₄ in an aim to compare the latter coating with its plain former. Characterization tests done include determining the structural and morphological properties using scanning electron microscopy and composition analysis with X-ray diffraction; then studies of chemical reactivity with respect to corrosion properties was studied using electrochemical impedance spectroscopy and potentiodynamic polarization. The discovery given was indicative that the micron particle size was not small enough to fill open pores and holes, allowing the diffusion of chloride through the surface, and any marginal corrosion rate improvement presented was an aftermath of covering the metal surfaces with particles, disabling the electrolyte to react directly with the metal.

[19] studied the effects of the electrodeposition of nickel-cobalt with composite coating of nanoparticles of Si₃N₄. The nanoparticles were characterized using a transmission electron microscope, and the polarization behavior of the bath was examined using a PAR-273A potentiostat. The developed samples evolved as a result of the coating process were characterized using a scanning electron microscope, it appeared that the nanoparticles developed as spherical grains on the surface of the sample. The nanoparticles also greatly improved the microhardness and tribological properties of the alloy substrate. The increased strength, hardness, wear resistance and corrosion resistance were attributed to the inclusion of Si₃N₄ particles into the bath.

Many experiments have been done regarding the electrodeposition of metals on other metals, especially of Zinc deposition as it is an industrially standard practice. [20] studied the effects of zinc coating on the corrosive and mechanical properties of mild steel. It was concluded by the author that the ubiquitous application of zinc coatings on steel is majorly due to its evolved properties, and observed in an experimental analysis inclusive of the microhardness, polarization and surface properties indicative of the protection offered by doubling the hardness of steel and reduction in its corrosion rate.

There is currently a field of research surrounded on the present and possible potential applications of the magnetism of multilayered films or ultra-thin films developed through the process of electrodeposition. By [21], electroplating here is important due to its ability to develop thin films on objects on a Nano-scale and relies on the developed magnetic measurement instruments to observe the evolution of the physical properties. Through the ability to magnetize objects, electroplating is used in various research and applications that require a material to have that special character. An example is give by the development of micromachined actuators using electrodeposited permalloy by [22]. These actuators are capable of exerting large forces and their invention has been made possible through electroplating of the permalloy – Ni₈₀Fe₂₀, enabling the actuator processes to make use of this material for magnetic interaction and force creation. These magnetic actuators are applied as valves, in pump/compression actuation, locking mechanisms and vibration generations.

In the design of devices such as thermoelectric generator and coolers, electroplating is the technique recommended to be used when synthesizing the engineered Nano thermoelectric materials due to its ability to work economically and efficiently by [23], while still producing the desired results. These thermoelectric devices perform better than their conventional others in areas of compactness, scalability, solid-state operations, with no emissions and high reliability. Although electrodeposition was feared before its involvement in the semiconductor industries due to the application of a wet process, it is now undoubtedly extensively applied in the microelectronics industries, recounting the important devices such as switches made by large electronics producers which used techniques of electrodeposition as well as physical methods [12]. Therefore, these instrumental plays by electrodeposition in the world of electronics makes it widely recognized as it is a less expensive and simpler method of microsystem filming compared to various dry processes. Its scalability and coating time also serve as a factor to its newfound popularity as it presents mostly advantages for various industrial applications.

From [24], tin electrodeposition is also gaining ground due to its ability to perform in core areas of: corrosion prevention, fabrication of electronics and plating of equipment and cooking utensils. It is stated that these last two decades have seen an advance in the knowledge of the science of tin plating, and given
applications such as the development of a new type of lithium ion batteries based off the tin electroplated negative electrodes in [25], which concludes that electroplating is a viable synthesizing tool for monitoring the structure of lithium ion electrodes.

Electrodeposition has many capable fields of application and has established an impact in the lives of every human. The need to design and manufacture new materials, which have enhanced mechanically and electrochemically properties falls in line with the natural need for humans to acquire better standards of living has brought about a field of material engineering concerning the co-deposition of refractory particles alongside the components of the electrodeposition electrolyte, such as co-deposition using Silicon nitride nanoparticles are compounds from the chemical combination of silicon and nitrogen. Si3N4 is known to be thermally stable with low chemical reactivity, hence its resistance to acids [26]. It is used in various industries such as the automobile industry to develop parts that require low wear, and used in making bearings due to their hardness being higher than metals. Silicon nitride is a common addition to many coating applications due to the enhanced strength and temperature stability given by the refractory particles.

4 Conclusion
Electroplating is a coating technique, easily reproducible, cheap and effective method of corrosion prevention. It is a process that provides protection and evolution of positive physical characteristics of a material, and when compared to other methods of coating, shows more scalability and promise due to its simplicity and duplicability.

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