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Influence of Ni additions and age-hardening treatment on the corrosion resistance of Al-Cu-Si alloy

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Abstract

The quest for materials with high strength, toughness, light weight, cost effectiveness and good corrosion resistance is one of the major challenges facing materials engineers. Al-Cu-Si alloys have a combination of all these properties except corrosion resistance. In this work, the effects of Ni addition and age-hardening treatment on the corrosion resistance of the alloy were investigated. The results obtained from both gravimetric and linear polarization established 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.

Keywords: Shingling, linear polarization, gravimetric, transpassed, solutionised.

Introduction

One of the properties of critical interest for structural metals is their strength [1-3]. 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. Therefore, to overcome these short falls, other elements are primarily added to improve strength of aluminium [4]. 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) [4-6]. 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 [3, 7, 8]. However, Totten & Mackenzie [4] and Callister [9] reported that both cold deformation and alloying tend to diminish resistance to corrosion.

The Al-Cu family, in which copper is the major alloying element [10], have good mechanical properties, high temperature strength, and fatigue life. They are difficult to cast [11-12], however, and their long freezing range makes them extremely susceptible to hot cracking [13]. In addition to their low castability shortcoming, Al-Cu alloys exhibit the lowest corrosion resistance amongst all aluminium alloys [14]. 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. The 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 [15].

However, in these alloys, copper contributes to strength, and presence of silicon improves castability and reduces hot shortness.

The interest devoted to the study of the casting Al-Cu alloys is based on the extensive use of these materials. Riani *et al* and Zhao and co-workers [16-17] claimed that 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. The present study is aimed at investigating the influence of Ni and thermal treatment on the corrosion resistance of Al-Cu-Si alloy.

2. Materials and methods

2.1 Materials

A multicomponent alloy of Al-Cu-Si-Ni, with nominal composition shown in Table 1, was produced. The aluminium used was in form of wires while high purity elemental powders of Si and Ni were used for the production. Copper was added in form of Al-Cu master alloy (50/50 w% ligand). Others include NaCl, ethanol, nylon strings and plastic beakers.

2.2 Casting and preparation of specimens

The melting was carried out in a charcoal-fired crucible furnace. After the melt had attained the required temperature of 800^{o}C for super heating, it was then chilled-cast into preheated split cylindrical steel molds of diameter 22mm and length 350mm. No modifier was used during the casting.

A total of two hundred and ten (210) corrosion coupons of average thickness and diameter 5mm and 10mm respectively were cut and prepared according to ATSM G4 standards.

Table 1: Composition of the produced alloy

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

2.3 Gravimetric corrosion rate determination

Two hundred (200) cylindrical corrosion coupons were used for the gravimetric corrosion evaluation of the five different compositions of the alloy. In each of the five alloy composition, forty (40) coupons were cut and prepared according to ASTMG31, ASTM G4 and ANSI/NACE TM0177-96 [18-20]. From each alloy composition, twenty (20) coupons were heat treated while the remaining twenty (20) coupons were used in the as-cast condition. The heat treated samples were solutionized at 510^{o}C±5, soaked for 3hours and then quenched in water at ambient temperatures as specified in ASTM B917/B917M [21]. Thereafter, the quenched samples were aged at a temperature of 170^{o}C ±5^o as prescribed in ASTM standards and then allowed to cool in air. 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 [18]. 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 (3.5%NaCl) 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:

$$W = w_1 - w_2 \qquad (2.1)$$

And hence the corrosion rate (CR), in mils per year (mpy), according to ASTM G1 [22] was calculated using equation 2.2:

$$CR\ (MPY) = \frac{KW}{\rho AT} \qquad (2.2)$$

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) [20], T is the exposure time in hours.

2.4 Linear Polarization

For the potentiodynamic polarization, 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. 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 and the curves were 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.

3.0 Results & discussions

3.1 Gravimetric Studies

The weight loss corrosion curves in Figures 1 and 2 revealed that corrosion resistance of the as-cast and age-hardened alloy increases with increasing Ni up to a maximum of 2.9%Ni content. The increase in the corrosion resistance of the alloy may be associated 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; such as $NiAl_3$, Ni_3Si and others that passivate easily and hence bring about reduction in corrosion of the alloy. As reported elsewhere [23], the intermetallics and the α-matrix both oxidize rapidly forming protective oxide films and also the 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 containing 0%Ni. 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 was probably due to the fact that many fine precipitates of intermetallic compounds and formation of dispersoids induced by excess Ni addition cause 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 Al-Rawajfeh and Al-Qawabah [5] report who claimed that finer particles are more susceptible to corrosion than coarse ones. It should be noted from Figures 1 and 2 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 contain 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 tend to envelop the precipitated intermetallics thus serving as a protection against corrosion—a process called shingling [23]. This is supported by the work of Wislei, *et al* [24]. As it is reported by Wislei and European Aluminium Association [24, 25] that both Al_2Cu and Al_3Ni are cathodic with respect to the Al-rich α-phase, 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. The work of Wislei, *et al* [24] has also supported this idea.

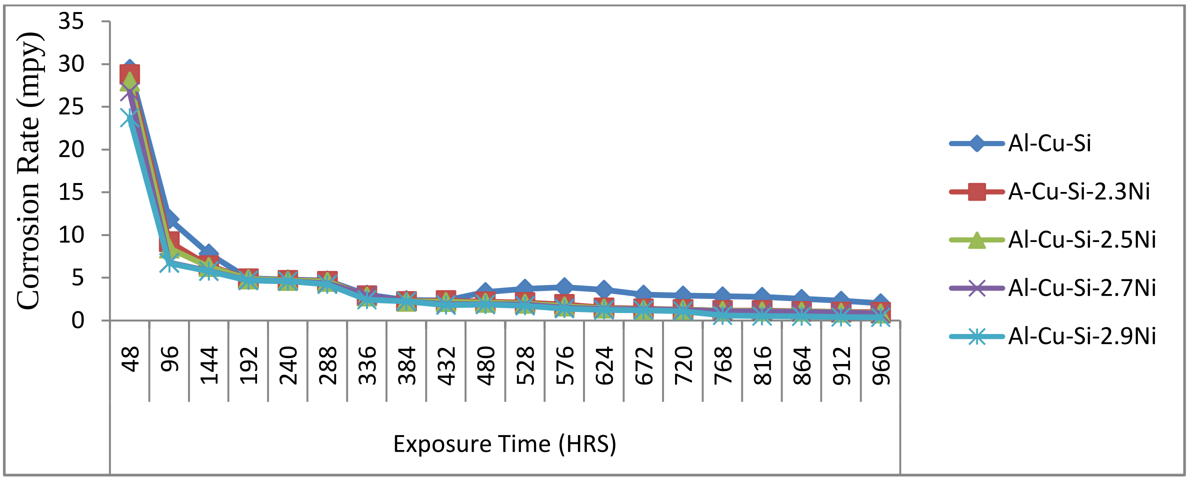

Figure 1: Weight loss Corrosion Rate Curves for As-Cast Al-Cu-Si Alloy with Ni Additions in Simulated Seawater.

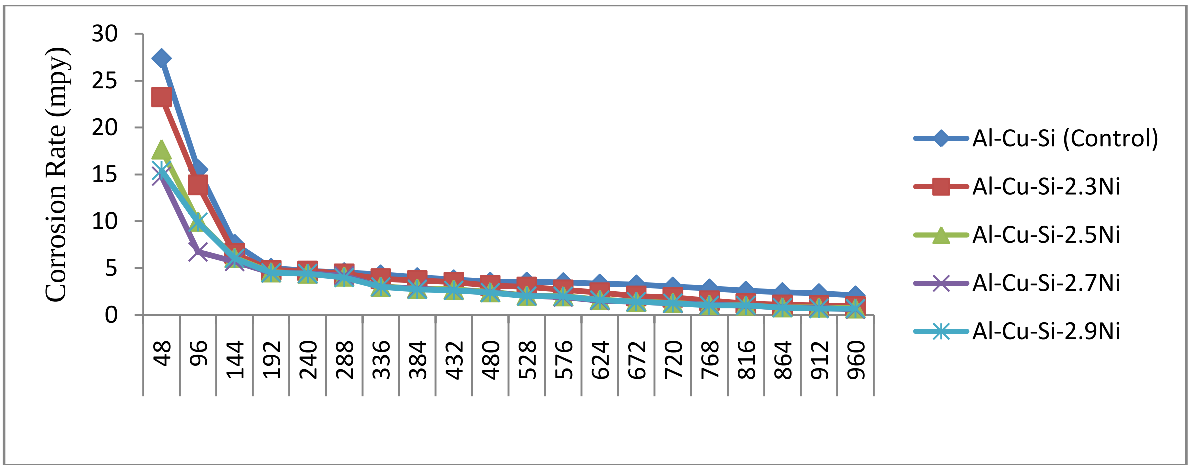

Figure 2: Weight loss Corrosion Rate Curves for Heat-Treated Al-Cu-Si Alloy with Ni Additions in Simulated Seawater

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 react with aluminium, copper and silicon from the alloy to form Al_3Ni, Al_6Cu_3Ni, Ni_3Si and $Al_3(Ni, Cu)_2$ [14, 26]. These intermetallic compounds formed are responsible for the alloy's resistance to high temperature oxidation, 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 reported elsewhere [26].

3.2 Linear Polarization

The linear polarization data and curves for Al-Cu-Si alloy with addition of different percentages of Ni in simulated sea water are shown in Tables 2-3 and Figures 3-4. 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 ($\boldsymbol{j}_{\mathbf{corr}}$) were obtained from polarization curves in Figures 3 and 4 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 2 and 3.

From the linear polarization (LP) curves in Figures 3 and 4, 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 [28]. However, for each of the alloy composition, of either condition—as-cast or age 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 Al_2O_3 and NiO_2, and according to Schweitzer [28], once NiO_2 is formed, it cannot be removed easily by either cathodic treatment or chemical dissolution. For the as-cast, the LP curves are similar and hence the same trend was observed. 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 up scan of potential, the alloy lost its passivity and transpassed where the current densities increase with rise in corrosion potential before moving into the secondary passive region.

Table 2: 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/cm²)	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

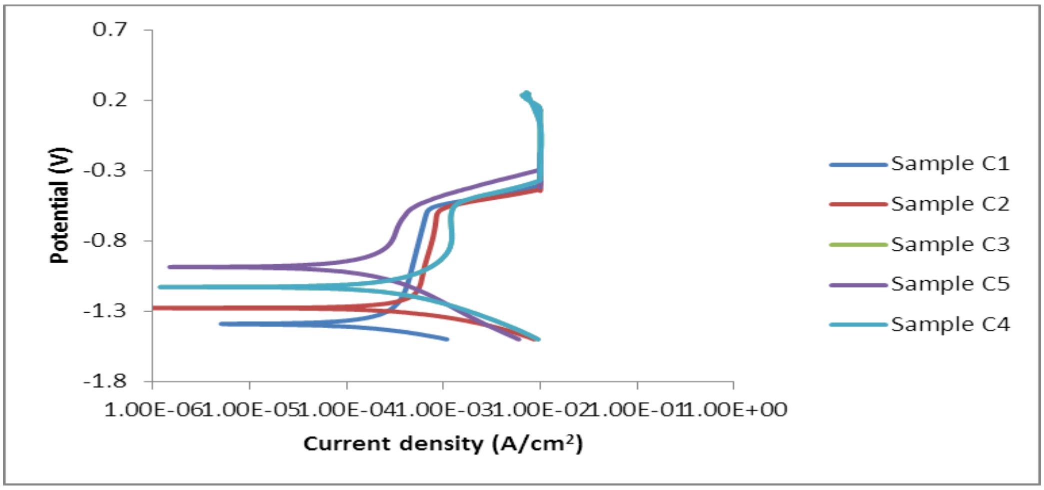

Figure 3: Linear Polarization Curves for As-Cast Al-Cu-Si Alloy with Ni Additions

Table 3: Linear Polarization Parameters of Heat Treated Al-Cu-Si with Ni Additions

Alloy Sample	%Ni addition	E_{corr}, Calc (V)	E_{corr}, Obs (V)	j_{corr} (A/cm²)	i_{corr} (A)	Corrosion rate (mm/year)	R_p (Ω)
D1	0	-0.85712	-0.85982	2.85E-06	8.95E-06	0.019328	1006.5
D2	2.3	-0.8539	-0.85982	2.20E-06	6.92E-06	0.014955	663.86
D3	2.5	-0.56149	-0.55698	5.69E-07	1.79E-06	0.002827	7145.7
D4	2.7	-0.5609	-0.55698	2.70E-07	8.48E-07	0.001112	4748.8
D5	2.9	-0.67532	-0.67335	1.61E-06	5.05E-06	0.005063	952.35

As a corollary, the corrosion rate from the LP curves decreases with Ni content for both as-cast and heat treated alloy samples. For example, the corrosion rates for as-cast and age hardened control alloys are 0.0587mm/yr and 0.0193mm/yr respectively. This corrosion rates decrease to as low as 0.009mm/yr and 0.0011mm/yr for a-cast and heat treated Al-Cu-Si-Ni alloy composition containing 2.9%Ni and 2.7%Ni respectively (i.e. the corrosion resistance increases by 83% and 94% for as-cast and heat treated alloys respectively). See Tables 2-3 and Figures 3-4. This clearly showed that addition of Ni to Al-Cu-Si helps in reducing the corrosion rate of the alloy.

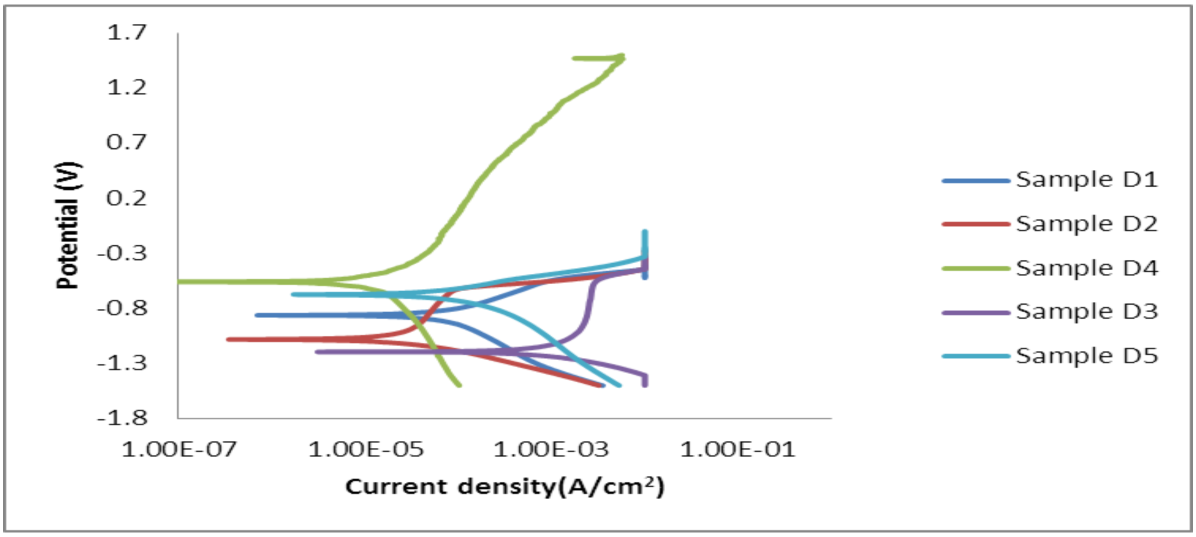

Figure 4: Linear Polarisation Curves for Aged Hardened Al-Cu-Si Alloy with Ni Additions

The heat treated 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 intermetallic compounds, such as $CuAl_2$, Ni_3Si and Al_3Ni, are enveloped by the α-matrix which acts as a protection against corrosion. This is in relation with the investigation carried out by Wislei *et al* [24]. Moreover, the presence of the intermetallics Al_3Ni, which possessed a very good corrosion resistance [27] may be responsible for the improvement in the corrosion resistance. Consequently, for either conditions (i.e. as-cast and age hardened) the Al-Cu-Si alloy containing Ni showed an improvement in the corrosion resistance than the control alloy.

Conclusion

Gravimetric and linear polarizations have been employed to study the effect of Ni addition on the corrosion behavior of Al-Cu-Si. From the experimental result obtained, it was observed 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.

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