CORROSION OF NANOCOMPOSITE Sn/Ag COATING ON COPPER SUBSTRATE

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UNIVERSITI SAINS MALAYSIA
2022

SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

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Dissertation submitted in partial fulfillment of the requirements for the degree of

Bachelor of Engineering with Honours

(Materials Engineering)

Universiti Sains Malaysia

September 2022

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled ‘Thesis Title’. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

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Witness by

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Date:

ACKNOWLEDGEMENT

First and foremost, I would like to express my deepest gratitude to Almighty Allah for giving me the strength to complete my final year project. There are a number of people without them this project might not have been accomplished, and to whom I am greatly indebted. Assoc. Prof. Dr Nurulakmal Mohd Sharif, my supervisor for her guidance throughout this entire project and thesis writing process. To Mr. Kong, thank you so much for a great experience, for believing in me and for your insight and help.

I would like to deliver my appreciation to all the laboratory technicians in School of Materials and Mineral Resources Engineering who spent time to facilitate me in operating testing machines and software to complete my project especially to Mr. Mohd Azam Rejab. I would like to take this opportunity to thank all my friends for their kindness and support during my academic journey. Thanks for the sincere friendship and memories.

A special thanks to my parents, who encourage me all the time to finish this final year project. I would thank to my beloved mother and respected father for theirs' pray, love and supports during my academic journey.

Lastly, to those who contributed directly or indirectly in this project, I appreciate your kindness.

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ABSTRAK

Salutan Stanum atau Sn biasa digunakan sebagai salutan perlindungan tembaga. Bagi memperbaiki kekonduksian elektrik, Argentum atau Ag boleh ditambahkan membentuk salutan komposit Sn/Ag. Walaubagaimanapun, penambahan nano partikel perlulah tidak memberi kesan negatif kepada sifat-sifat saduran lain seperti perlindungan kakisannya. Kajian ini dilakukan bagi melihat kesan penambahan nano partikel Ag ke atas sifat kakisan penyaduran Sn pada substrat kuprum (Cu). Semasa proses penyaduran elektro, tetapan operasi yang digunakan dalam kajian ini termasuk ketumpatan arus 2A dan voltan 1.5 V, kelajuan pengacauan (400 rpm), proses penyaduran elektro selama 4 minit dan suhu 24 ℃. Kesan kadar kakisan substrat kuprum yang disalut dengan salutan nanokomposit Sn dan Sn/Ag dengan saiz 10 nm dan 100nm telah dikaji melalui ujian kakisan rendaman dan polarisasi potentiodinamik. Sifat kakisan terbaik diperoleh dengan salutan Sn berbanding salutan Sn/Ag. Kadar kakisan yang lebih tinggi bagi sampel bersalut Sn/Ag telah disahkan melalui ujian rendaman selama 7, 14 dan 21 hari, dan teknik polarisasi potentiodinamik menggunakan elektrolit NaCl 1M. Ketebalan salutan telah dicirikan menggunakan SEM. Kehilangan berat dan kadar kakisan dikira daripada kedua-dua eksperimen . Kaedah ekstrapolasi Tafelmenggunakan sampel kuprum sebagai elektrod kerja, elektrod platinum sebagai elektrod kaunter dan elektrod calomel standard sebagai elektrod rujukanBerdasarkan keputusan rendaman, peningkatan tempoh pendedahan bersalut Sn dan Sn/Ag kepada larutan menghakis menyebabkan kadar kakisan yang lebih tinggi. Kadar kakisan Sn/Ag 10 nm adalah lebih tinggi daripada Sn dan Sn/Ag 100. Berdasarkan plot Tafel, kadar kakisan kuprum yang disalut dengan Sn/Ag 10nm adalah lebih tinggi daripada salutan Sn/Ag dan salutan Sn. Sampel

bersalut Sn mempunyai kadar kakisan yang paling rendah berbanding sampel Sn/Ag yang lain iaitu 0.10262 mm/tahun dan mempunyai nilai Ecorr yang lebih tinggi, -0.80923V berbanding sampel Cu-Sn/Ag10 nm dan 100 nm, -1.0305V dan -0.96093V masing-masing. Ini menunjukkan bahawa sampel Sn/Ag lebih reaktif dan lebih mudah terhakis daripada sampel bersalut Sn.

CORROSION OF NANOCOMPOSITE STANUM/ARGENTUM COATING ON COPPER SUBSTRATE

ABSTRACT

Sn coating is commonly used as corrosion protection for copper. To improve electrical conductivity, Argentum or Ag can be added into the coating to form composite coating Sn/Ag. However, the addition of nanoparticles must not lead to negative effect to the coating's properties such as the corrosion resistance. This study is carried out to evaluate effect of adding nanoparticles Ag to the corrosion behavior of Sn coating on copper (Cu) substrate. During electrodeposition process, the operating parameters includes current density 2A and voltage of 1.5 V, stirring speed (400 rpm), 4 minutes electrodeposition process and temperature of 24°C. The effect to corrosion rate of copper substrate coated with Sn and Sn/Ag 10 nm and 100nm nanocomposite coating were studied via immersion and polarization potentiodinamic corrosion tests.

The best corrosion properties were obtained with Sn coating compared to Sn/Ag coating. The higher corrosion rate of Sn/Ag coated samples was confirmed by immersion test for 7, 14 and 21 days and potentiodynamic polarization technique was caried out with 1M NaCl electrolyte. The thickness of the coating was also characterized by using SEM. The weight loss and corrosion rate were calculated from these experiments. The Tafel extrapolation method used copper sample as working electrode, platinum electrode as counter electrode and standard calomel electrode as reference electrode.

Based on immersion results, increasing duration of Sn and Sn/Ag coated exposure to the corrosive solution causes higher corrosion rate. The corrosion rate of Sn/Ag 10 nm is higher than Sn and Sn/Ag 100. Based on Tafel plot, corrosion rate of copper coated with Sn/Ag 10nm is higher

than Sn/Ag coating and Sn coating. Sn coated sample has lowest corrosion rate compared to other Sn/Ag samples which is 0.10262 mm/year and has a higher Ecorr value, -0.80923V compared to Cu-Sn/Ag10 nm and 100 nm samples, -1.0305V and -0.96093V respectively. This indicates that Sn/Ag samples are more reactive and corroded more easily than Sn coated sample.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The deterioration of metal structures due to corrosion is one of the most serious problems in the world. Corrosion causes durability reduction for steel structures which leads to loss of billions of dollars every year. Corrosion is defined as destructive attack of a material by chemical or electrochemical reaction with its environment (Robarge, 1999). Various techniques were used to prevent corrosion damage. These include coating, cathodic and anodic protection, alternation of environment using inhibitors, design of structure (wall thickness allowance) and materials selection of metal and alloy for particular service (Sulaiman, 2014).

Coating is one of the most widely used techniques in corrosion control of the metals. The motivation for using coating on steel structures is to improve the properties of steel surface by reducing corrosion and abrasion effects in which the service life of steel structure could be extended (Fauchais et al., 2014). The coating is cost effective technique, easy to apply on metal surface and offers barrier between the metal surface and environment. These advantages make the coating preferable technique in corrosion control. The coating can be classified into organic and metallic coatings. Organic coatings are not effective enough for protecting of metals from corrosion. In fact a poor adhesion of organic coatings, under film corrosion and mechanical damage of the coating could reduce the ability of the organic coatings in protecting of metal surfaces. A satisfactory protection can be provided by metallic coatings in which barrier between metal and its environment can be formed (Uhlig and Revie, 1985). Two types of metallic coatings namely noble and sacrificial coating are used in industry applications. Noble coatings such as copper, chrome, lead, silver and nickel are noble in galvanic series with respect to steel. A barrier layer on steel surface can be provided by noble coatings. This layer should contain minimum number of pores to prevent access of water underneath the metal coating and initiate the corrosion at steel surface. The second type of metallic coatings are sacrificial coatings. These include zinc, tin, aluminum and cadmium which are more active than steel in galvanic series and hence protect steel surface by galvanic protection. Various processes are used to deposit metallic coatings such as electrodeposition, hot dipping, flame spraying and vapor deposition process (Fontana, 1986).

Electrodeposition technique is the most common technique used for applying metallic coatings on steel surface due to low cost of operation, controlling the coating thickness easily, complex structures can be deposited by this process, low energy consumption and high production rate (Tuaweri and Wilcox, 2006; Jean et al., 1999 Ullal and Hegde, 2013). One of the main purposes of electrodeposition process is to enhance the characteristics of metal surface by providing a coating that be able to resist corrosion agents and withstand the abrasion or a combination of them.

Copper is one of the world's oldest metals. It is now used in one of the most innovative industries which is electronics. Copper is the world's third-most-consumed metal, with electronics accounting for three-quarters of its consumption. Electronic connectors, circuit wirings and contacts, printed circuit boards, computer chips, semiconductors, and commutators are all examples of copper-based products.

Nowadays, metallic corrosion which is a constant and continuous process becomes a severe problem of worldwide significance that affects many sectors, especially in numerous industrial applications due to their enormous economic losses (B. El Ibrahimi, 2020). According to research guided by the NACE, the current economic loss of corrosion has been increased up to $ 2.5 trillion per year that equates to around 3.4% of the gross domestic product (GDP) (G. Koch, 2016). As mentioned before, copper is an extensively material utilized for a wide range of applications such as electronic industries and communications as a conductor in electrical power lines, component in building construction, industrial machinery, and transportation, pipelines for domestic and used extensively in seawater distribution systems, due to their high thermal and electrical conductivity remarkable, and good mechanical workability.

However, copper loses this property in the presence of large amounts of aggressive chloride ions particularly in the marine environment, and suffers severe corrosion (L. Guo, 2014), due to the tendency of the chloride ion to form an unstable film with copper CuCl covers the metal surface which is subsequently attacked by a chloride anion to produce soluble chloride complex CuCl2− and diffuses to the bulk solution leaving the surface unprotected (Khaled, 2008). Systematic research on the long-term atmospheric corrosion behavior of copper and its alloys has been conducted. When exposed to an aqueous environment with carbon dioxide and oxygen, copper is particularly prone to forming cuprite (Cu2O) (B. Hammouti, 2012), which can be presented as following:

$$2Cu + 1/2O_2 \rightarrow Cu_2O \tag{1}$$

$$Cu_2O + 2H^+ \rightarrow Cu_2 + H_2O \tag{2}$$

$$Cu + 2H^+ \frac{1}{2O_2} \rightarrow H_2O + Cu^2 \tag{3}$$

$$4\ Cu^2 + SO_2 - 4 + 6H_2O \rightarrow Cu_4SO_4(OH_6) + 6H \tag{4}$$

It is widely believed that sulfates are the major corrosion products of copper and its alloys in the rural and urban atmospheres. The sulfates include but are not limited to brochantite, antlerite and posnjakite. However, in the marine atmosphere, atacamite is the common corrosion product. In the marine atmosphere containing a high concentration of water-soluble chloride, the cuprite (Cu_2O) initially generated in the thin film are oxidized into the cupric Cu^{2+} ions , and then react with water-soluble chloride, forming $\mathrm{CuCl_2}$. Whereafter, $\mathrm{CuCl_2}$ transforms into $Cu_2Cl(OH)_3$ through the subsequent dissolution, ion pairing and redeposition process (J.J.S. Rodrıguez, 2003).

One highly effective route to avoid the above-mentioned corrosion concerns is applying protective coatings on the metal surface. A variety of materials have been employed for protecting copper from corrosion. Sn is the metal coating usually used for copper and copper alloys due to low cost and very good solderability. Improved corrosion and chemical resistance are also an advantage of tin coating but is dependent upon coating thickness. Sn has a relatively low melting temperature and therefore provides little, if any, improvement to the operating temperature range of copper. However, Sn has relatively low conductivity and, when coated over copper, forms an inter-metallic layer which will increase resistance compared to bare or silver-plated wire.

Electrodeposition of β-Sn and its alloys is a common practice in the solder industries in connector finishes and electronic components on printed circuit boards. Despite the excellent solderability and good surface finish, β-Sn coatings are prone to whisker formation, cracks and void formation, and corrosion (] X. Zhong, 2013). Because of that, a lot of research goes into improving the corrosion resistance properties and suppressing the whisker formation by changing the microstructure of β-Sn electrodeposits. Electrodeposition parameters such as electrolyte composition, pH, deposition temperature, mode of electro-deposition, alloying elements, and applied current density are very influential in deciding the final morphology, microstructure, and therefore the corresponding corrosion properties of the β-Sn coatings (Abhay Gupta, 2022).

The high corrosion resistance of the Sn and Ag electrodeposits is an essential requirement in the electronics industry. While most studies comprehensively discuss the role of morphology, grain size, and grain orientations in determining the corrosion resistance of electrodeposits, the influence of grain boundary constitution is often neglected despite intergranular corrosion being one of the most probable modes of failure of many alloys in corrosive conditions. In the present report, Sn and Sn-Ag electrodeposited coatings were fabricated at different current densities and how the crystallographic texture of the coating surface exposed to the corrosive medium influence the corrosion resistance of the Sn and Sn-Ag coatings (Abhay Gupta, 2022).

1.2 Problem Statement

The leading users of tin plating are divided between electronics, mechatronics, hardware, fasteners, food equipment and, most recently, solar. Here are a few examples from each industry: terminals and housings used in avionics, circuit breakers and interconnects used in construction of new homes and buildings, screws, nuts and bolts used on marine hardware in naval vessels, baking sheets and bowls used in food manufacturing and home cookware, and now solar panels.

Tin has many strengths making it a desirable choice due to its corrosion protection such as fretting, which means surface to surface corrosion, environmental which refers to sulfur bearing environments that cause tin to tarnish decent contact resistance and excellent solderability no known toxicity to life on Earth and also Sn coating is the lowest cost choice as compared to its rivals up the food chain. (Sun, 2021)

Because of its good corrosion resistance and solderability, tin coating is widely used in various industrial fields as a protective coating for all kinds of metal devices . However, in a relatively harsh environment, the protective effect of a single tin coating on the metal substrate is limited, how to further improve the quality of tin coating has become a hot issue in the field of surface engineering technology. Fretting corrosion is a possible degradation mechanism for tin coated contacts. Degradation of the contact interface accelerates when tin is mated to gold or other noble metals like palladium, and these mismatches should be avoided. However, there are several sources which indicate that a tin to silver interface is an exception to this rule.

At present, most of the research is to improve the coating quality of tin coating by doping metal elements and nanoparticles. However, there is no research on corrosion of Sn-Ag nano-coating at present. In order to prove the potential of Sn-Ag nanocomposite coatings, Sn-Ag nanocomposite coating were prepared by electrodeposition, and the effects of different size of nanoparticles which is 10 nm and 100 nm of Ag on tin coatings were studied.

1.3 Objectives

The objectives of this research are as follow:

I. To evaluate corrosion behavior of Sn-coated and uncoated Cu sheet.

II. To assess effect of Ag additives to the corrosion behavior of Sn plating.

1.4 Project Overview

This thesis is further divided into five chapters which comprises the introduction part, literature review, experiment procedures, results and discussions and conclusion and recommendation’s part. In Chapter 1, readers will be exposed to the introduction, the background information, as well as the aim and scope of this thesis. Next, in the literature review, the findings of the general research that was done on this topic will be presented, focusing the details on the past and current studies that was done by other researchers, as well as insights on the corrosion and metal coating technologies. Chapter 3 details the sample preparation procedures, overall experimental procedures and characterization techniques used in this research study. Chapter 4 presents the experimental results and discussions on the corrosion rate of Sn and Sn/Ag coating on copper substrate by carried out immersion test potentiodynamic polarization technique. Lastly, in Chapter 5, conclusion and recommendations are presented for future studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Corrosion is the destructive attack of a metal on its environment. Corrosion is a natural process in which metals and alloys try to return to a more stable thermodynamic state because of chemical attack or interaction with their environment. To put it another way, metals, except for platinum and gold, are found in nature in impure forms, primarily as stable oxides, or sulphides. Energy is consumed in most processing techniques to obtain pure metals, resulting in pure metals having a greater energy state than their ore. So, corrosion is the easiest and quickest route for metals to reach their most stable condition.

Metal corrosion is defined as the natural and unavoidable loss of desired metal properties because of interaction with specific substances in the environment. Corrosion has been shown to be harmful to the environment as well as human health. Electrochemical reactions are common in corrosion processes. The two most common processes that keep a corrosion process moving in acidic media and neutral/alkaline environments, respectively, are hydrogen evolution and oxygen reduction. A range of factors contribute to metal and alloy corrosion.

2.2 Corrosion principle and protection

2.2.1 Corrosion of metal (electrochemical process)

Corrosion is an electrochemical process in which electrons are transported between a metal surface and a liquid electrolyte solution, resulting in the deterioration of the substrate in both aqueous and atmospheric environments. Metals have a strong ability to react electrochemically with oxygen, water, and other substances in the atmosphere, resulting in corrosion. The term anode is used in this context to describe the section of the metal surface that is really corroding, whereas the term cathode is used to describe the metal surface that consumes the electrons formed by the corrosion reaction.

An electrochemical reaction is outlined as a reaction involving the transfer of electrons. It's also a reaction that involves oxidation and reduction. The very fact that corrosion consists of a minimum of one chemical reaction and one reduction reaction isn't entirely obvious because both reactions are usually combined in one piece of metal for example electrochemical reaction during the corrosion of Cu in HCl.

Anode: $Cu\ (s)\ \rightarrow Cu^{2+} + e^{-}$ (2.1)

Cathode: $2H^{+} + 2e^{-} \rightarrow H_2\ (g)$ (2.2)

These equations describe the characteristics of a copper electrochemical reaction. Electrons are transferred during such a reaction, or to put it another way, an oxidation reaction occurs in conjunction with a reduction process.

Overall corrosion equation: $Cu +\ 2H^{+} \rightarrow Cu^{2+} + H_2(g)$ (2.3)

2.2.2 Types of corrosion

2.2.2(a) Uniform corrosion

This corrosion happens when the anode and cathode areas of a metal's surface that is in contact with the electrolyte are constantly moving, and it results in a virtually uniform corrosive attack on the entire surface. The rusting of steel plate in seawater is an illustration of this type of corrosion. If the rate of metal loss is known, provisions for corrosion can be made during design and maintenance. Despite being known as uniform corrosion, it is distinguished by an average surface loss.

2.2.2(b) Galvanic corrosion

A variation in electrical potential occurs when two different metals are subjected to a corrosive environment. The more electrically active metal will function as the anode in the resulting galvanic cell and experience higher corrosion if the two metals are electrically connected. The installation of steel fasteners to join copper plates together is an example of such a corrosion cell. Galvanic corrosion is not always harmful. Galvanizing, or applying a zinc coating to steel, is used to protect it rather than prevent corrosion since the zine, which is anodic to the steel, corrodes preferentially. As a result, the steel is cathodically protected by converting any exposed steel to a cathode. (Lu Chang, 2022)

It is generally good practice not to use dissimilar metals unless it is necessary, but if it is, the following precautions should be used:

- Attempt to electrically isolate the metals.
- Use protective coatings on the metal surface(s), generally the cathode
- Cathodically protect the less noble metal.
- Put corrosion inhibitors into the system.
- Use design in which anodic part may be replaced easily.
- Keep out moisture.
- Use metals that are close to one another in the galvanic series.
- Design so that the anode/cathode area ratio is high.

- Use design allowances to account for the corrosion.

Galvanic corrosion is also known as one of the most common types of corrosion, which occurs when a metal comes into contact with another conducting substance in a corrosive media. It can be found at the intersection of a water main where a copper pipe meets a steel pipe, or in a microelectronic device where different metals and semiconductors are combined, or in a metal matrix composite material where reinforcing materials, such as graphite, are dispersed in a metal, or on a ship where various components immersed in water are made of different metal alloys. Galvanic corrosion can cause metals to deteriorate quickly in some situations, but it can also protect an associated metal from corrosion, which is the basis of cathodic protection by sacrificial anodes. (ZHANG, 2011)

When two dissimilar conducting materials in electrical contact are exposed to an electrolyte, the galvanic current passes from one to the other. Galvanic corrosion is the corrosion that occurs at the anodic member of such a couple and is directly related to the galvanic current according to Faraday's law. Local corrosion refers to the additional corrosion that occurs simultaneously on the couple's anode during a coupling state. Local corrosion may or may not be equivalent to typical corrosion that occurs when the two metals are not electrically connected. The difference effect, which can be positive or negative, is the difference between local and normal corrosion. The total corrosion rate of the couple's cathodic member is usually reduced by a galvanic current. The cathodic part is cathodically protected in this situation. (ZHANG, 2011)

The corrosion potential Ecorr is the electrode potential of any metal or alloy placed in a corrosive environment. The galvanic series (in seawater) is an ordered list of corrosion potentials experimentally measured in natural seawater for both pure and alloyed metals. Metals and alloy with more positives potentials (like platinum) are called noble metals, and metal with more negative potentials (like magnesium) are called active metals. Standard half-cell electrode potentials are often referred to as the standard hydrogen electrode, whereas electrode potentials in galvanic series (Figure 2.1) are measured relative to a saturated colonel electrode (but any acceptable reference electrode can be used). (Swain, 1997)

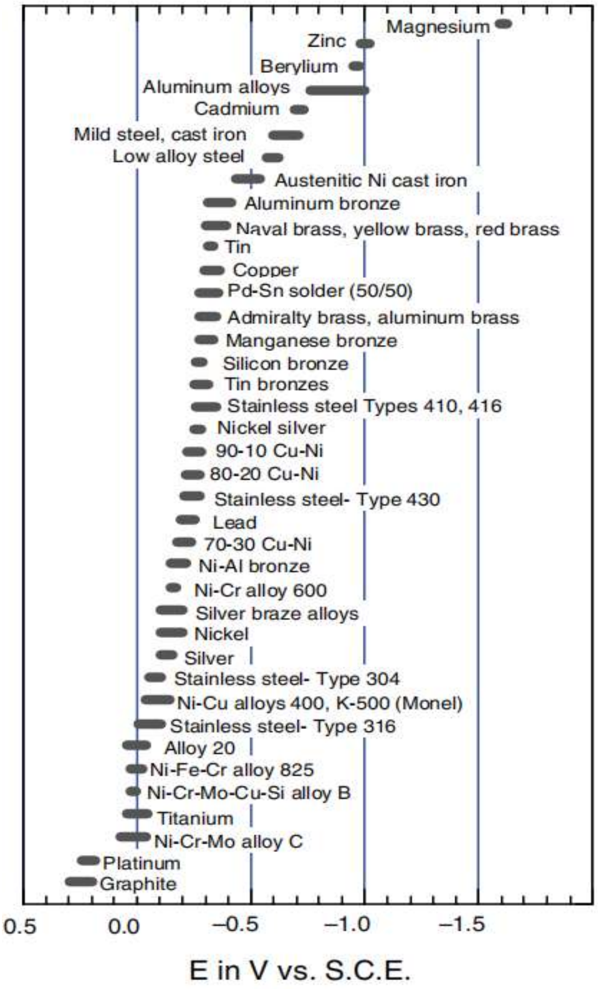

Figure 2.1 The Galvanic Series in Seawater (Johnse, 2007)

In addition to the potential difference between the two linked metals, many other factors play a part in galvanic corrosion. Some or all the factors shown in Figure 2.2 may be included which is depends on the situations. In general, the elements in categories (a)–(c) fluctuate less from one situation to another for a particular pair than the factors in categories (d)– (g).

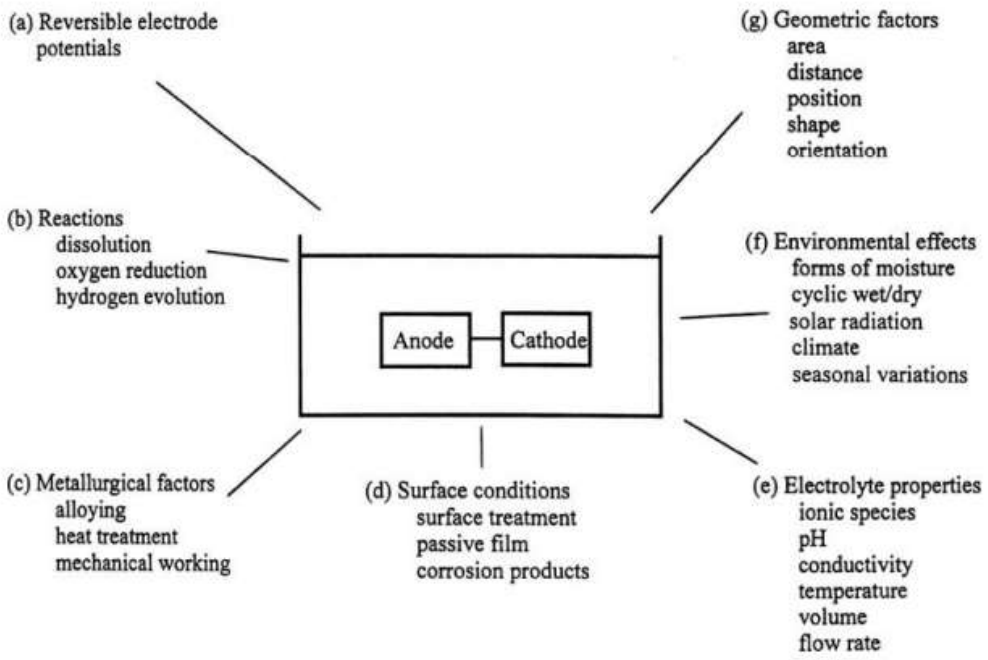

Figure 2.2 Factors That Contribute to Bimetallic Couple Galvanic Corrosion. (Whitman, 1924)

In many circumstances, the effects of geometric factors on galvanic actions can be analytically studied. However, determining the effects of electrode surface characteristics on reaction kinetics in real-world circumstances can be challenging. Galvanic corrosion is more complicated than normal corrosion because it includes geometrical factors in addition to material and environmental factors.

All factors impacting electrode characteristics, such as those described in categories (a)–(g), have an impact on galvanic activity between any two metals, as shown in Figure 2.2. Because the actual potential (the corrosion potential) of a metal in an electrolyte is usually very different from its thermodynamic equilibrium value due to kinetic processes, the intrinsic polarity of a galvanic couple is determined by the reversible electrode potentials of the two coupled metals, while the reactions, metallurgical factors, and surface conditions determine the actual polarity under a given situation. (Whitman, 1924)

Other parameters, such as reaction kinetics and the formation of corrosion products, are significant in determining the galvanic corrosion rate, in addition to the potential differences between the two metals. Different galvanic corrosion rates of an anode connected to varying cathode materials can be explained by different oxygen diffusion rates through the oxide layers when the cathodic reaction is oxygen reduction and diffusion limited. Changes in galvanic corrosion rates can arise from differences in cathodic efficiency of oxygen reduction in the oxide scale on the cathode surface, which may or may not be dependent on the corrosion potential. As a result, the difference in corrosion potentials between uncoupled metals is not a good measure of galvanic corrosion rate. (ZHANG, 2011)

2.2.2(c) Crevice corrosion

When areas of partial shielding or gaps created by lapped joints are exposed to corrosive conditions, a localized attack known as crevice corrosion results. Concentration cells are the name given to these resultant cells. Metal-ion cells and oxygen cells are two such examples. Oxygen concentration cells develop when the protected area loses oxygen and starts to behave like an anode in comparison to the oxide region. Figure 2.3 shows how this occurs. Because the shielded area is so small in comparison to the unshielded section, corrosion happens relatively quickly. (Iannuzzi, 2019)

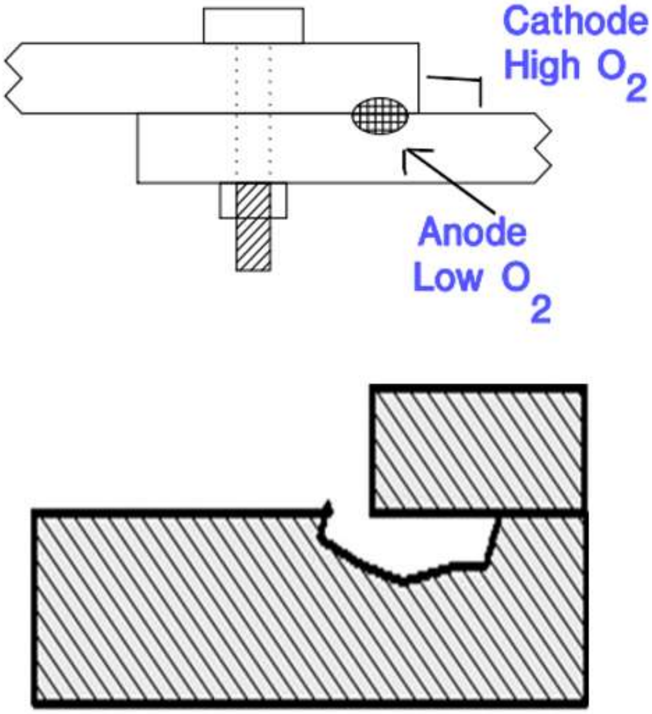

Figure 2.3 Schematic diagram represent crevice corrosion (Makhlouf, 2014)

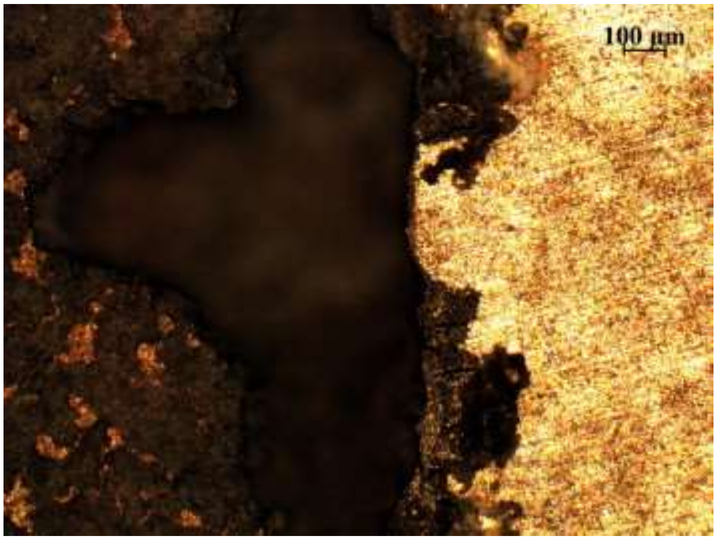

Figure 2.4 An example of crevice corrosion on AZ91D magnesium alloy coated with stannate (under specific conditions) after 7 days of immersion in 3.5% NaCl solution. (Makhlouf, 2014)

The oxygen cell is the main trigger for this corrosion. The accumulation of acidic, hydrolysed salts within the crevice (frequently created by the same reasons that produced the low oxygen level) promotes the ongoing growth. Oxygen cell crevice corrosion can happen to alloys like 18-8 stainless steels.

Copper alloys are used most often to create metal-ion cells. The shielded area accumulates corrosion products and becomes cathodic to the regions outside of the crevice where corrosion products are kept washed away. This style of concentration cell is depicted in the illustration below.

Another instance of metal-ion cell corrosion is called metal-ion crevice corrosion, which happens when the relative speeds of the electrolyte on the metal surface are different at different points. A metal disc whirling rapidly in water serves as a nice illustration. Whereas metal-ion concentration is low and linear velocities (v=r) are highest, corrosion occurs close to the edge (since the ions are repeatedly swept away). The metal-ions are swept away by the high velocity, which is higher than in areas closer to the disc hub, creating anode zones. (This should not be confused with the discussion on "immunity" from corrosion where the low ion concentration was one of the main reasons.) At the centre of the disc, where velocities are lower, the metal functions as a cathode and is protected. An equilibrium concentration existed there. Because we can't reach an equilibrium concentration in this situation, metal ions keep forming. (ZHANG, 2011)

The two concentration cells, however, corrode in various places along the crevice. While the metal-ion cell corrodes outside of the protected area, the oxygen cell corrodes inside. As previously mentioned, either the oxygen or the metal-ion cell is the primary cause of the corrosion. The build-up of corrosion byproducts, clacareous deposits, and salts within the fissure controls its continuous expansion. The two concentration cells, however, corrode in various places along the crevice. While the metal-ion cell corrodes outside of the protected area, the oxygen cell corrodes inside. As previously mentioned, either the oxygen or the metal-ion cell is the primary cause of the corrosion. The accumulation of corrosion by products, clacareous deposits, and salts within the fissure controls its continuous expansion. (Swain, 1997)

2.2.2(d) Pitting corrosion

Many engineering alloys, such as stainless steels and Al alloys, are useful only because of passive films, which are thin (nanometre scale), oxide layers that form naturally on the metal surface and greatly reduce the rate of corrosion of the alloys. Such passive films, however, are often susceptible to localized breakdown resulting in a Passive films, which are very thin oxide layers (on the order of nanometres in thickness), which naturally grow on the metal surface and significantly slow the rate of corrosion of the alloys, are the only reason that many technical alloys, such as stainless steels and aluminium alloys, are functional. However, these passive films are frequently vulnerable to localised disintegration, which accelerates the dissolving of the underlying metal. If the assault starts on an exposed surface, it is referred to as pitting corrosion; if it starts in an obstruction, it is referred to as crevice corrosion. These forms of localised corrosion, which are closely linked, can cause structural elements to fail more quickly by perforating them or by serving as a starting point for cracks. Accelerated dissolution of the underlying metal. If the attack initiates on an open surface, it is called pitting corrosion; at an occluded site it is called crevice corrosion. These closely related forms of localized corrosion can lead to accelerated failure of structural components by perforation, or by acting as an initiation site for cracking. (Fernández-Domene, 2014)

Pitting is an extremely localized attack that eventually results in holes in the metal. It is one of the most destructive and insidious forms of corrosion. Basically, the alloys subject to pitting are those that rely on an oxide film for protection, such as stainless steels. The initiation of a pit can be the result of any of the following:

a) Chemical attack, such as ferrous chloride or aerated seawater on stainless steel.

b) Mechanical attack such as an impact or scratching that removes small areas of the protective film.

c) Crevice corrosion resulting from tiny deposits on the surface, especially in stagnant seawater.

Figure 2.5 example of pitting corrosion of a steel plate. (Markova, 2016)

2.2.2(e) Other localized corrosion

In addition to the pitting and the crevice corrosion, the following are also localized corrosion:

- Poultice corrosion - attack which occurs at the edge of a damp fabric.
- Deposition corrosion - corrosion process in which a more noble metal deposits on a less noble metal and causes attack due to a bimetallic cell. It is common in copper/aluminium systems

- Filiform corrosion - localized attack of a metal surface beneath a coating due to oxygen concentration cells.

2.2.2(f) Selective Leaching aka Dealloying

Selective Leaching corrosion happens when some regions of a metal surface are metallurgically different from other, nearby areas. For instance, brass is an alloy made of copper and zinc in a "solid solution". It can corrode if the copper is left behind after the zinc is selectively removed from the alloy. It degrades the alloy's mechanical characteristics and renders it porous. When the yellow natural colour of brass changes to a reddish or coppery appearance, it can be recognised. Tin can be added to an alloy in modest amounts to help prevent dealloying.

Such selective leaching is known as "dezincification". Cast irons can corrode in such a matter that the iron is selectively corroded away, leaving behind a soft graphite layer. This is referred to as "graphitization". Other examples are referred to as dealuminification, denickelification, decobaltification, etc. where the terms refer to the metallic element that is selectively corroded away.

The mechanism of selective leaching has been explained as follows for a brass alloy:

a) the brass corrodes
b) the zinc ions stay in solution
c) the copper plates back on as a solid layer

Dealloying refers to selective removal of one or more less noble elements from an alloy through a corrosion mechanism. For this reason, dealloying is traditionally regarded as a destructive process in electrochemistry field, which frequently leads to materials failure, such as stress corrosion cracking. This type of corrosion is also called parting and, after the most common example, the selective leaching out of zinc from brass, dezincification as mention before. For other alloys undergoing selective leaching names such as dealuminumification and denickelification are also used. Another important and somewhat misleading name for a form of selective leaching suffered by gray cast iron when iron is selectively leached out leaving behind a graphite matrix is graphitization. (Kruger, 2001)

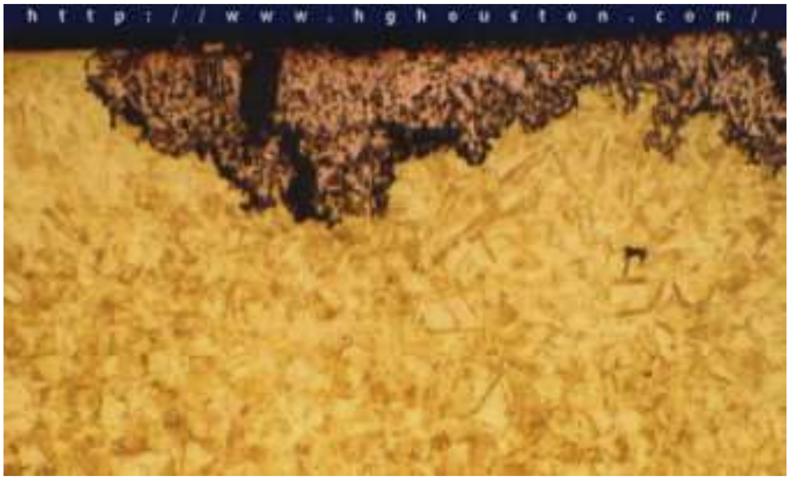

Figure 2.6 Dezincification of brass. (Coker, 2015)

2.2.2(g) Erosion-Corrosion

High velocity electrolyte flow causes erosion-corrosion, which is accelerated by the flow's abrasive impact. When materials in suspension are present in the electrolyte, this corrosion is particularly severe. The result is the removal of a protective oxide from the film surface, leaving a new alloy vulnerable to corrosion. Pitting on a wider scale could be compared to erosion-corrosion. In actuality, the maximum electrolyte velocity that a given metal can withstand exists. Selection of copper nickel alloys for use in seawater is based on resistance to erosion-corrosion.

In addition to example of erosion corrosion, besides being widely used in various cable conductors and precision instruments (Z. Gao, 2022), copper is also frequently used in air conditioning, heating and refrigeration, and water distribution networks to fabricate tubing where it serves in flowing fluid and suffers erosion corrosion (J. Zhou, 2018). The corrosion resistance of copper is dependent on the corrosion product film formed on its surface which is mainly composed of a compact $\mathrm{Cu_2O}$ inner layer and a porous $\mathrm{Cu_2(OH)_3\,Cl}$ outer layer (R.F. North, 1970). However, copper is shown to be susceptible to a critical surface shear stress or a critical flow velocity in a hydrodynamic system where the corrosion product film is peeled off and accelerated corrosion attack is initiated (D.D. Macdonald, 1978). Thus, thoroughly understanding the erosion corrosion behaviour of copper is important to develop protective measures and/or optimize the corrosion resistance of copper flow-handling components.

Erosion corrosion is also can be understand as a synergistic outcome that accelerates the corrosion attack in the surface of the metal due to the motion of the corrosive fluid. For this corrosion to happen, there must be interaction between the material, corrosive fluid, and solid particles. To better understand this concept, Fig. 2.5 explains how erosion corrosion happens. Fig. 2.5 shows a solder drip left inside the pipeline after the soldering was completed. The fluid flow in a pipe is moving in an x direction, meanwhile the flow is in contact with the drip. When this happens, the soldering drip causes turbulence inside the pipe and because the fluid has some abrasive particles, they start to wear out the surface of the pipe, leaving the material exposed to corrosion drivers. The material begins to corrode and degrade because of the corrosive fluid inside the pipe. (Abdel Salam H. Makhlouf, 2018)

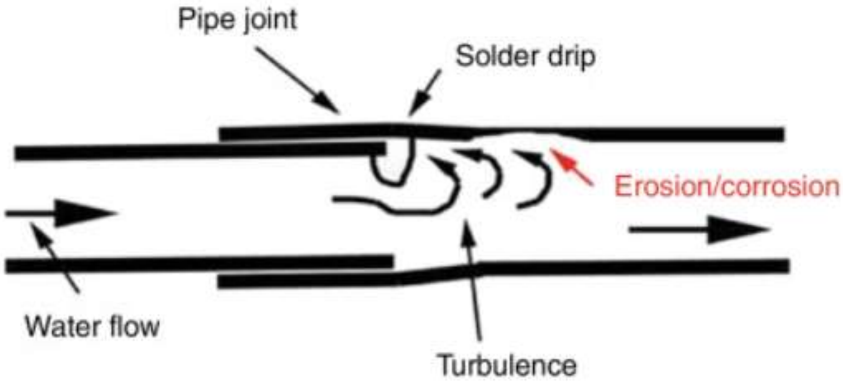

Figure 2.7 Mechanism of erosion corrosion inside a pipe. (Abdel Salam H. Makhlouf, 2018)

2.2.2(h) Stress Cracking Corrosion

Stress corrosion cracking (SCC) is the formation and growth of crack through materials subjected to tensile stress and a specific corrosive medium. It can lead to unexpected sudden failure of normally ductile metals. Specific metal-environment combinations can lead to cracking. This indicates that not all environments affect every alloy with SCC. Additionally, under normal circumstances, the surroundings that lead to this form of cracking have no impact on the alloy's corrosion. Unwanted metallurgical and environmental changes have created metal-environment combinations that are sensitive to SCC in some states. The SCC sites on the metal surfaces may not be visible by visual inspection, while metal parts are being filled with microscopic cracks. These invisible cracks progress rapidly and lead the component and structures to catastrophic failures. (Khalifeh, 2019)

This phenomenon is associated with a combination of tensile stress, environment, and some metallurgical conditions as described in Figure 2.6. The metal or alloy is virtually unaffected over the most of its surface during stress corrosion cracking, while fine and branch cracks spread through the bulk of the material. It is shown in Figure 2.7. This cracking phenomenon can happen at stresses that are substantially lower than design stresses, which can cause equipment and structures to fail before they should.

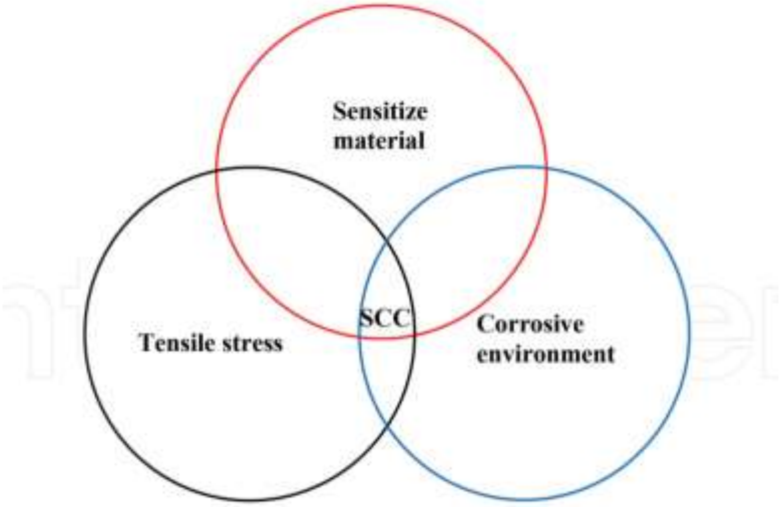

Figure 2.8 The essential requirements for SCC. (Khalifeh, 2019)

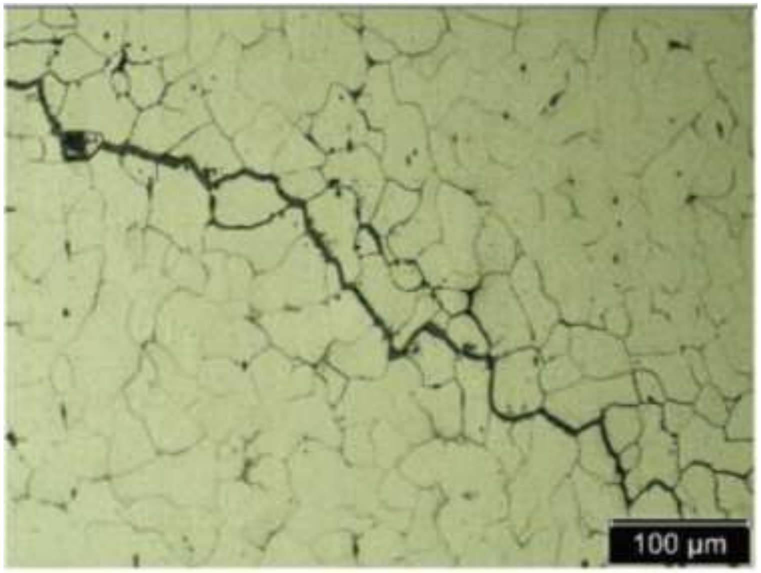

Figure 2.9 Crack development in carbon steel exposed to nitrate solution. (al, 2011)

Not all metal-environment combinations are prone to cracking. In other words, each metal or alloy has a specific environment where SCC might form. Additionally, the sources of stress for every failure case may vary. Another well-known example of SCC is the seasonal cracking of brass during the rainy season in an ammoniacal atmosphere. This was first identified on the brass cartridge used by the British Army in India. Since it is usually identified during the rainy season, it is also called seasonal cracking (MG., 2005). Alpha brass is an alloy of Cu-Zn. It can crack either intergranular or trans granularly in non-tarnishing ammonia solutions, depending on its zinc content (JR., 2001). Trans granular stress corrosion cracking, TGSCC, is observed in alloys with 20 or 30% Zn but not in alloys with 0.5 or 10% Zn (Craig J, 1968). Stress corrosion cracking of Cu-Zn and Cu-A1 alloys in cuprous ammonia solutions can only occur when the parting limits for dealloying are exceeded. The parting limits are about 14 and 18 a/o for Cu-A1 and Cu-Zn, respectively. Cu-A1 and Cu-Ga alloys have shown similar behaviours (Craig J, 1968).

2.2.2(i) Intergranular Corrosion

An interfacial deterioration phenomenon known as intergranular corrosion has the potential to cause far more harm than homogeneous corrosion (Fontana and Staehle, 1972). Intergranular corrosion-prone materials frequently show a considerable reduction in cross section and grain dropping, which can result in significant mass loss, quick structural integrity degradation, and unanticipated catastrophic collapse. Many factors have been known to affect intergranular corrosion including electrochemical environment (Osozawa et al., 1966), grain boundary structure (Paiurnbo and Aust, 1990), impurity segregation (Aust et ai., 1966) and second phase particles (Erb and Aust, 1984), and residual stress (Erb et al., l982).