EFFECTS OF Ni ADDITIONS ON THE MECHANICAL PROPERTIES AND CORROSION RESISTANCE OF Al-Cu-Si ALLOY

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BY

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Declaration

I hereby declare that the work in this thesis entitled "EFFECTS OF Ni ADDITIONS ON THE MECHANICAL PROPERTIES AND CORROSION RESISTANCE OF Al-Cu-Si ALLOY" has been carried out by me in the Department of Metallurgical and Materials Engineering, under the supervision of Professor S. A. Yaro and Dr. M. Abdulwahab. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this work has been presented for another degree diploma at this or any other Institution.

Mohammed, Abdullahi ______________________ ______________________
Signature Date

Certification

This thesis entitled EFFECTS OF Ni ADDITIONS ON THE MECHANICAL PROPERTIES AND CORROSION RESISTANCE OF Al-Cu-Si ALLOY by Abdullahi MOHAMMED meets the regulations governing the award of the degree of Masters of Science of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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Dedication

I dedicate this Thesis to my wife—Jamila and my children—Aisha Karima, Mohammed Faisal and Mohammad Ammar.

Abstract

This study was aimed at investigating the influence of Ni addition on the mechanical properties and corrosion characteristics of Al-Cu-Si alloy and the prime focus was to obtain a material that possessed good mechanical properties with adequate corrosion resistance. In this research, gravimetric and linear polarization methods were used to assess the corrosion behavior of the alloy in 3.5%NaCl. Microstructural properties of the coupons were studied with the aid of optical metallurgical microscope, while hardness and impact strength were measured with Rockwell scale F universal testing machine and Hounsfield impact tester machine respectively. The results obtained from both gravimetric and linear polarization indicates that corrosion resistance of the alloy was enhanced by Ni addition and thermal treatment. The reason might be due to the formation of intermetallics such as $NiAl_3$ and Ni_3Si, which passivate easily to form oxides that protect the alloy from further corrosion; and also the enveloping of the cathodic intermetallics by the α-matrix—a process called shingling may be responsible for improvement in the corrosion resistance of the alloy. The hardness of the alloy also increased with Ni up to a maximum of 2.5%Ni and then decreased, while the impact strength tends to decrease with increasing Ni content. The rise in hardness may equally be associated with the intermetallic compounds that are formed which tend to pin-down dislocation movement and hence higher hardness was achieved.

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Abbreviations, Definitions, Glossary and Symbols

Abbreviations

AC	As-cast
AH	Age-hardened
ANSI	American National Standard Institute
GP-zone	Guinier-Preston zones
LP	Linear Polarization
NACE	National Association of Corrosion Engineers
NOCACO	Northern Cable Company
OPM	Optical Metallurgical Microscope
SCC	Stress Corrosion Cracking
SHT	Solution Heat Treatment
SSSS	Super Saturated Solid Solution
HRF	Rockwell Hardness, Scale F
wt	Weight

Symbols

%	Percent
^{O}C	Degrees Celsius
Ɵ□	Metastable Precipitate
Ɵ´	Incoherent Precipitates
Ɵ	Coherent precipitate

Glossary

Alclad—to coat aluminium alloy or any other metal with liquid aluminium melt for corrosion protection.

Shingling—to cover something with anothe

CHAPTER ONE

1.0 INTRODUCTION

One of the properties of critical interest for structural metals is their strength. However, like all other pure metals, aluminium has low strength (about 90Mpa) and elastic modulus and therefore cannot be used in applications where resistance to deformation and fracture is essential (Aye, *et al*., 2008; Dwight, 1999; Kissel and Robert, 2002). Therefore, to overcome these short falls, other elements are primarily added to improve strength of aluminium (Totten and Mackenzie, 2003). Even though, mechanical strength of aluminium may be enhanced not only by alloying but also by cold deformation. During cold deformation, crystal defects are generated leading to improved strength properties; and in alloy formulation, strength can be impacted by reinforcement with intermetallic compounds, solid solution strengthening, and precipitation hardening (aging) (Al-Rawajfeh and Al-Qawabah, 2009; David and James, 1998; Totten and Mackenzie, 2003). The strength imparted during cold deformation and alloying, coupled with the light weight— 2.7g/cm^3 (approximately one-third as much the density of steel—7.83 g/cm^3, copper—8.93 g/cm^3, or brass—8.53 g/cm^3) makes aluminium and its alloys particularly advantageous for structural applications where dead load is a concern (Kissel and Robert, 2002; Roberge, 2000; Rooy, 1990). However, Totten and Mackenzie, (2003) and Callister, (2001) reported that both cold deformation and alloying tend to diminish resistance to corrosion.

Although most metals are alloyed with aluminium, few comparatively have sufficient solid solubility to serve as major alloying additions. Among the commonly used elements, only zinc (Zn), magnesium (Mg) (both greater than 10 atomic %), copper (Cu) and silicon (Si) have significant solubility. However, several other elements with solubility below one atomic percent confer important improvements to alloy properties. Examples are some of the transition metals, e.g. chromium (Cr), manganese (Mn) and zirconium (Zr) used primarily to form compounds that control grain structure (Mathers, 2002; Polmear, 2006). Others are nickel (Ni), titanium (Ti), lead (Pb), scandium (Sc) and beryllium (Be) (Polmear, 2006; Vargel, 2004). The effects of these alloying elements in aluminium are well known and documented in literatures (Kosgey *et al*., 2007). For instance, it is known well that Cu addition increases the strength and hardness of aluminium alloys, which is due to the influence of Cu on the behavior of the alloys during the age-hardening treatment. However the element exhibit detrimental effect; like reduction in general corrosion resistance, to hot tearing and in castability (Li, et al., 2006; Totten and Mackenzie, 2003). Silicon, on the other hand, increases castability characteristics of aluminium alloys (Totten and Mackenzie, 2003; Vadims, *et al*., 2007); it improves fluidity, hot tearing resistance and feeding behavior (Mathers, 2002). Magnesium imparts solid solution strengthening, enhances the ability of the metal to work-harden (David and James, 1998) and increases corrosion resistance of aluminium and its alloys (Vadims, *et al*., 2007). Nickel increases creep resistance and in combination with copper, it enhances high temperature properties. In the presence of copper, nickel forms such compounds as Al_6Cu_3Ni or $Al_3(Ni,Cu)_2$ and these are some of the most thermally stable compounds which exerts positive influence upon mechanical properties at elevated temperatures. Nonetheless, the formation of these compounds is accompanied by the reduction of copper concentration in aluminium and, correspondingly, lowers strength at room temperature (Vadims, *et al*., 2007). Titanium is used extensively to refine grain size in aluminium castings. It is employed commonly in combination with boron as titanium boride, TiB_2 or Al-Ti-B master alloy (Kwon and Lee, 2003; Totten and Mackenzie, 2003; Vadims, *et al*., 2007).

However, in some aluminium alloys, addition of alloying elements only will not give optimum and required properties, but in order to achieve the desired properties, these alloys are given proper heat treatment. These types of alloys are called heat- treatable aluminium alloys. Many of these heat-treatable aluminium alloys require a rapid quench from the solution heat treatment (SHT) temperature by either immersion in, or spraying using cold water to achieve optimal mechanical properties. This rapid quench maintains a supersaturated solid solution, which then decomposes in a controlled manner through either natural aging or artificial aging. Whilst the retention of good mechanical properties is desirable during heat treatment, in thick sections the varying cooling rate can lead to large thermal gradients that not only cause property inhomogeneity in quench sensitive alloys, but can also lead to high level of residual stresses. These residual stresses can have a detrimental effect on the component; leading to warping or cracking during the quench, dimensional instability during machining, reduced fatigue life and increased susceptibility to stress corrosion cracking (SCC) (Dolan and Robinson, 2004). In Al-Cu alloys, which as of today remain the strongest and most thermally stable among all standard casting aluminium alloys (Vadims *et al.*, 2007), the solid solution of Cu in aluminium gives the increase in strength. Nevertheless, the bulk of the strength is achieved by the formation of precipitates of copper aluminides, $CuAl_{2,}$ during heat treatment; and to gain the full benefits of this precipitates it should be present as a finely and evenly distributed sub-microscopic precipitates within the grains which is achieved by solution treatment followed by a carefully controlled ageing heat treatment (Mathers, 2002).

Accordingly, the present study can be considered as an attempt to investigate the effect of Ni addition on the corrosion resistance and mechanical properties of Al-Cu-Si alloy.

1.1 STATEMENT OF THE PROBLEM AND JUSTIFICATION OF THE RESEARCH WORK

For structural applications, aluminium requires a combination of strength, toughness, corrosion resistance and cost effectiveness. These mechanical and physical properties are determined by the nature and kind of microstructure of an alloy. Consequently, the performance of a cast component is determined by the quality of the microstructure of the alloy. Ouyang, *et al* (2009) reported that Al-Cu-Si based alloys have high specific strength, low thermal expansion coefficient and good mechanical properties. These alloys have low corrosion resistance and components made of this alloy have to be alcladded for corrosion protection (Li *et al*., 2006; Totten and Mackenzie, 2003), however, it is easy to produce flat clad products at a good and reasonable cost but impracticable with section and forgings. Therefore, the introduction of Ni into the alloy may improve the corrosion resistance as well as some mechanical properties. This is because Ni is known to have excellent corrosion resistances, even at high temperatures. This lends motivation for the present research work.

1.2 AIM AND OBJECTIVES OF THE RESEARCH WORK

The main objective of this research work is to investigate the effects of Ni on the corrosion resistance and mechanical properties of the mentioned alloy. Other specific objectives include:

i. To produce and Al-Cu-Si alloy with different percentages of Ni added and subject them to artificial aging conditions,

ii. To study the mechanical properties of the alloy in the as-cast and age-hardened conditions,

iii. To investigate the corrosion behavior of the alloy in simulated seawater,

iv. To study the microstructure of the alloy using optical metallurgical microscope (OPM).

1.3 SCOPE OF THE RESEARCH WORK

This research work covered the production of the alloy Al-Cu-Si-Ni by chill casting method, and aging the alloy artificially. Mechanical properties and corrosion characteristic of the alloy were also studied. The mechanical properties measured are hardness, and impact strength, since the alloy may find applications in automobile and aerospace industries. On the corrosion analysis, weight loss and Linear Polarization electrochemical method of estimating corrosion rate were used in studying the corrosion behavior of the alloy. These were carried out in simulated seawater (3.5%NaCl) as the alloy is also intended for use in oil and gas offshore industries. Microstructural characterization of the alloy was also conducted.

1.4 CONTRIBUTION TO KNOWLEDGE

To the best of my knowledge, no previous research work was carried out on the effect of Ni addition to Al-Cu-Si alloy up to 2.9% in order to improve the corrosion resistance and the mechanical properties of the alloy. Consequently, this research work has tremendously, to some extent, improved the corrosion resistance and some mechanical properties of the alloy by alloying and heat treatment.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 ALUMINIUM AND ALUMINIUM ALLOYS

Aircraft engines, fuselage, automobile parts, and energy saving strategies in general, have promoted the interest and research in the field of lightweight materials, typically on alloys based on aluminum (Riani, *et al*., 2009; Sarhan, *et al*, 2013). This metal, aluminium, has low density, high ductility, high thermal and electrical conductivity, good corrosion resistance, attractive appearance, and it is nontoxic (Abdulwahab, *et al.*, 2012; Abdulwahab, *et al.*, 2013; David and James, 1998; Mohammed, *et al.*, 2013). Despite its cost, this remarkable combination of qualities makes it an ideal material for use in conventional and critical novel applications such as in aerospace, automobiles, food handling, building, heat exchange, and electrical transmission (Abdulwahab, 2008; David and James, 1998; Hassan and Aigbodion, 2009; Liu, *et al*., 2013; Pokova, *et al.*, 2012; Totten and Mackenzie, 2003; Zeren and Karakulak, 2009). The pure metal is, however, deficient in two respects: mechanical strength and elastic modulus (Aye, *et al*., 2008; David and James, 1998 and Einar, 2004); and aluminium alloy development was driven by the need to improve them without sacrificing other qualities; for example, to improve strength for aerospace, marine, and civil engineering applications without losing corrosion resistance. The success of these endeavors has secured the status of aluminium alloys as second only to steels in economic value (Einar, 2004).

2.2 CLASSIFICATION AND DESIGNATION OF ALUMINIUM ALLOYS

Aluminium alloys may be divided into two broad classes: cast and wrought products. These two classes can be further subdivided into families of alloys based on chemical composition and finally on temper designation. The temper designations are used to identify the *condition* of the alloy, in other words the amount of cold work the alloy has undergone or its heat treatment condition (Mathers, 2002). Wrought alloys are those that are worked to shape, while cast alloys are those that are poured in a molten state into a mold that determines their shape (Kissel and Robert, 2002; Totten and Mackenzie, 2003; Zaki, 2006; Dwight, 1999).

The Aluminum Association, AA, maintains an internationally recognized designation system for each category, described in the American National Standard Institute, ANSI H35.1, Alloy and Temper Designation Systems for Aluminum. The Aluminum Association’s designation system for aluminium alloys was introduced in 1954 (Kissel and Robert, 2002). Under this system, a four-digit number is assigned to each alloy registered with the Association (Zaki, 2006; Smallman and Bishop, 1999; Cayles, 1988). After these digits a hyphen and the basic temper designation follows—a letter and possibly a one- to three-digit number, which indicates the mechanical and/or heat treatment to which the alloy has been subjected to (Callister, 2001). In general, heat-treatable alloys receive T-tempers while work hardening alloys are given H-tempers (Totten and Mackenzie, 2003). Subdivisions of the basic tempers are also given by one or more numbers following the letters (Kissel and Robert, 2002).

2.2.1 WROUGHT ALUMINIUM ALLOYS

For wrought alloys, a four-digit system is used to produce a list of wrought composition families as shown in Table 2.1 (Roberge, 2000).

Table 2.1: Wrought aluminium alloy classification system

Series	Content
1xxx	Commercially pure aluminium
2xxx	Copper
3xxx	Manganese
4xxx	Silicon
5xxx	Magnesium
6xxx	Magnesium and Silicon
7xxx	Zinc
8xxx	Reserve for other elements
9xxx	Unassigned

Source: Schweitzer, P. A., 2007.

The first digit defines the major alloying class of the series. The second digit in the designation indicates alloy modification. If the second digit is zero, it indicates the original alloy; integers 1 through 9, assigned consecutively, indicate modifications of the original alloy. The last two of the four digits have no special significance, but serve only to identify the different aluminium alloys in the group. Variations are defined by one or more alloying elements (Zaki, 2006; Cayles, 1988).

2.2.2 CAST ALUMINIUM ALLOYS

A system of four-digit numerical designations incorporating a decimal point is used to identify aluminium and aluminium alloys in the form of castings and foundry ingot as shown in Table 2.2 (Cayles, 1988; Zaki, 2006).

Table 2.2: Cast aluminium alloy classification system

Series	Content
1xx.x	Commercially pure aluminium
2xx.x	Copper
3xx.x	Silicon with addition of magnesium and/or copper
4xx.x	Silicon
5xx.x	Magnesium
6xx.x	Unused
7xx.x	Zinc
8xx.x	Tin
9xx.x	Reserve for other alloying elements

Source: Schweitzer, P. A., 2007.

The first digit indicates the alloy group (Cayles, 1988). For the 2xx.x through 9xx.x alloy groups, the second two of the four digits in the designation have no special significance but serve only to identify the different alloys in the group. The last digit, which is to the right of the decimal point, indicates the product form: whether casting or ingot. The decimal .0 in all cases pertains to casting alloy limits. Decimals1and 2 concern ingot compositions (Roberge, 2000). A serial letter preceding the numerical designation indicates a modification of an original alloy, or of the impurity limits for unalloyed aluminium. The serial letters are assigned in alphabetical sequence starting with A but omitting I, O, Q and X, where X is being reserved for experimental alloys (Cayles, 1988).

2.2.3 DESIGNATIONS FOR EXPERIMENTAL ALLOYS

Experimental alloys also are designated in accordance with the system for wrought and cast alloys, but they are indicated by the prefix X (Wessel, 2004). The prefix is dropped when the alloy is no longer experimental. Nonetheless, during development and before they are designated as experimental; new alloys may be identified by serial numbers assigned by their originators. Use of the serial number is discontinued when the ANSI H35.1 designation is assigned (Cayles, 1988).

2.3 HEAT TREATMENT OF ALUMINIUM ALLOYS

Heat treatment in its broadest sense refers to any of the heating and cooling operations that are performed for the purpose of changing the mechanical properties, the metallurgical structure, or the residual stress state of a metal product. When the term is applied to aluminium alloys, however, its use frequently is restricted to the specific operations employed to increase strength and hardness of the precipitation-hardenable wrought and cast alloys (Brooks, 1982). The strongest aluminium alloys are, however, strengthened by precipitation hardening and the basic requirement for an alloy to be susceptible to precipitation hardening or age hardening is a decrease in solid solubility of one or more alloying elements with decreasing temperature (David and James, 1998; Totten and Mackenzie, 2003; Smallman and Bishop, 1999).

Heat treatment to increase strength and hardness of aluminium alloys is a three-step process: solution heat treatment, quenching and age hardening (Totten and Mackenzie, 2003; Brooks, 1982). Solution heat treatment consists of heating the alloy to a temperature between 460 and 550°C, at which all the alloying elements are in solid solution (Roberge, 2000; David and James, 1998). The alloy is then rapidly cooled, usually by quenching in water or some other cooling media (Hassan, *et al*., 2008; Kissel and Robert, 2002; Smallman and Bishop, 1999). Being the metal is in an unstable state, the alloying elements are forced to precipitate from solution as hard, intermetallic particles, a process known as natural aging, which takes about 5 days to complete. Conversely, some alloys naturally age too slowly and incompletely; so the process needs to be accelerated by a precipitation treatment. This consists of raising the temperature of the alloy to a temperature lower than 200°C, usually 5^{o}C below the solvus temperature (Totten and Mackenzie, 2003), for a specified time. Under these conditions, artificial aging is promoted (Roberge, 2000). Also, the aging must be accomplished not only below the equilibrium solvus temperature, but also below a metastable miscibility gap called the Guinier-Preston (GP) zone solvus line (Brooks, 1982). Heat treatment involving quenching and aging is the most widely used method for improving strength properties of aluminium alloys. The aging is a term covering the processes of precipitation hardening which can occur at room temperature or at higher temperatures requiring special heating. The advantages of the artificial aging over natural aging are that the material ends up being stronger but less ductile, and the final properties are achieved in hours rather than days (Dwight, 1999).

During age-hardening process, the supersaturated solid solution decomposes or transforms to a series of phases or coherent and incoherent precipitates (David and James, 1998; Totten and Mackenzie, 2003; Hernandez-Rivera, *et al*., 2012), and the precipitation sequence originally established by Guinier and Preston (GP) in Al-Cu alloys after rapid quenching is accepted as: supersaturated solid solution (SSSS) transforming to GP zones plates and to the coherent precipitate θ'', followed by semi-coherent θ' and to final equilibrium precipitate $\theta(Cu_2Al)$ (Biswas, *et al*., 2011; David and James, 1998; Klobes, *et al*., 2010; Smallman and Bishop, 1999; Totten & Mackenzie, 2003; Wang and Starink, 2005;), that is,

SSSS→GP→ (θ'') → θ'→θ(Cu_2Al)

The formation of GP zones and subsequent precipitation of metastable phases plays dominant roles in strengthening the age-hardenable aluminium alloys (Hirano, 1989). Based on this fact, Mostaed *et al*., (2013) and David and James (1998) reported that aluminium alloys are strengthened as dislocation movements are inhibited by matrix lattice strains building up around the GP zones and transition precipitates, but as these transition species are progressively replaced by equilibrium precipitates, the lattice strains are relaxed and the alloy softens.

GP-zones have been recognized as microstructural aggregates of solute atoms in the aluminium matrix (Berg, *et al*., 2011) which are develop during the initial stages of precipitation by "natural aging" at room temperature and in the early stages of "artificial aging" at temperatures in a range 100-180^{o}C (Ravi and Wolverton, 2004). However, their precise role in the formation of hardening precipitates is still not clear in most alloys (Berg, *et al*., 2011).

On the other hand, non-heat-treatable alloys are strengthened by means of cold work applied during manufacture (Dwight, 1999); nonetheless, these alloys may also undergo a heat treatment called annealing to soften the metal so that it can be more easily formed. This heat treatment is used only to stabilize properties so that strength does not decrease over time—behavior called age softening—and is required only for alloys with an appreciable amount of magnesium (Kissel and Robert, 2002).

2.4 ALLOYS BASED ON THE ALUMINIUM–COPPER SYSTEM

The Al-Cu family, in which copper is the major alloying element (Crook, 2005), have excellent mechanical properties, high temperature strength, and fatigue life. They are difficult to cast (Martin, 2006; Yawei, *et al.*, 2010), however, and their long freezing range makes them extremely susceptible to hot cracking (Sigworth and Kuhn, 2007). In addition to their low castability shortcoming, Al-Cu alloys exhibit the lowest corrosion resistance amongst all aluminium alloys (Vadims *et al*., 2007). This is because copper reduces corrosion resistance of aluminium more than any other alloying element and this arises mainly because of its presence in micro-constituents, and these micro-constituents are usually the source of most problems with electrochemical corrosion in alloys as they lead to non-uniform attack at specific areas of the alloy surface (Polmear, 2006). However, in these alloys, copper contributes to strength, and presence of silicon improves castability and reduces hot shortness.

Aluminum-copper alloys with more than 3 to 4% Cu are heat treatable, but usually heat treatment is used only with those alloys that also contain magnesium, which enhances their response to heat treatment (Brooks, 1982; Warmuzek, 2004). Alloys of this type were the first heat treatable high-strength aluminum-base materials and have been used for more than 75 years in structural applications (Crook, 2005).

The limit of solid solubility of copper in aluminium is ~5.8% at 548°C temperature; and at ambient, this copper is present as a saturated solid solution with particles of the hardening phase, copper aluminide, ($CuAl_2$) within the grains as a fine or coarse precipitate or at the grain boundaries (Mathers, 2002).

The interest devoted to the study of the casting Al-Cu alloys is based on the extensive use of these materials. Riani *et al* (2008) and Zhao and co-workers (2007) said these alloys have a combination of high strength and fracture toughness, and permit the design of products characterized by low and very complex geometries in modern industries particularly in the latest generation of the military and civilian aircraft, spacecraft and combustion engines of ground transportation vehicles.

2.5 MECHANICAL PROPERTIES OF ALUMINIUM AND ITS ALLOYS

Pure aluminium is weak, with low tensile strength and elastic modulus (Dwight, 1999; Kissel and Robert, 2002). These mechanical properties may be improved by alloying (Dwight, 1999), strain hardening (Roberge, 2000; Omotoyinbo and Oladele, 2010), thermal treatment, or by combinations of all three techniques (Roberge, 2000). These techniques used to alter the properties of aluminum are intended to improve mechanical and physical properties, but these techniques may actually cause degradation of corrosion resistance (Snodgrass, 2003).

For solid-solution type alloys, mechanical properties are highly dependent on the primary grain size and in most instances; a uniform and fine grain size is sought (Al-Rawajfeh and Al-Qawabah, 2009) in order to obtain optimal properties in the wrought and cast products. Accordingly, the size of the primary grains resulting from solidification is reduced by the use of grain refinement techniques. These techniques include such mechanical methods as mold vibration, stirring, and control of metal flow, which provide nuclei by detachment of dendrite arms. In addition, use of grain refining inoculants may also change the structure from coarse non-uniform to a fine, uniform one and the grain-refining inoculants commonly used in the aluminium industry are master alloys containing titanium or titanium plus boron (Stefanescu and Ruxandale, 2004). For Al-Cu alloys, the mechanical properties are much dependent on copper content and the subsequent heat treatment processes. It should be noted that copper is added to aluminium alloys to increase their strength, hardness, fatigue and creep resistance and machinability; (Wislei, *et al*., 2007; Al-Rawajfeh and Al-Qawabah, 2009) however, at the expense of corrosion (Li, *et al*., 2006).

2.6 CORROSION PROPERTIES OF ALUMINIUM AND ITS ALLOYS

Aluminium is a very active metal thermodynamically (Fontana, 2005), and therefore pure aluminium and all its alloys depend on a naturally occurring aluminium oxide film to provide corrosion protection (David and James, 1998; Roberge, 2000; Zaki, 2006; Snodgrass, 2003; Abdulwahab, *et al.* 2012). This oxide film is adherent, transparent, and stable in aqueous media in the pH range of approximately 4 to 9 (European Aluminium Association, 2002). It is also said to be self-healing, and an electrical insulator, and as the oxide film is naturally self-renewing, any accidental abrasion or other mechanical damage of the surface film is rapidly repaired (Roberge, 2000; Snodgrass, 2003; Weidmann and Guesnier, 2008). The conditions that promote corrosion of aluminum and its alloys, therefore, must be those that continuously abrade the film mechanically or promote conditions that locally degrade the protective oxide film and minimize the availability of oxygen to rebuild it (Roberge, 2000).

Aluminium and its alloys suffer from the most common form of corrosion called pitting. This form of corrosion occurs when a corrosive species such as chloride ions compromises the integrity of the oxide film at local sites (Snodgrass, 2003) and as the concentration of the chloride ions is increased, the passive film undergoes active dissolution due to adsorption of chloride ions; and corrosion is enhanced (Zaki, 2006). However, in severe (acidic) industrial atmospheres, a mixture of pitting and uniform corrosion may take place (Einar, 2004).

Corrosion of aluminium and its alloys may occur as a result of either metallurgical or environmental factors (Nada and Vanja, 2006). Metallurgical effects on corrosion of aluminum are classified into two categories. In the first category are effects from insoluble, intermetallics constituent particles. These can be formed from trace impurity elements, most notably iron, and/or from purposely added alloying elements. These constituent particles play a predominant role in pitting corrosion. In the second category are effects from precipitation of secondary phases, usually as a result of a controlled thermal process such as age hardening. This includes both intergranular and intragranular precipitations, as well as effects from solutes remaining in solid solution. Constituent particles are well known sites for pit initiation, due to galvanic interaction with the surrounding matrix and depending on initial composition; some constituent particles are cathodic to the matrix while others are anodic.

However, some micro-constituents exhibit a changing galvanic effect as the corrosion process ensues (Moran, 2003). Environmental factors such as the acidity or alkalinity significantly affects the corrosion behavior of aluminium alloys as they corrodes more rapidly both in acids and in alkalis compared to distilled water; with the rates in acids depending on the nature of the anion (Revie and Uhlig, 2008). At lower and higher pH, aluminum is more likely to corrode but by no means always does so. For example, aluminium is quite resistant to concentrated nitric acid. When aluminum is exposed to alkaline conditions, corrosion may occur, and when the oxide film is perforated locally, accelerated attack occurs because aluminum is attacked more rapidly than its oxide under alkaline conditions; and the result is pitting. In acidic conditions, the oxide is more rapidly attacked than aluminium, and more general attack should result (Roberge, 2000). The pitting behavior caused by acidic or alkaline attack is predominantly determined by the constituent particles. Thus pitting susceptibility is related to copper content. Hence, lower copper alloys exhibit significantly better pitting resistance than higher copper alloys (Moran, 2003). For example, in Al-Cu alloys, pitting is initiated when traces of the reduced Cu^{2+} ions are deposited at local sites on surface of the alloy; and being copper an efficient cathode, it shifts the corrosion potential in the noble direction to the critical potential thereby both initiating pitting and, by galvanic action, stimulating pit growth (Revie and Uhlig, 2008) (see Equation 2.8). *A*l-Cu alloys are also susceptible to SCC due to the precipitation of intermetallic compounds at the grain boundaries during heat treatments. These precipitate particles are aligned along the grain boundaries and surrounded on both sides by very narrow bands of metal that are depleted in the alloy components contributing to the precipitates. These narrow bands are known as the grain boundary denuded zones. There is thus established a continuous network of three closely adjacent bands of metal with different compositions—the precipitate, the denuded zone and the matrix, between which there are possibilities for electrochemical interactions (see Fig. 2.1). The role of the specific agent now, the chloride ion in this case, is to initiate these interactions by assisting in local de-passivation. In aluminum-copper-silicon alloys, the grain boundary precipitate includes the compound, $CuAl_2$, and the denuded zone is anodic to both the precipitate and the matrix, creating possibilities for local action electrochemical cells, somewhat similar in action to the bi-metallic cells (David and James, 1998; Schweitzer, 2007).

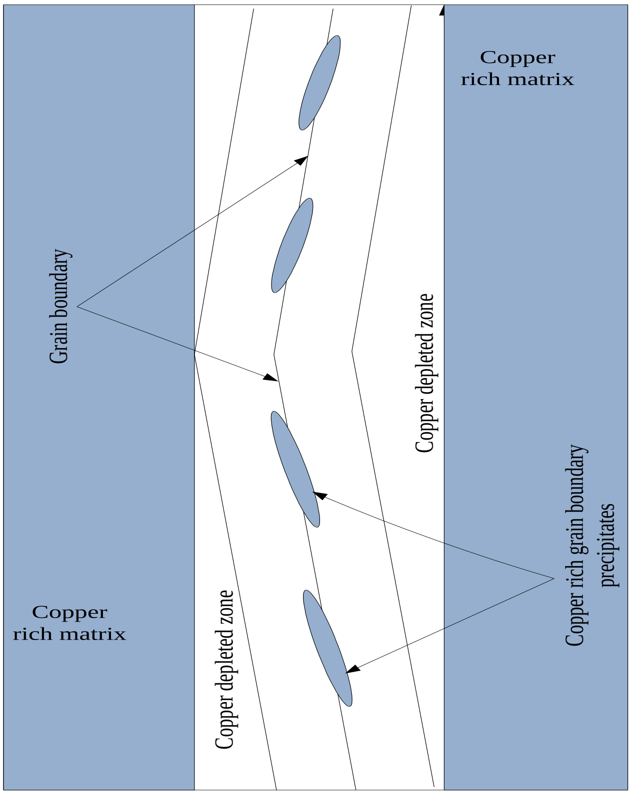

Fig. 2.1 Grain boundary and copper depleted regions in 2xxx/2xx.x alloys.

Source: Schweitzer, P. A. 2007.

Note that Precipitation of the very-high-copper-content precipitates at the grain boundary causes a copper-depleted zone on either side of the boundary, and the difference in the electrochemical potentials of the copper-depleted zone and the copper-rich matrix form a strong galvanic cell. Furthermore, the anodic copper-depleted area is smaller in area compared with the cathodic grain matrix, resulting in a high driving force for rapid intergranular corrosion (Schweitzer, 2007).

Galvanic corrosion is another major practical corrosion problem of aluminium and its alloys. The reason for this is that aluminium is thermodynamically more active (less noble) than most other common structural materials, and that the passive oxide which usually protects aluminium may easily be broken down locally when the potential is raised due to contact with a more noble material (Einar, 2004). Perez (2004) said galvanic corrosion could also occur in polycrystalline alloys due to differences in microstructural phases. Perez explained that, the different phases present leads to galvanic-phase coupling or galvanic microcells between the precipitates and the matrix since each phase has different electrode potentials and atomic structure. Therefore, distinct localized anodic and cathodic microstructural areas develop due to microstructural inhomogeneity, which act as micro-electrochemical cells in the presence of a corrosive medium (electrolyte). For instance in alloys of 2xxx and 2xx.x series, the copper precipitates (Al_2Cu) acts as a cathodic site to the alloy matrix and this initiates galvanic action, which decreases the corrosion resistance of the aluminium alloy (Zaki, 2006). This cathodic precipitates formed in Cu-alloyed aluminium will cause the alloy to corrode intergranularly in polluted industrial atmospheres, in severe marine atmospheres, and in seawater (Einar, 2004). The detrimental effects of copper in these series of aluminium alloys in the solid solution form is attributable to selective dissolution phenomena during the corrosion process, whereby copper was locally enriched on the surface as copper-rich particles providing efficient cathodic sites (Al-Rawajfeh and Al-Qawabah, 2009; Zaki, 2006); though this problem can be overcomed by alcladding components made of these alloys. However, it is easy to produce clad flat products but impracticable for sections and forgings (David and James, 1998). Another form of corrosion in aluminium alloys is exfoliation corrosion, which usually propagates in grain boundaries parallel to the surface (Einar, 2004). Generally, aluminum alloys, particularly the 2xxx/2xx.x series, are less corrosion resistant, because the Al_2Cu intermetallics is cathodic (Wislei, *et al*., 2007 and Roberge, 2000) with respect to the aluminium matrix in these alloys (Andreatta, *et al*., 2003).

2.6.1 MECHANISM OF CORROSION OF ALUMINIUM AND ALUMINIUM ALLOYS

Pure aluminium is found to have good corrosion resistance to seawater. This is because the passive film resists attack by chlorides, probably because of the much greater chemical affinity of aluminium for oxygen than for chlorine (David and James, 1998). However, Revie and Uhlig (2008) reported that the corrosion behavior of aluminium, in general, is sensitive to the presence of small amounts of impurities in the metal such as alloying elements. They said all these impurities with the exception of magnesium tend to be cathodic to aluminum matrix and thus the high-purity metal is much more corrosion-resistant than commercially pure aluminum, which in turn, is usually more resistant than aluminum alloys. Also David and James (1998) explained that corrosion of aluminum alloys is more structure sensitive than for most other alloy systems because the highly reactive metal depends on passivity for protection and is vulnerable to reactive pathways provided by the proliferation of intermetallics compounds more noble than the aluminum matrix. For this reason, David and James (1998) said, the form the attack takes is influenced not only by alloy composition but also by the influence of heat-treatments and of working operations on the microstructure.

Aluminium and its alloys corrode in different ways and forms, depending on the condition of operation and electrolyte. For example, aluminium tends to pit in waters containing Cl^-ions, particularly at crevices or at stagnant areas where passivity breaks down through the action of differential aeration cells (Revie and Uhlig, 2008). The initiation of pits occurs at localized sites on the metal surface defects, which may be due to coating failure, mechanical discontinuities or microstructural phase heterogeneities such as secondary phase precipitates. The microstructural phase heterogeneities, most especially, lead to local galvanic cells coupling between the particles of compound and the adjacent matrix and, once pits are nucleated their growth can be autocatalytic (Perez, 2004; Revie and Uhlig, 2008; Vargel, 2004), (see Fig. 2.1). During the corrosion of aluminium and its alloys in neutral, alkaline or acidic media; it is assumed that many anodic and cathodic reactions take place at localized sites. For instance, in a water-base electrolyte containing chloride ions and oxygen molecules, the Cl^- ions migrate towards the bottom and oxygen molecules react with water molecules on the metal surface. Therefore, metal chloride and hydroxyl ions are produced. This is an oxidation process known as metal dissolution. The mechanism of this corrosion process is expressed in the following equations (Baboian, 2005; Batchelor and Loh, 2002; Bunshah, 1994; McCafferty, 2010; Perez, 2004; Schweitzer, 2010; Vargel, 2004):

Dissolution of aluminium in water proceeds according to the equation

$$Al \rightarrow Al^{3+} + 3e^{+} \qquad 2.1$$

Reduction in neutral or alkaline solutions containing dissolved oxygen

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4(OH)^{-} \qquad 2.2$$

Reduction in acidic solutions containing dissolved oxygen,

$$O_2 + 4H^{+} + 4e^{+} \rightarrow 2H_2O \qquad 2.3$$

Reduction in de-aerated neutral or alkaline solutions (Kelly *et al*. 2003; European Aluminium Association, 2002),

$$2H_2O + 4e^{-} \rightarrow 2(OH)^{-} + H_2 \uparrow \qquad 2.4$$

Reduction in acidic solutions containing no dissolved oxygen (Bunshah, 1994; Kelly *et al*. 2003),

$$2H^{+} + 2e^{+} \rightarrow H_2 \uparrow \qquad 2.5$$

The dissolve aluminium ions then combine with the chloride ions to form an amphoteric compound called aluminium chloride.

$$Al^{3+} + Cl^{-} \rightarrow Al^{3+}Cl^{-} \qquad 2.6$$

Subsequently, $Al^{3+}Cl^{-}$ is hydrolysed by water molecules as follows:

$$2Al^{3+}Cl^{-} + O_2 + 4H_2O \rightarrow 2Al(OH)_3 + 2H^{+}Cl^{-} \qquad 2.7$$

The free acid $H^{+}Cl^{-}$, migrates to the bottom of the pits which increases the acidity at these locations thereby increasing the size of the pits and hence corrosion rate (Callister, 2007; Perez, 2004; Vargel, 2004).

Aluminium alloys of 2xxx/2xx.x, in which copper is the major alloying element, are less resistant to corrosion than alloys of other series, which contain much lower amounts of copper or none. Electrochemical effects on corrosion can be stronger in these alloys because of two factors: greater change in electrode potential with variations in amount of copper in solid solution and, under some conditions, the presence of nonuniformities in solid-solution concentration. However, that general resistance to corrosion decreases with increasing copper content is not primarily attributable to these solid-solution or second-phase solution-potential relationships, but to galvanic cells created by formation of minute copper particles or films deposited on the alloy surface as a result of corrosion. As corrosion progresses, copper ions, which initially go into solution, re-plate onto the alloy to form metallic copper cathodes (Revie and Uhlig, 2008; Crook, 2005). The reduction of copper ions and the increased efficiency of O^{2+} and H^{+} reduction reactions in the presence of copper increase the corrosion rate (Crook, 2005; Bunshah, 1994).

Aluminium alloys also suffer from intercrystalline corrosion in which galvanic cells are being formed because of heterogeneity in alloy structure which may arise from trace alloying additions or minor elements present. For example, in the aluminium copper type alloys, precipitation of Cu_2Al, particles at the grain boundaries leaves the adjacent solid solution anodic and prone to corrosion. However, serious intercrystalline attack in this alloy is not usual, provided that correct manufacturing and heat treatment conditions are observed (Batchelor and Loh, 2002; Shreir *et al*. 1994).

2.7 EFFECTS OF ALLOYING ELEMENTS ON MECHANICAL PROPERTIES, MICROSTRUCTURE AND CORROSION RESISTANCE OF ALUMINIUM ALLOYS

The presence of impurities, alloying constituents, defects, multiple phases, and other metallurgical features, sometimes in very small amounts, can have a profound influence on the corrosion resistance of a material; affecting the susceptibility, rate, mechanism, form of corrosion and mechanical properties (Noel, 2003). The properties of aluminium alloys depend on a complex interaction of chemical composition and microstructural features developed during solidification, thermal treatment and (for wrought products) deformation processing. Although pure aluminium is very resistant to corrosion because of the presence of a thin oxide film of aluminium oxide, Al_2O_3, corrosion resistance generally decreases with increasing alloy content, so tempers have been develop to improve the corrosion resistance of the highly alloyed materials (Totten and Mackenzie, 2003). In general, practices that result in non-uniform microstructure will lower corrosion resistance, especially if the microstructural effect is localized (Al-Rawajfeh and Al-Qawabah, 2009; Totten and Mackenzie, 2003).

All strengthening techniques of aluminium alloys rely on simple principle: restricting or hindering dislocation motion, which renders the material harder and stronger (Warthi, *et al*. 2013). Solid solution, strain hardening, precipitation hardening, and grain size reduction are the mechanisms for strengthening aluminium alloys (Al-Rawajfeh and Al-Qawabah, 2009; Totten and Mackenzie, 2003). In terms of grain size strengthening, fine grain size is often desired for high strength (Mitrašinović and Robles Hernández, 2012). The mechanism of strengthening from precipitation involves the formation of coherent clusters of solute atoms (i.e. the solute atoms have collected into a cluster but still have the same crystal structure as the solvent phase). This causes a great deal of strains because of mismatch in size between the solvent and solute atoms. Consequently, the presence of the precipitate particles, and even more importantly the strain fields in the matrix surrounding the coherent particles, provide higher strength by obstructing and retarding the movement of dislocations. The characteristic that determines whether a precipitate phase is coherent or non-coherent is the closeness of match or degree of mismatch between atomic spacing on the lattice of the matrix and on that of the precipitate. These changes in properties result from the formation of solute-rich microstructural domains or GP zones (Brooks, 1982).

2.8 APPLICATIONS OF ALUMINIUM AND ALUMINIUM ALLOYS

Aluminium alloys are considered as high performance materials in automotive and aerospace industry where damage tolerance is essential (Katarina, *et al*. 2012), and the increasing demand from industries for improved properties in materials has stimulated the development of new materials. For aerospace and automotive industries the properties most required are reduced weight (Zhen and Kang, 1997; Desmukh, *et al*. 2006), low thermal expansion coefficient, excellent mechanical properties; mainly wear resistance at high temperatures (Santos, *et al*. 2005) and corrosion resistance (Tsau and Chen, 2002; Zhen and Kang, 1997). Consequently, because of its light weight, aluminium and its higher-strength alloys are extensively used for structural components and fuselage coverings in aircraft and aerospace vehicles (Al-Rawajfeh and Al-Qawabah, 2009; Dobrzański, *et al*. 2008; Huda, 2009; Jones, 1996; Kumar, *et al*. 2007; Mansourinejad, *et al*. 2012; Seyedrezai, *et al*. 2009; 92), and automotive engines and skin sheet (Hirth, *et al*. 2001). Also rising fuel cost and environmental concerns have motivated the development of alloys with high strength-to-weight ratio in order to reduce vehicle weight (Ye, 2003; Seyedrezai, *et al*. 2009; LaDelpha, *et al*. 2009) which improves fuel efficiency and in turn reduces emission (Gaber, *et al*. 2004). In car engines, aluminium alloys are used frequently in the manufacture of cylinder heads (Ovono, *et al*. 2006), pistons, and sumps. Al–Si casting alloys of the 3xx.x series are being used in automotive industry frequently for engine blocks and pistons with cast iron cylinder liners for wear resistance ((Abdulwahab, *et al*., 2011; Djurdjevic, *et al*., 200; He, *et al.,* 2012 and Liao, *et al.,* 2013). Aluminium wheels, vacuum-cast or forged, are replacing conventional steel wheels in sports and conventional cars because of its light- weight, resistance to atmospheric attack and surface finish (Smallman and Bishop, 1999).

Aluminum and its alloys have some special properties that make this metal and its alloys the most economical and attractive for a wide variety of uses. These include appearance, light weight, high strength, fabricability, castability, fluidity and excellent formability (in rolling, drawing and extrusion). Others are high corrosion resistance in many environments, colorless and non-poisonous corrosion products, good physical and mechanical properties (Abdulwahab, *et al*. 2012; Al-Rawajfeh and Al-Qawabah, 2009; Callister, 2001; Durmus and Meric, 2007; Einar, 2004; Gbenebor *et al*. 2012; Mamatha, *et al*., 2011; Rooy, 1990; and Tsau and Chen, 2002). Also when compared with structural steels, aluminium alloys have much higher specific strength-to-weight ratio and corrosion resistance (Durmus and Meric, 2007). Therefore, the high strength-to-weight ratio of this metal has favored the use of aluminium and its alloys in such diverse applications as in marine environment for bridge rehabilitation ((Popoola, *et al*. 2012; Kissel and Robert, 2002; Rooy, 1990), as well as shipping and defense industries (Durmus and Meric, 2007)—in armor plates manufacture (Wang, *et al*. 2009). In addition to the various fields of applications, aluminium is used in helicopter decks and living quarters on offshore oil platforms, and in superstructures on ships. Also special aluminium alloys have been developed for sacrificial anodes (Einar, 2004).

CHAPTER THREE

3.0 MATERIALS, EQUIPMENT AND METHODOLOGY

3.1 MATERIALS

Materials used in this research work include high purity aluminium and copper wires obtained from Northern Cable Company (NOCACO); Kaduna, high purity nickel and silicon powders, Al-Cu (50/50) master alloy, distilled water, ethanol. Others include Sodium chloride granules and etchants.

3.2 EQUIPMENT

The following are equipment used during this research work: charcoal fired crucible furnace, split cylindrical steel moulds, molding boxes, Rockwell universal testing machine, and Hounsfield Balanced Impact machine, optical metallurgical microscope, heat treatment furnace, plastic containers, nylon strings, and wooden sticks. Others include analytical balance, and electrochemical corrosion kit.

3.3 METHODOLOGY

3.3.1 CASTING

A model multi-component Al-Cu-Si-Ni alloy with nominal chemical composition shown in Table 3.1 was produced using high purity Al wires, pure Si and Ni powders and Al–Cu (50/50w% ligand) master alloy. The alloy was melted in a charcoal-fired crucible furnace and chill cast into preheated split cylindrical steel molds of diameter 22mm and length 350mm. The pouring temperature was about 830^{o}C for a homogeneous melt.

Table 3.1: Composition of alloy produced

Alloy	Cu wt.%	Si wt.%	Ni wt.%	Al wt.%
1	4.00	2.00	—	94.00
2	4.00	2.00	2.30	91.70
3	4.00	2.00	2.50	91.50
4	4.00	2.00	2.70	91.30
5	4.00	2.00	2.90	91.10

3.4 HEAT TREATMENT

A total of 131 samples were Aged Hardened out of 262 samples prepared. The Aged Hardened sample were solutionized at 510^{o}C $\pm 5^{o}$C, soaked for 3hours and then quenched in water at ambient temperatures as specified in ASTM B917/B917M. Thereafter, the quenched samples were aged at a temperature of 170^{o}C $\pm 5^{o}$Cas prescribed in ASTM standards and then allowed to cool in air. Table 3.2 gives a summary of the as-cast and the Aged Hardened samples for the various tests and analysis carried out.

Table 3.2: Experimental Design

Analysis	Weight Loss		Hardness		Impact Strength		Microstructures		SEM		Electrochemical Linear Polarization	
Alloy Condition	AC	AH	AC	AH	AC	AH	AC	AH	AC	AH	AC	AH
Number of Samples	100	100	5	5	15	15	5	5	1	1	5	5

AC = As-Cast
AH = Aged Hardened

3.5 MECHANICAL PROPERTIES

The mechanical properties investigated are hardness and impact strength which were correlated with the microstructures of the alloy.

3.5.1 HARDNESS

Hardness values of ten (10) samples were measured using Rockwell hardness scale F with major load of 60kg and minor load of 15kg. Also hardness values of ten (10) as-corroded samples were taken. Thus a total of twenty samples were evaluated for hardness. For each of the samples, three readings were taken and the average was calculated. This test was conducted according to ASTM E18 Standards.

3.5.2 IMPACT STRENGTH

Impact strength values of thirty (30) samples were measured using a Hounsfield Balanced Impact Testing Machine. The samples used are cylindrical in nature and measured 45mm in length and 10mm in diameter. They were notched at the centre and the notch angle is $45^{o}\pm0.005$ as recommended by ASTM E23 and NACE standard with a notch depth of 1mm. For each alloy composition, impact strength of 6 samples was determined, whereby 3 samples were Aged Hardened while the remaining 3 were in as-cast condition.

3.6 METALLOGRAPHY

Metallographic samples were prepared in accordance with standard procedures specified in ASTM E3, and etched with Keller's reagent (5ml HNO_3, 3ml HCl, 2ml HF & 90ml H_2O) for 10−30s at room temperature as prescribed in ASTM E7, E340 and E407. Microstructures were viewed and captured using an Optical Metallurgical microscope. See Appendix A.

3.7 CORROSION

Both weight loss and Linear Polarization, LP methods were used in evaluating the corrosion behavior of the five different composition of Al-Cu-Si-Ni alloy as described in subsequent sections (control inclusive).

3.7.1 GRAVIMETRIC/WEIGHT LOSS METHOD

About two hundred (200) cylindrical corrosion coupons were used for the weight loss corrosion evaluation of the five different compositions of the alloy. In each of the five compositions of the alloy, forty (40) coupons were cut and prepared according to ASTM G1, G4 and ANSI/NACE TM0177-96. From each alloy composition, twenty (20) coupons were Aged Hardened while the remaining twenty (20) coupons were used in the as-cast condition.

The machine-finished coupons were first of all cleansed of any dirt, such as grease and oxides using detergent and ordinary water in accordance with ASTM G4 standards. Distilled water was then used followed by ethanol. The coupons were dried in the air and the initial weight, w_1 was then taken using digital chemical balance. Thereafter, the coupons were immersed in a simulated seawater environment by suspending them with nylon strings for a total period of 960 hours. At forty-eight hour (48hrs) interval, a set of coupons were removed from the corrosive environment and the corrosion products were removed by scrubbing with a soft bristle brush. The coupons were rinsed with ethanol followed by distil water and then dried in the air. The weight w_2 was then recorded. From the initial weight w_1 and the final weight w_2, the weight loss, W was deducted as follows:

$$W = w_1 - w_2 \tag{3.1}$$

And hence the corrosion rate (CR), in mils per year (mpy), according to ASTM G31 was calculated using equation 3.2:

$$CR\ (MPY) = \frac{KW}{\rho A T} \tag{3.2}$$

Where,

K is a constant given as 3.45×10^6 in mils per year,

W is the weight loss (i.e. w_1-w_2) in g,

ρ is the density of the alloy in g/cm^3,

A is the area of the test coupon in cm^2; given as $\frac{\pi}{2}(D^2 - d^2) + t\pi D + t\pi d$: (D = coupon's diameter, d = diameter of mounting hole and t = thickness) (ASTM G1), T is the exposure time in hours.

3.7.2 LINEAR POLARIZATION METHOD

A total of ten (10) samples consisting of five (5) as-cast and five (5) age-hardened were subjected to electrochemical technique to characterize the corrosion rate of the alloy. This comprised of cyclic scan employing the linear polarization technique. A potentiostat coupled to a computer system, a glass corrosion kit with graphite rods as counter electrodes and saturated Ag/Ag^+ reference electrodes were used. The alloy samples were made as the working electrodes.

The samples were positioned at the glass corrosion cell kit, leaving a $3.11cm^2$ alloy surfaces in contact with the solution. Polarization test was carried out in 3.5%NaCl at room temperature in a static solution for a period of 30 minutes using a potentiostat. The polarization curves were determined by stepping the potential at a scan rate of 0.0016V/s. The polarization curves plotted using AutoLab data acquisition system (AutoLab Model: Aut71791 and PGSTAT30), and both corrosion rate and potential were estimated by the Tafel extrapolation method using the anodic and cathodic branches polarization curves,

CHAPTER FOUR

4.0 RESULTS AND DATA PRESENTATION

4.1 RESULTS

Results obtained for hardness, impact strength, weight loss corrosion rate and electrochemical corrosion rate data are presented in both tabular and graphical forms.

Table 4.1 shows the variation of hardness values with alloy composition. Impact strength values obtained for the as-cast and Aged Hardened samples are shown in Table 4.2. Weight loss corrosion rate values for a span period of 960 hours are presented in Tables 4.3-4.4 for as-cast and Aged Hardened samples of the alloy. Also corrosion rate analyses for linear polarization are recorded in Tables 4.5-4.6. All the data obtained in Tables 4.1-4.6 have also been represented graphically in Figures 4.1-4.2. The micrographs obtained from are shown in Plates 1-6 in Appendix A. The experimental data obtained is presented in the next section.

4.2 DATA PRESENTATION

Table 4.1: Hardness values of as-cast and Aged Hardened Al-Cu-Si with Ni addition

	Average Hardness Values, HRF	
%Ni Addition	As-Cast	Aged-hardened
0	26.3	29.3
2.3	27.5	29.9
2.5	37.2	42.5
2.7	30.6	31.6
2.9	29.4	30.3

Table 4.2: Impact Energy in Joules for As-cast and Age-hardened Al-Cu-Si Alloy with Ni additions.

	Average Impact Energy, Joules	
%Ni Addition	As-Cast	Aged-hardened
0	10.6	20.1
2.3	14.6	20.5
2.5	15.5	18.7
2.7	11.9	16.3
2.9	9.1	10.2

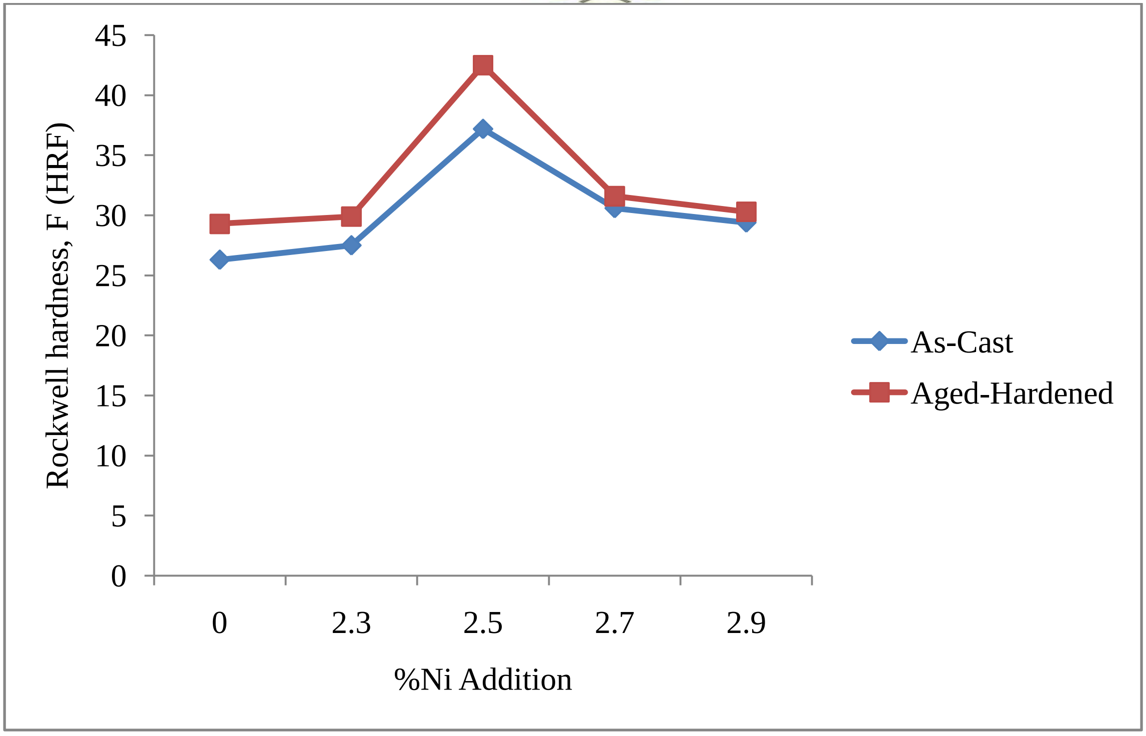

Figure 4.1: Hardness Curves for As-Cast and Aged-Hardened Samples of Al-Cu-Si with Ni Additions.

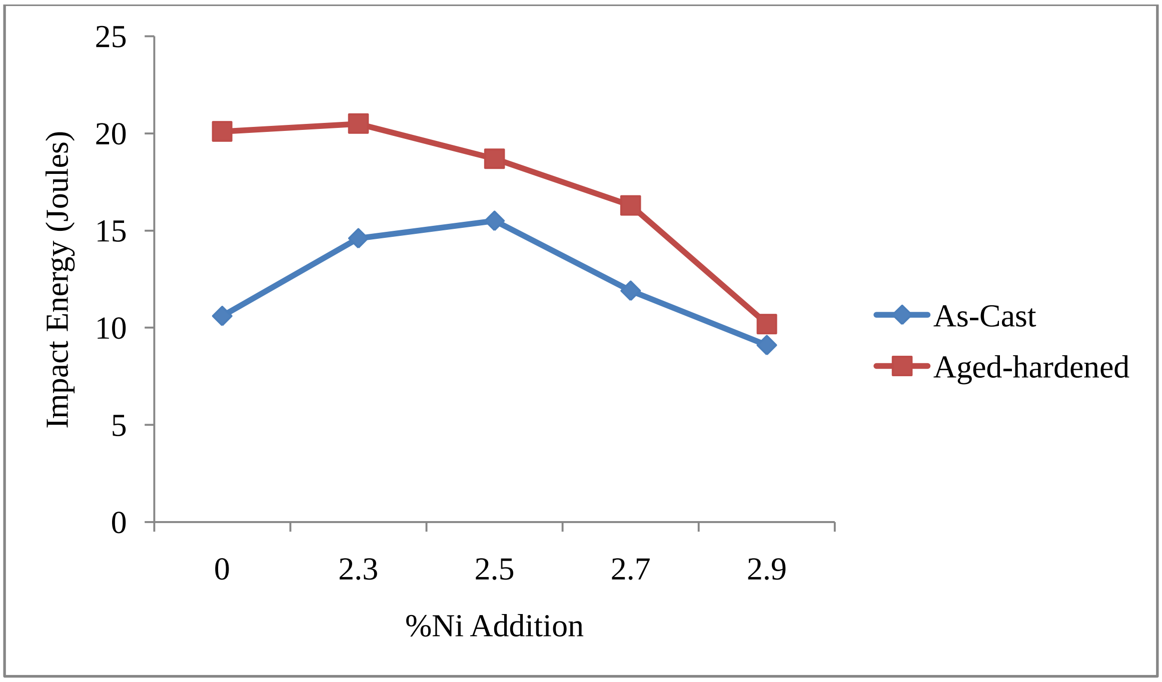

Figure 4.2: Variation of Impact Energy with Respect to %Ni in Al-Cu-Si of As-Cast and Aged-Hardened Alloy.

Table 4.3: Weight Loss Corrosion Rate Data for As-Cast Al-Cu-Si with Ni Additions in Simulated Seawater over Exposure Time

%Ni addition	Exposure Time (Hrs)																			
	48	96	144	192	240	288	336	384	432	480	528	576	624	672	720	768	816	864	912	960
	Corrosion Rate (mpy)																			
0	29.401	11.856	7.817	4.91	4.776	4.663	2.996	2.368	2.339	3.308	3.7	3.88	3.58	3.003	2.901	2.806	2.746	2.509	2.29	1.998
2.3	28.759	9.216	6.439	4.875	4.713	4.6	2.9	2.251	2.33	2.209	2.104	1.88	1.488	1.37	1.281	1.18	1.175	1.092	1.009	0.976
2.5	28.003	8.46	6.3	4.862	4.669	4.56	2.847	2.241	2.201	2.109	2.001	1.674	1.438	1.303	1.29	1.169	1.105	1.08	0.96	0.866
2.7	26.748	6.755	5.788	4.688	4.601	4.306	2.934	2.23	1.901	1.901	1.853	1.491	1.341	1.29	1.2	1.069	1.029	1.001	0.901	0.801
2.9	23.731	6.702	5.768	4.68	4.599	4.202	2.405	2.222	1.801	1.87	1.701	1.376	1.208	1.193	1.09	1.004	0.501	0.488	0.391	0.36

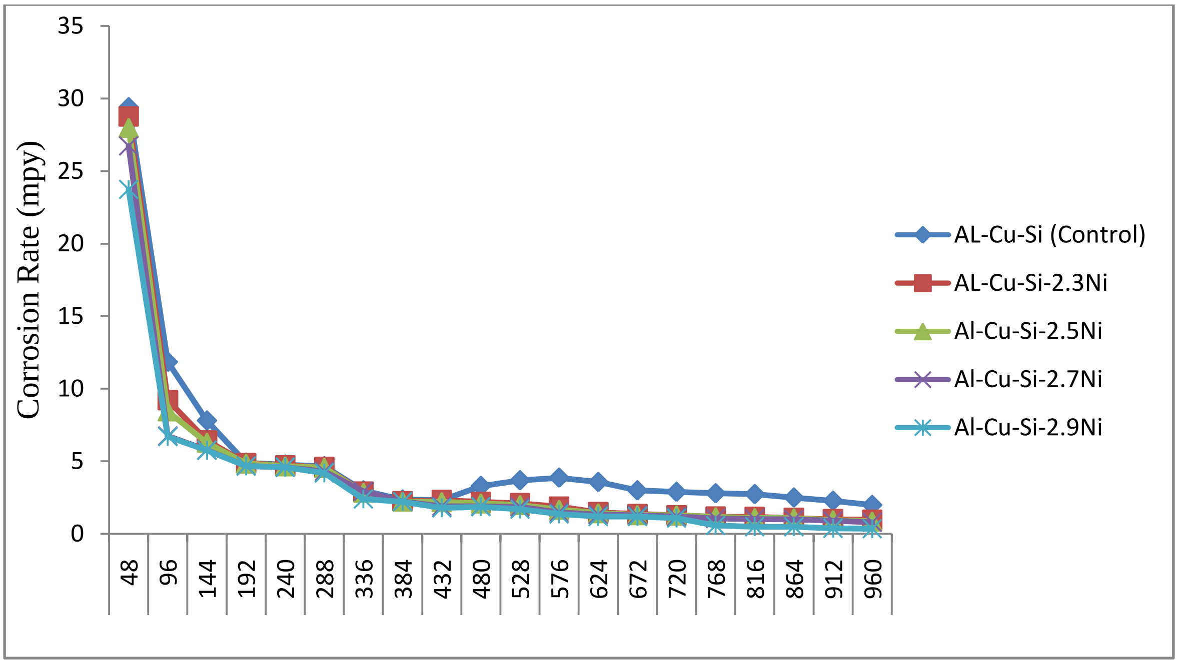

Figure 4.3: Weight Loss Corrosion Rate Curves for As-Cast Al-Cu-Si Alloy with Ni Additions in Simulated Seawater.

Table 4.4: Weight Loss Corrosion Rate Data for Aged-Hardened Al-Cu-Si with Ni Additions in Simulated Seawater over Exposure Time

%Ni addition	Exposure Time (Hrs)																			
	48	96	144	192	240	288	336	384	432	480	528	576	624	672	720	768	816	864	912	960
	Corrosion Rate (mpy)																			
0	27.376	15.516	7.565	4.998	4.697	4.531	4.303	3.998	3.776	3.512	3.525	3.466	3.319	3.223	3.008	2.796	2.564	2.408	2.294	2.054
2.3	23.22	13.857	6.545	4.752	4.69	4.378	3.851	3.671	3.495	3.135	2.986	2.681	2.358	2.008	1.847	1.518	1.214	1.056	0.996	0.901
2.5	17.669	9.964	6.094	4.548	4.416	4.099	3.014	2.809	2.695	2.425	2.063	1.995	1.61	1.416	1.282	1.081	1.007	0.814	0.795	0.697
2.7	14.787	6.698	5.686	4.506	4.407	4.184	2.983	2.801	2.6	2.411	2.051	1.891	1.511	1.401	1.234	1.071	0.991	0.801	0.73	0.603
2.9	15.417	9.893	6.026	4.484	4.401	3.976	2.971	2.711	2.595	2.356	2.001	1.976	1.591	1.391	1.235	1.001	0.992	0.771	0.677	0.662

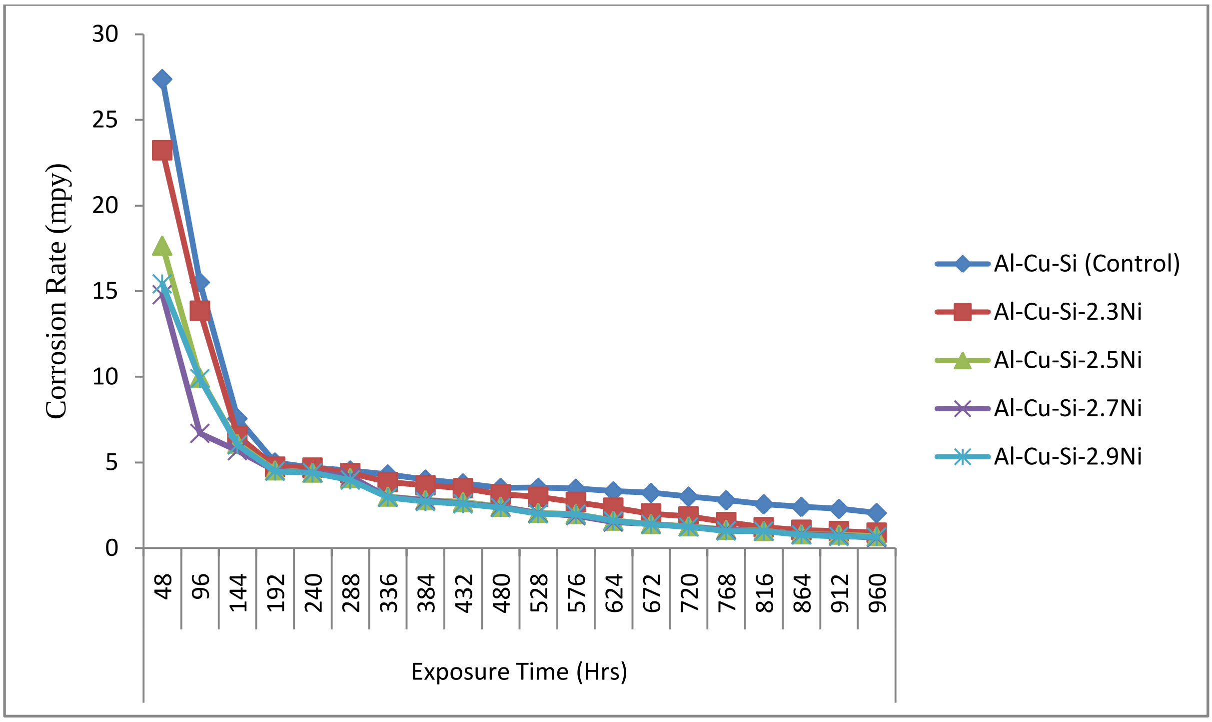

Figure 4.4: Weight Loss Corrosion Rate Curves for Heat-Treated Al-Cu-Si Alloy with Ni Additions in Simulated Seawater.

Table 4.5: Linear Polarization Parameters of As-Cast Al-Cu-Si with Ni Additions

Alloy Sample	%Ni Addition	Ecorr, Calc (V)	Ecorr, Obs (V)	j_{corr} (A/cm^2)	i_{corr} (A)	Corrosion rate (mm/year)	R_p (Ω)
C1	0	-1.387	-1.3887	4.68E-06	1.47E-05	0.021532	297.53
C2	2.3	-1.2693	-1.2753	1.03E-05	3.22E-05	0.054681	49.857
C3	2.5	-1.1284	-1.1262	5.88E-06	1.85E-05	0.032055	212.77
C4	2.7	-0.98816	-0.98423	4.68E-06	1.47E-05	0.029479	478.17
C5	2.9	-0.98113	-0.98423	2.44E-06	7.67E-06	0.009173	481.22

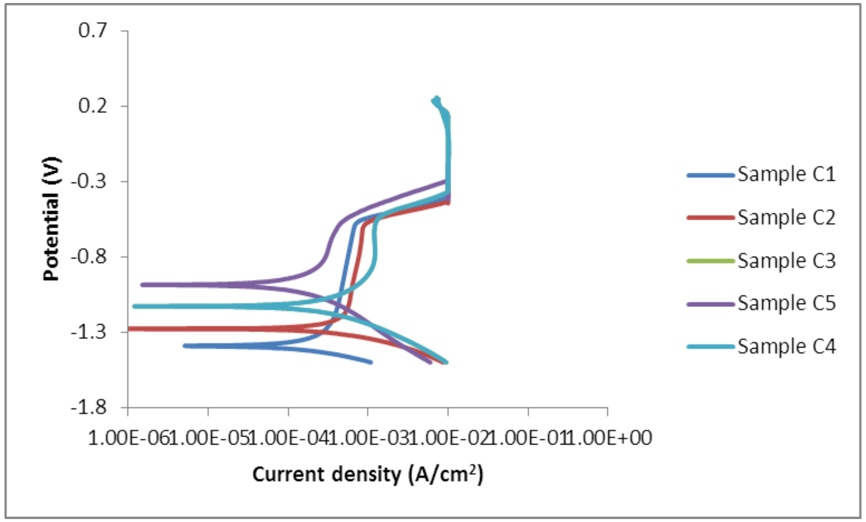

Figure 4.5: Linear Polarization Curves for As-Cast Al-Cu-Si Alloy with Ni Additions.

Table 4.6: Linear Polarization Parameters of Heat Treated Al-Cu-Si with Ni Additions

Alloy Sample	%Ni Addition	Ecorr, Calc (V)	Ecorr, Obs (V)	j_{corr} (A/cm^2)	i_{corr} (A)	Corrosion rate (mm/year)	R_p (Ω)
C1	0	-1.387	-1.3887	4.68E-06	1.47E-05	0.021532	297.53
C2	2.3	-1.2693	-1.2753	1.03E-05	3.22E-05	0.054681	49.857
C3	2.5	-1.1284	-1.1262	5.88E-06	1.85E-05	0.032055	212.77
C4	2.7	-0.98816	-0.98423	4.68E-06	1.47E-05	0.029479	478.17
C5	2.9	-0.98113	-0.98423	2.44E-06	7.67E-06	0.009173	481.22

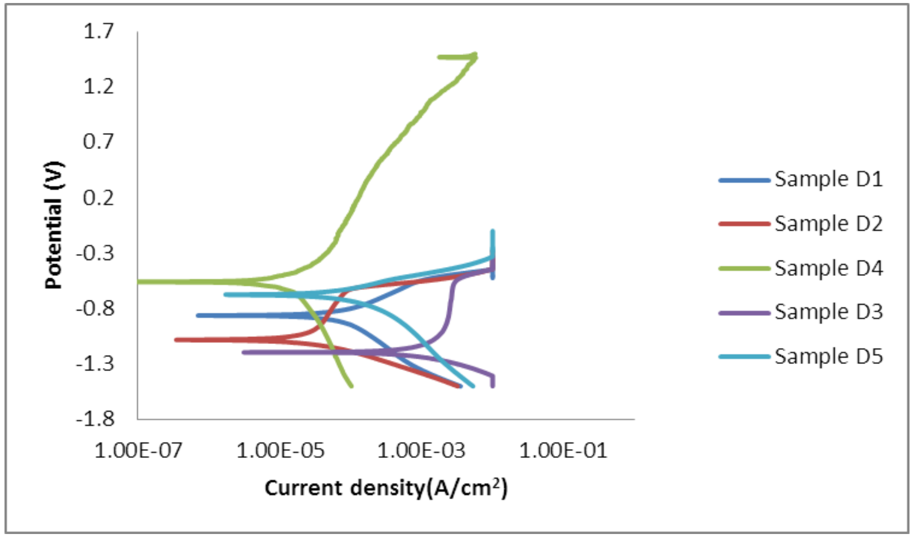

Figure 4.6: Linear Polarization Curves for Aged-Hardened Al-Cu-Si Alloy with Ni Additions.

CHAPTER FIVE

5.0 DISCUSSIONS

5.1 HARDNESS

To understand the effect of nickel content and heat treatment, hardness values of alloy samples were measured both in as cast and aged hardened conditions. The hardness result obtained in this research indicates that the hardness of the alloy increases with Ni content for both as-cast and aged-hardened conditions up to a maximum of 2.5%Ni and then the hardness dropped sharply at 2.7%Ni. The increase in hardness was probably due to combination of Ni and $CuAl_2$ to form intermetallics, which are even stronger than the $CuAl_2$ which is the main strengthening constituent of this series of alloys such as $NiAl_3$ and Ni_3Si. On the other hand, the sudden decrease in hardness of the alloy beyond 2.5%Ni for either condition may not be unconnected with the fact that Ni reduces significantly the sole strengthening agent, $CuAl_2$, in this type of alloy to form ternary phases such as Al_7Cu_4Ni, Al_6Cu_3Ni, Al_7CuNi, Al_9Cu_3Ni, Al_3Cu_2Ni and Al_3CuNi. These ternary phases are said to reduce the mechanical properties of this type of alloy series at room temperature. This follows the fact that the formation of Al_2Cu in Al-Cu alloys is responsible for their good mechanical properties, so any attempt to reduce the Cu concentration in the matrix will consequently result into a decrease in mechanical strength of the alloy. Also the decrease in hardness of the alloy may be explained in terms of the increase in inter-particle spacing between the constituent particles and or dispersoids (Risanti *et al.*, 2007), which may lead to easy dislocation bowing across these particles. In addition, increase in Primary Dendrite Arms (λ_1) and Secondary Dendrite Arm Spacing (SDAS) (λ_2) can result in lower mechanical properties and vice versa. This was attested for in a research conducted by Kaya, *et al* (2008) and Totten and Mackenzie, (2003). Furthermore, Nickel has low solubility in solid (Al) and hence slow diffusion rate. Therefore, during solidification it enters various phases, in particular those containing iron and copper

(Eskin, *et al*. 2005; Smallman and Ngan, 2007). Another mode of explanation for the decrease in hardness of the alloy beyond 2.5%Ni for both as-cast and age-hardened conditions can be in terms of the amount, size, shape and distribution of eutectics formed. The eutectics produced due to excess addition of Ni, which is one of the eutectic formers, affects the mechanical properties of a cast component as reported by Khajeh and Maijer (2011). This large volume of elongated eutectics in the alloy may form softer phases which consequently may lead to reduction in hardness and strength of the alloy. This has been explicitly reported elsewhere (Kermendis, *et al*. 2010).

Nonetheless, from Table 4.1, it can be seen that the hardness values of the age-hardened alloy is higher than those for as-cast. The increase in hardness with Ni addition after age-hardening may be associated with the formation of harder precipitated phases such as Ni_3Al and Ni_3Si during the aging process as reported by Kaya, *et al*. (2008) and US Department of Health and Human Services, (2000) in the α-Al matrix. The nickel aluminide, $NiAl_3$, which has been used for long as a strengthening constituent in high-temperature nickel-base superalloys, owes its outstanding strength to a fine dispersion of precipitation particles of the ordered Ni_3Al embedded in a ductile α-matrix (ASM Specialty Handbook, 2000), and as Warmuzek (2004) reported, the micro-hardness of the intermetallic compound Ni_3Al is about 10,000HV. In addition, the precipitation of phases such as Cu_2Al (with micro-hardness of 7,600HV) (Warmuzek, 2004), also adds to the increase in hardness of the alloy. Therefore, the precipitation of Cu_2Al, Ni_3Si and Ni_3Al are responsible for the increase in hardness with Ni content as these constituent particles hinders dislocation movement. However this increase in hardness may have a negative effect on the corrosion resistance of the alloy.

5.2 IMPACT STRENGTH

In this research work, the impact energy of the alloy, with varying composition, was determined in order to assess the shock absorbing property of the alloy as well as to study the effect of stress concentration and high velocity load application.

Equally from the trend of curves trend in Figure 4.2, it can be deduced that age-hardened samples of the alloy exhibit higher impact toughness than their as-cast counterparts. However the impact energy decreases with nickel content for both as-cast and age-hardened conditions of the alloy. This fall in impact energy, basically, may be linked to the fact that nickel exerts positive influence upon mechanical properties at elevated temperatures for Al-Cu alloys and it (nickel) lowers strength at room temperature as adduced by Vadims *et al*. (2007) and since the test was carried out at room temperature, the impact strength decrease with Ni content.

5.3 MICROSTRUCTURE CHARACTERISTICS

The micrographs of Al-Cu-Si alloy with the addition of different percentages of Ni are shown in Appendix, Plates 1-6 for both the as-cast and aged-hardened conditions. The microstructure of this type of alloys is generally said to be characterized by primary (λ_1) and secondary (λ_2) dendrite arms (Wislei, *et al*., 2007) as can be observe in Plates 1-5 in Appendix A. From the micrographs, it can be seen that the microstructures of the age-hardened alloy have finer grains and consequently more grain boundaries than the as-cast alloy. This is based on the fact that there is an increase in the volume of the precipitated intermetallic compounds during ageing process and also refinement of the precipitated constituent particles.

5.4 GRAVIMETRIC ANALYSIS

Table 4.3 and 4.4 containing the weight loss corrosion data in Appendix A revealed that corrosion resistance for the as-cast alloy increases with increasing Ni content up to 2.9%Ni. The continuous increase in the corrosion resistance of the as-cast alloy may be connected with the fact that Ni is a corrosion resistant element and thus react with the alloy Al-Cu-Si to form phases— constituent particles, intermetallics and dispersoids, that passivate easily and hence a reduction in corrosion rate of the alloy. As reported elsewhere by Anthony *et al* (2011), the intermetallics and the α-matrix both oxidize rapidly forming protective oxide films, and also the α-matrix provides a protection to the precipitates via a process called shingling. Thus the Al-Cu-Si alloy containing Ni have lower corrosion rates in comparison with the control alloy. On the other hand, the corrosion resistance of the age-hardened alloy also increases with Ni but at 2.9%Ni, the resistance dropped. The reason for the fall in the corrosion resistance at 2.9%Ni may be due to the fact that many fine precipitates of intermetallic compounds and formation of dispersoids induced by excess Ni addition caused the alloy to have so many corrosion paths to be initiated both in the grains interiors and at the grain boundaries. This is in line with the claim of Al-Rawajfeh and Al-Qawabah, (2009) work who reported that finer particles are more susceptible to corrosion than coarse ones.

It should be noted from Tables 4.3-4.4 and Figures 4.3 and 4.4 that the corrosion resistance of the age-hardened alloy is higher than those in the as-cast condition. This is based on the fact that the age-hardened alloy contained high volume of fine precipitates of intermetallic compounds—GP zones, formed during the precipitation hardening session. However it is expected that a metal with finer precipitated particles is more susceptible to pitting, intercrystalline, intergranular and grain boundary corrosion, but in this case the aluminium matrix probably enveloped the precipitated intermetallics—a process called shingling

(Anthony, *et al*. 2011), thus serving as a protection against corrosion. This is supported by the work of Wislei, *et al*. (2007). As it is reported by Wislei and European Aluminium Association, (2002) that both Al_2Cu and Al_3Ni are cathodic with respect to the Al-rich α-phase, and perhaps the rise in corrosion potential of α-phase reduces the galvanic coupling between Al_2Cu, Al_3Ni and the α matrix and thus reducing the driving force for pitting corrosion. This idea was supported elsewhere (Wislei, *et al*. 2007). The low corrosion resistance of Al-Cu-Si alloys is much attributed to the formation of the intermetallic compounds Al_2Cu due to the reaction between copper and aluminium during casting and during precipitation hardening. However in the presence of Ni, less Al_2Cu is formed because Ni tend to combine with Cu and Si from the alloy to form Al_3Ni, Al_6Cu_3Ni, Ni_3Si and $Al_3(Ni, Cu)_2$ (Nunomura *et al*. 2004; Vadims, *et al*. 2007) and others. These intermetallic compounds and dispersoids formed are responsible for the alloy's resistance to corrosion over a wide range of temperature, because Ni_3Al and Ni_3Si in particular are said to have excellent corrosion and oxidation resistance in a wide range of temperatures owing to formation of stable surface alumina and silica oxide layers, respectively as contained in Nunomura *et al*. (2004) work.

5.5 LINEAR POLARIZATION RESISTANCE

The linear polarization data and curves for Al-Cu-Si alloy with additions of different percentages of Ni in simulated seawater are shown in Tables 4.5-4.6 and Figures 4.5-4.6, Appendix A. From the data obtained, it can be seen that the corrosion rates of all the studied samples, in either conditions, showed a smaller passive region (cathodic arm) and a prolonged active arm (anodic arm). This is because the samples were cast and solidified in a similar manner. The corrosion current densities (j_{corr}) were obtained from polarization curves in Figures 4.5 and 4.6 by Tafel plots using both cathodic and anodic branches of the polarization curves. The current densities (corrosion rates) and their corresponding corrosion potentials are shown in Tables 4.5 and 4.6, chapter four.

From the linear polarization (LP) curves in appendix A, it can be seen that, at the base of the plot, the curves starts out with a gradually increasing current and potential as expected for most metals and alloys (Schweitzer, 2010). However, for each of the alloy composition, of either condition—as-cast or precipitation hardened, there is dramatic polarizing effect that drops the current as the potential increases to a point where corrosion is essentially halted. At this point, the alloy is said to passivate due to the formation of hard solid oxide films such as NiO_2, Al_2O_3 and SiO_2 from both the matrix and the intermetallics, and according to Schweitzer, (2010), once NiO_2 is formed, it cannot be removed easily by either cathodic treatment or chemical dissolution.

For the as-cast, the LP curves look alike and hence follow the same trend. Consequently, for the five as-cast alloy samples, the polarization curves rise rapidly and become fundamentally vertical at limiting current densities with a progressive increase in potential. However, with an upscan of potential, the alloy lost its passivity and enters into a transpassive region where the current densities increase with rise in corrosion potential before moving into the secondary passive region. As a corollary, the corrosion rate from the LP curves decreases with Ni content for both as-cast and aged-hardened alloy samples. For example, the corrosion rates for as-cast and aged-hardened control alloy are 0.0587mm/yr and 0.0193mm/yr respectively. These corrosion rates decreased to as low as 0.009mm/yr and 0.0011mm/yr for a-cast and Aged Hardened Al-Cu-Si alloy composition containing 2.9%Ni and 2.7%Ni respectively. See Tables 4.5-4.6 and Figures 4.5-4.6. This clearly showed that addition of Ni to Al-Cu-Si helps in reducing the corrosion rate of the alloy to certain extent because Ni binds a significant percentage of Cu in the alloy which is responsible for the high rates of corrosion experienced in this series of alloys.

The LP data tallies with the gravimetric analysis in that for the as-cast the corrosion rate decreases with Ni content up to a maximum of 2.9%Ni, while for the age-hardened alloy the corrosion rate started increasing at 2.9%Ni.

5.6 CORRELATION BETWEEN MICROSTRUCTURE, HARDNESS, IMPACT STRENGTH AND CORROSION RESISTANCE OF Al-Cu-Si WITH Ni ADDITIONS

In multiphase alloys, different types of microstructures result depending on the volume fraction, shape and the distribution of the phases (Gleiter, 1996). According to literatures, the microstructure of Al-Cu-Si alloys plays an important role in determining the mechanical properties and corrosion behavior of the alloy. Hence, the micrographs shown in Plates 1-10 can be used to interpret the variation of hardness, impact strength and corrosion resistance of the alloy in both the as-cast and precipitation-hardened conditions.

The as-cast microstructures may most likely consist of dendritic α-matrix with $CuAl_2$, Al_3Ni and other interdendritic eutectic regions which give rise to microsegregation pattern following a lamellar alternation of each. This is in accordance with the result obtained by Wislei, *et al*. (2007) and Zhao, *et al*. (2007). However there are several intermetallic phases precipitated inside the α-matrix responsible for the alloy's high strength such as $NiAl_3$, $Al_3(Cu, Ni)_2$, Al_3Cu and others due to addition of Ni for those containing Ni. The microstructure of the aged-hardened alloy showed a rather finer grains and hence more grain boundaries than those in the as-cast condition. This is why the hardness values of the aged-hardened alloy are higher in comparison with those of the as-cast as articulated by the investigation carried out by Reed-Hill, (1973) and Li, *et al*. (2013). See Plates 6-10. The finer grains obtained in the aged-hardened alloy creates more grain boundaries and according to Rösler, *et al*. (2007) and Li, *et al*. (2013) these grain boundaries interfere with dislocation movement and once a dislocation reaches a grain boundary, it cannot continue its slip motion into another grain because of the differences in orientation of the slip planes and directions between two neighboring grains (Ashby, *et al*. 2007; Rösler, *et al*. 2007). Hence, grain boundaries serve as obstacles to movement of dislocation which pile up near the boundaries (Ashby *et al*. 2007; Rösler *et al*. 2007; and Totten & Mackenzie, 2003). Therefore, with decreasing grain size (i.e. more finer grains) less distance is covered or travelled by a glissile dislocation before reaching a grain boundary, resulting in higher strength and hardness. This is called grain size hardness (Martin, 2006; Reed-Hill, 1973; and Totten & Mackenzie, 2003). In addition, there is a relationship between grain size and strength established by Hall and Petch called the Hall-Petch equation. This equation is given as (Jóni *et al*., 2013; Martin, 2006; Reed-Hill, 1973; and Totten & Mackenzie, 2003):

$$\delta_{\gamma} = \delta_{f} + k_{1} d^{-m} \tag{4.1}$$

Where δ_{γ} is yield stress, δ_{f} is frictional stress, k_{1} is constant that characterized the difficulty of transmitting slip across the grain boundary for a given alloy system, *d* is average grain size and *m* is 0.5 for grain size hardening.

Therefore, as *d* tends to infinity, δ_{γ} increases, hence the strength and hardness.

Literatures from different researchers agreed on the fact that there is a relationship between hardness, corrosion resistance and microstructural composition of a given alloy. As such, alloys with higher hardness values have finer grains size and are said to be more susceptible to corrosion than those with coarse grains (Wang *et al*. 2009). Nevertheless, in this research work, the aged-hardened alloy exhibit a finer grain structure but showed a better corrosion resistance than the coarse grain as-cast alloy. Furthermore, the Aged Hardened samples of the alloy containing Ni in different percentages gave a better corrosion rate values than the control alloy containing 0%Ni. This might be attributed to the fact that the precipitated intermetallics, such as $CuAl_2$, Ni_3Si and Al_3Ni, are enveloped by the α-matrix which acts as a protection against corrosion—a process called *shingling*. This is in relation with the investigation carried out by Wislei, *et al*. 2007). Moreover, the presence of the intermetallics

Al_3Ni, which possessed a very good corrosion resistance (Kumar, *et al*. 2011) may be responsible for the improvement in the corrosion resistance. Consequently, for either conditions (i.e. as-cast and Aged Hardened) the Al-Cu-Si alloy containing Ni showed an improvement in the corrosion resistance than the control alloy.

CHAPTER SIX

6.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 SUMMARY

Weight loss and potentiodynamic polarization consisting of linear polarization have been employed to study the effect of Ni addition on the corrosion behavior of Al-Cu-Si. Equally, hardness and impact toughness variation have been studied using various techniques mentioned in chapter three.

From the experimental result obtained for weight loss and linear polarization, it was clarified that the corrosion resistance of Al-Cu-Si improves for either conditions—as-cast and precipitation hardened up to 2.7%Ni content. However the age-hardened alloy containing Ni showed a better corrosion resistance than the as-cast. Comparatively, the hardness of the alloy increases with Ni content up to 2.5%Ni and then suddenly dropped sharply for reasons given in chapter five, section 5.1.

6.2 CONCLUSIONS

The study of the effects of Ni addition on the mechanical properties and corrosion behavior of Al-Cu-Si has lead to the following conclusions:

1. Ni addition has improved the corrosion resistance of the alloy, however excess addition tend to diminish the corrosion resistance.
2. The hardness of the alloy increased with Ni content up to 2.5%Ni and then suddenly falls. The sharp fall may not be unconnected with the fact that excess Ni in the alloy tend to remove or binds a significant proportion of the strengthening alloying element, copper to form other phases.
3. The result of the linear polarization and weight loss indicate that Ni addition to the alloy improves the corrosion resistance.

4. The result of hardness demonstrates that heat treatment— precipitation hardening, is a tool for enhancing both the corrosion resistance and some mechanical properties of the alloy.
5. The impact strength of the alloy decreases with Ni content.

6.3 RECOMMENDATIONS

1. The mechanical properties studied in this research are hardness and impact strength only; therefore other properties such as tensile strength, fatigue strength, torsional strength, and creep strength should be investigated and evaluated to know the effect of Ni addition on these properties.
2. The alloy, Al-Cu-Si with Ni additions should be subjected to different heat treatment cycles/conditions such as double or secondary thermal ageing, multistep thermal ageing, and interrupted quenching and ageing in order to determine if there is a more suitable method of heat treating this alloy other than single thermal ageing treatment—T6 (STAT) used in this research work.
3. Precipitation Volume Fraction (PVF) of the intermetallics in the alloy should be studied further using High Resolution Transmission Electron Microscope (HRTEM) in order to know the amount of precipitates involve, their location, and the Precipitate Free Zones (PFZ) if any.
4. Morphology, composition and distribution of the various constituent particles should further be investigated with the help of Transmission Electron Microscope, TEM.
5. Use of XRD should be made to identify the different strengthening constituents particles precipitated in this alloy.
6. Research should be carried out to determine the Brittle-Ductile Transition Temperature (DBTT) of this alloy.

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APPENDIX A

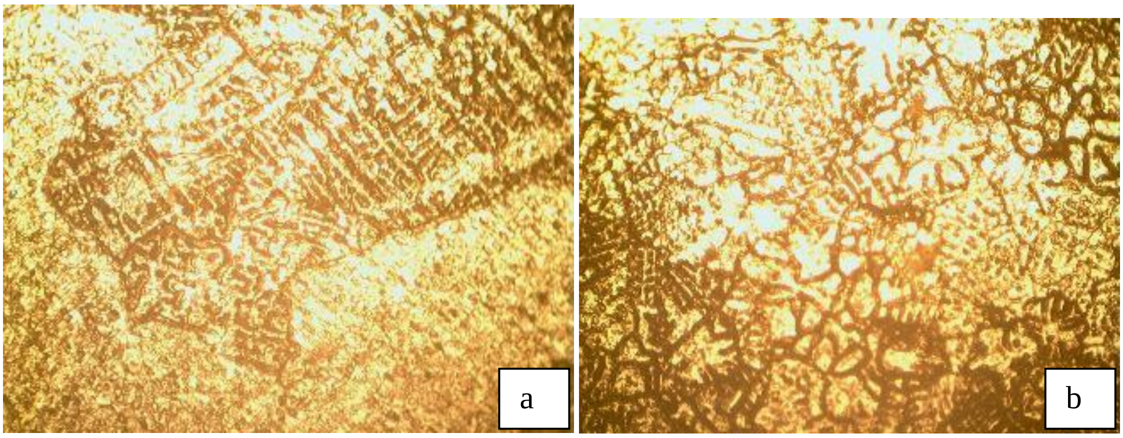

Plate 1: Microstructure of as-cast Al-Cu-Si (a) 0%Ni and (b) 2.3%Ni: Light-grey is α-Al matrix and dark-brown is precipitated intermetallics.

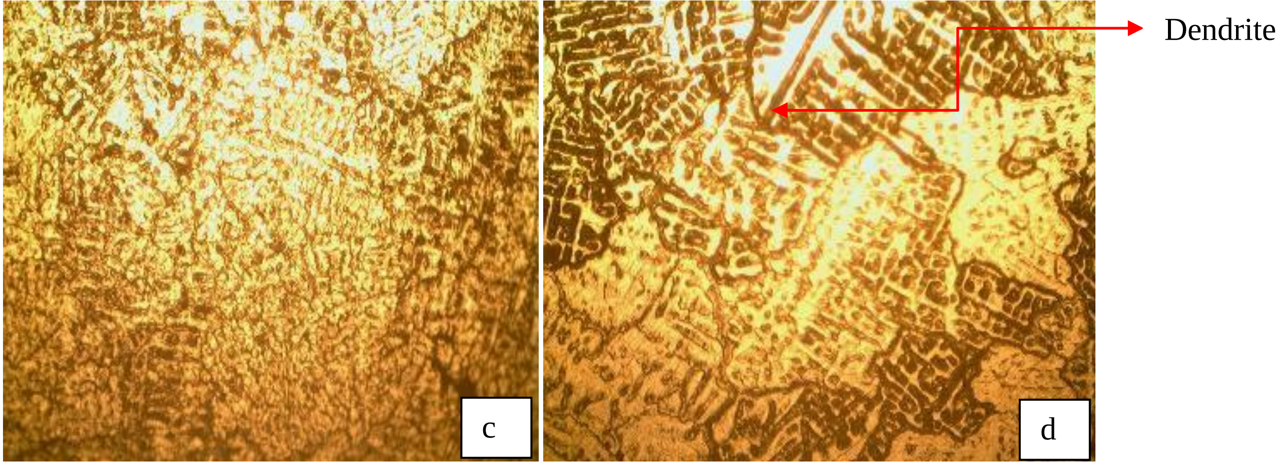

Plate 2: Microstructure of as-cast Al-Cu-Si (c) 2.5%Ni and (d) 2.7%Ni

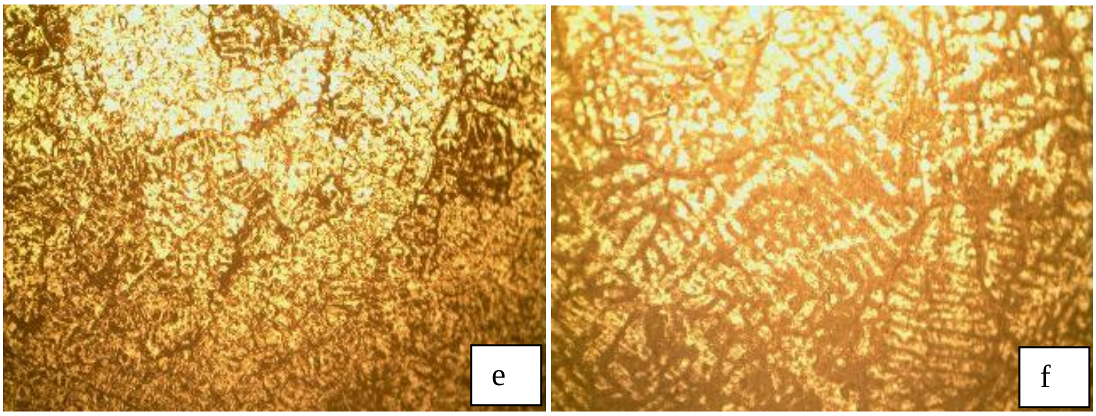

Plate 3: Microstructure of as-cast Al-Cu-Si (e) 2.9%Ni and (f) Age-hardened Al-Cu-Si-0%Ni

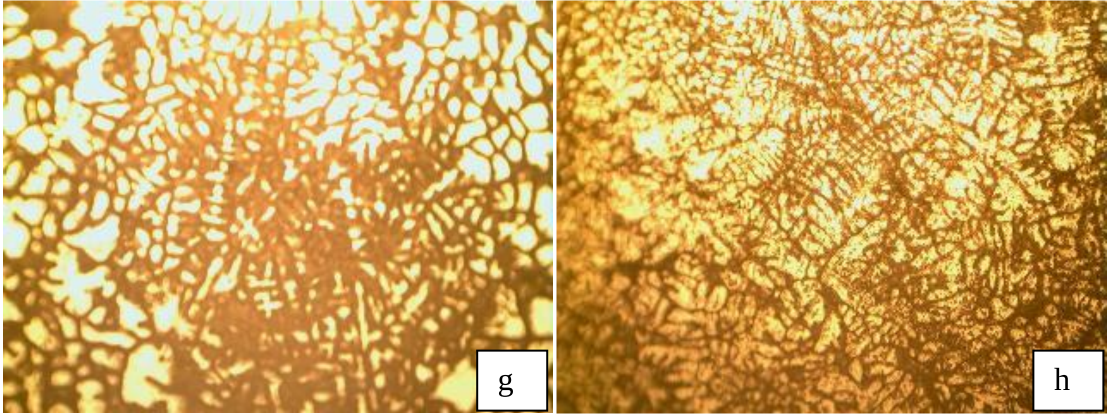

Plate 4: Microstructure of age-hardened Al-Cu-Si (g) 2.3%Ni and (h) 2.5%Ni

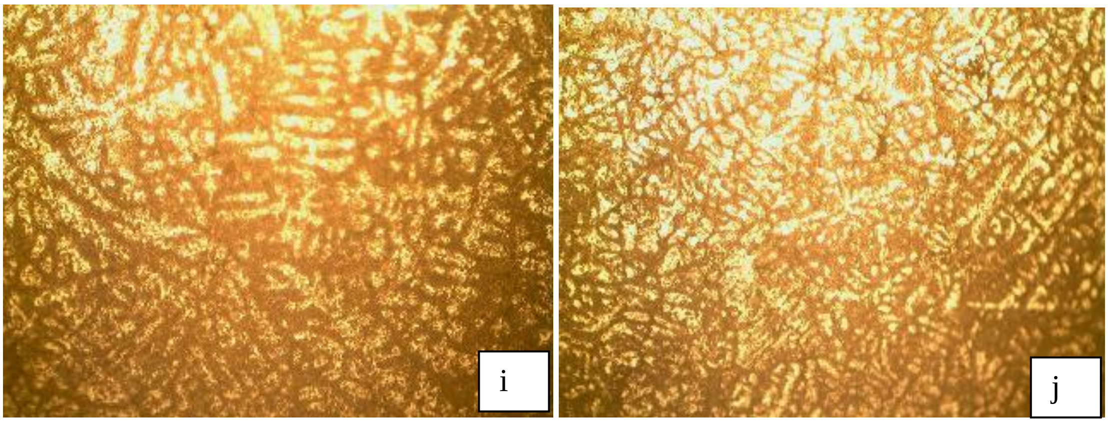

Plate 5: Microstructure of age-hardened Al-Cu-Si (i) 2.7%Ni and (j) 2.9%Ni showing a more finer precipitates.

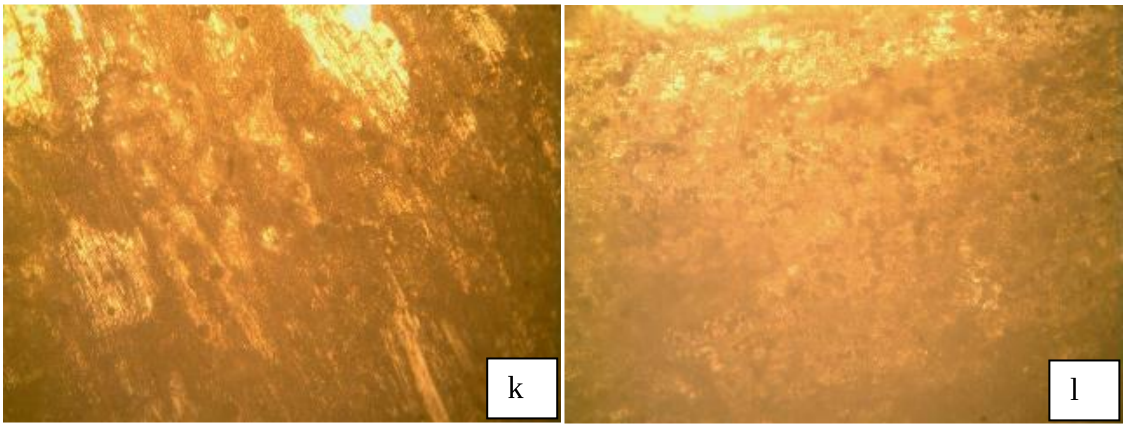

Plate 6: microstructure of as-corroded Al-Cu-Si after 480Hrs (k) 0%Ni as-cast showing uniform corrosion with a near evenly distributed shallow pits (l) 2.7%Ni age-hardened showing a more general corrosion with less pitting.