Corrosion Inhibition Study of Al-Cu-Ni Alloy in Simulated Sea-Water Environment

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ABSTRACT: A study on the inhibition of Al-Cu-Ni alloy in simulated sea-water environment was investigated using Sodium Chromate as inhibitor. The inhibitor concentration was varied as control, 0.25, 0.5, 1.0, 1.5 and 2.0 Molar. Al-Cu-Ni alloy was sand cast into cylindrical bars of 20 mm x 300 mm dimension. The corrosion of the sand-cast and treated alloys in 3.5wt% sodium chloride solution at temperatures 30°C, 50°C and 70°C over 1-5 hrs was evaluated using the weight loss method. It was observed that the corrosion rate of the treated alloys decreases with increase in inhibitor concentration. The decrease in corrosion rate on addition of the inhibitor can be attributed to the adsorption of the inhibitor onto the surface of the alloy. The attachment is by physical adsorption as the values of heat of adsorption were less than -10 kJ/mol. The plots obtained were linear meaning that they obey the Langmuir and Temkin adsorption isotherms. The inhibition efficiency increases generally with increase in temperature and inhibitor concentration.

I. INTRODUCTION

Corrosion and its control is a problem of great importance to the engineering industry with the rapid multiplying use of metals, the increasing occurrence of corrosive environment and the depletion of suppliers of ores (William and Javad, 2006). Corrosion is responsible for colossal loss of materials occurring everywhere and every moment involving billions of naira annually (Vijendra, 2009). Corrosion costs in the industrialized countries amount to about 4% of the gross national product. These include the cost, which can arise in the form of corrosion protection measures, through replacement of corrosion-damaged parts or through different effects deriving from corrosions, such as shut-down of production or accidents which lead to injuries or damage to property and occasional loss of lives (Einar, 1989).

As a consequence of the economics of production, environmental impact and ecological factors, it is becoming increasingly important to consider the "cradle-to-grave" life cycle of light alloy materials relative to the overall manufacturing process. This utmost necessitated the recent increase in research of the behaviour of Al alloys and other light metals subjected to different environments (Idenyi *et al*, 2009; Abdulwahab *et al*, 2011).

Inhibitors can be considered as a retarding catalyst and are used as a means of controlling and preventing corrosion. Inhibitor includes substances which on addition to the corrosive medium in very small amount retards the degradation of metals and can be used either in liquid media, gaseous media as well as to solid and semi-solid materials such as point file, packing material and protective greases (Kuznetsov, 2004).

In this work, the standard inhibitor (sodium chromate) has been found to be efficient for the Al-Cu-Ni alloy in reducing the corrosion rate by 65.7% and the mechanism of inhibition has been established from this result to be of physical adsorption.

II. MATERIALS AND METHODS

The materials used in this research include high purity aluminum and copper obtained from Northern Cable Company (NOCACO), Kaduna while the Nickel and sodium chromate (standard inhibitor) was obtained from a chemical shop in Zaria. Others include Kellers reagent as etchants were obtained from Metallurgical and Material Engineering Department of Ahmadu Bello University, Zaria. The equipment used for the heat treatment of the alloy was Muffle electrical resistance furnace with a capacity of 1200°C, Metallurgical Microscope for microstructural analysis, Digital Weighing Balance for weight loss determination and digital multimeter Corrosion Bath to maintain the temperature of the system during the corrosion process.

Al-Cu-Ni alloy was produced by sand casting method in which the percentage of Copper, and Nickel were kept constant as shown in Table 1.

Table 1: Charge calculation of the produced alloy (wt %).

Element	Al	Cu	Ni
Percentage	94	4.0	2.0

Melting of the alloy was done in a muffle resistance furnace that was allowed to heat up to 800°C for super heat to occur and then stirred thoroughly before pouring into the mould. The cast samples were prepared for corrosion test samples. The Al-Cu-Ni alloy samples were subjected to corrosion environment (3.5wt% NaCl solution) under the

influence of inhibitor (sodium chromate) at 30°C, 50°C, and 70°C for 1 – 5hrs. The corrosion was evaluated using weight loss technique. The standard expression for measurement of corrosion rate in Mils per Year (mpy) shown in eqn (1) was used (Fontana, 1987).

$$mpy = \frac{534W}{DAT} \qquad (1)$$

where
W = Weight loss (g)
D = Density of material (g/cm^3) = 2.7 g/cm^3
T = Time of exposure (hours)
A = Total surface area (in^2)

The efficiency of an inhibitor I, can be expressed as in eqn (2).

$$I = \frac{V_0 - V_i}{V_0} \times 100 \qquad (2)$$

where: V_o is the corrosion rate without inhibitor
V_i is the corrosion rate with inhibitor

The values of activation energy of inhibition (E_a) in eqn (3) were calculated using the Arrhending equation (Nnanna et al, 2010).

$$\log \frac{r_1}{r_2} = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (3)$$

where r_1 and r_2 are the corrosion rates in temperatures T_1 and T_2 respectively. R is the universal gas constant $(8.314kg/moy^{-1}/c^{-1})$. Free energy of adsorption and heat of adsorption were also calculated.

Optical microscope was used to analyse the various microstructures of the samples. Metallographic samples were sectioned from the as-cast samples and ground on grades of emery paper (240, 320, 400 and 600 grit-sizes using water as coolant. The ground samples were then polished with 1µm and 0.5µm sizes alumina powder suspension in distilled water. The polishing samples were then etched using Keller's reagent (190 ml H_2O + 5 ml HNO_3 + 3 ml HCl + 2 ml HF). The microstructures of the samples were obtained using an optical microscope with an in-built camera.

III. RESULTS AND DISCUSSION

The results of the corrosion rates of Al-Cu-Ni alloy at 30°C, 50°C and 70°C are shown in Tables 2-4. In Tables 5-7 the calculated values of inhibition efficiency with inhibitor concentration of Al-Cu-Ni alloy at 30°C, 50°C and 70°C are presented. Tables 8-10 show the calculated values of the activation energy, free energy and heat of adsorption with inhibitor concentrations of Al-Cu-Ni alloy. Equally, Tables 11 - 13 show the values of thermodynamics and kinetic parameter. Figure 1 shows the microstructure of as-cast Al-Cu-Ni alloy. The structure in the figure consists of Aluminium solid solution matrix, (orange), and grain boundary consisting of interdendritic network of $CuAl_2$ (dark) with grain boundary formations (x200).

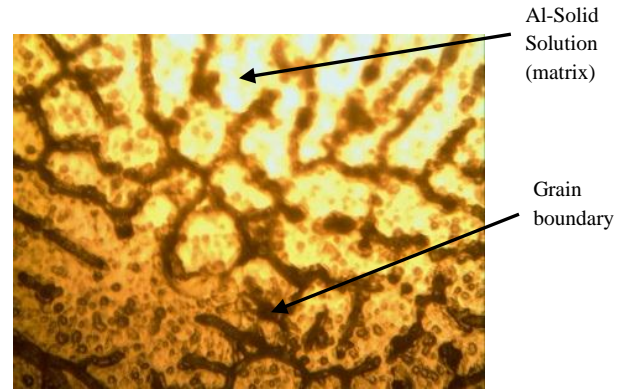
Figure 1: Micrograph of the as-cast Al-Cu-Ni alloy.

A. Effect of Inhibitor Concentration on Corrosion Rate

Inorganic inhibitors such as silicates, chromates, borates, etc, suppress the rate of corrosion by interfering between the anodic and cathodic reaction sites (Dara, 1986). This occurs as a result of the thin film formed on the surface of the alloy, which retards the corrosivity. The concentration of the inhibitor was varied (0.25, 0.5, 1.0, 1.5 and 2.0M) from 1-5hrs at 30°C, 50°C and 70°C. Tables 2 - 4 show the corrosion rate against inhibitor concentration of the cast Al-Cu-Ni alloy at various temperatures.

Table 2: Corrosion rates (mpy) of Al-Cu-Ni alloy at 30°C.

Inhibitor Conc. (M)	Exposure time (hrs)				
	1	2	3	4	5
Control	3.52	1.76	1.54	1.46	0.70
0.25	3.42	1.68	1.32	1.29	0.64
0.5	3.20	1.32	0.88	1.05	0.42
1.0	3.15	1.18	0.71	0.88	0.42
1.5	3.02	1.54	0.50	0.72	0.39
2.0	3.16	1.58	0.44	0.69	0.52

Table 3: Corrosion rates (mpy) of Al-Cu-Ni alloy at 70°C.

Inhibitor conc. (M)	Exposure time (hrs)				
	1	2	3	4	5
Control	1.93	1.56	1.32	1.24	0.99
0.25	1.67	1.40	1.10	1.00	0.61
0.5	1.21	1.15	1.08	0.92	0.88
1.0	0.76	0.94	0.88	0.74	0.52
1.5	0.41	0.52	0.44	0.35	0.21
2.0	0.57	0.53	0.48	0.42	0.39

Table 4: Corrosion rates (mpy) of Al-Cu-Ni alloy at 70°C.

Inhibitor conc.(M)	Exposure time (hrs)				
	1	2	3	4	5
Control	1.93	1.56	1.32	1.24	0.99
0.25	1.67	1.40	1.10	1.00	0.61
0.5	1.21	1.15	1.08	0.92	0.88
1.0	0.76	0.94	0.88	0.74	0.52
1.5	0.41	0.52	0.44	0.35	0.21
2.0	0.57	0.53	0.48	0.42	0.39

It was observed that the corrosion rate decreases generally with an increase in inhibitor concentration at 30°C, 50°C and 70°C for 1-5hrs. These results show that the behaviour of the inhibitor in the environment resulted in the formation a protective layer on the metal surface thereby reducing the corrosion rate. This finding is in conformity with that reported by Ihebrodike *et al* (2010) and Nnanna *et al*, (2010).

B. Effect of Inhibitor Concentration on Inhibition Efficiency

The inhibitor efficiency increases with an increase in inhibitor concentration, tending to saturate at higher values of inhibitor concentration as shown in Tables 5-7.

Table 5: Inhibition efficiency of Al-Cu-Ni alloy (%) at 30°C.

Inhibitor concentration (M)	1hr	2hrs	3hrs	4hrs	5hrs
0.25	4.60	3.03	35.23	6.82	17.14
0.5	18.39	13.64	42.05	38.64	40.00
1.0	25.86	33.33	52.27	56.82	54.29
1.5	41.95	44.70	63.64	68.18	65.71
2.0	30.46	15.15	57.95	22.73	17.14

Table 6: Inhibition efficiency of Al-Cu-Ni alloy (%) at 50°C.

Inhibitor concentration (M)	1hr	2hrs	3hrs	4hrs	5hrs
0.25	4.60	3.03	35.23	6.82	17.14
0.5	18.39	13.64	42.05	38.64	40.00
1.0	25.86	33.33	52.27	56.82	54.29
1.5	41.95	44.70	63.64	68.18	65.71
2.0	30.46	15.15	57.95	22.73	17.14

Table 7: Inhibition efficiency of Al-Cu-Ni alloy (%) at 70°C.

Inhibitor concentration (M)	1hr	2hrs	3hrs	4hrs	5hrs
0.25	13.47	10.26	16.67	19.35	11.11
0.5	37.31	26.28	18.18	25.81	38.38
1.0	60.62	39.74	33.33	40.32	47.47
1.5	73.06	71.79	68.94	71.77	78.79
2.0	70.47	66.03	63.64	66.13	60.61

This indicates that the effectiveness of the sodium chromate, as an inhibitor, in retarding the corrosion rate of cast Al-Cu-Ni alloy in the sodium chloride solution does not improve indefinitely with increase in inhibitor concentration. A point is reached at which an increase in the inhibitor concentration produces a small increase in the value of the inhibitor efficiency. This is attributed to the fact that at high temperature of 70°C, the inhibitor constituent tends to dissociate and hence a drop in efficiency. A similar conclusion was reached in (Ameer *et al*, 2000; Callister, 1997).

C. Effect of Inhibitor Concentration on Activation Efficiency

The values of the activation energy of adsorption, E_{ads}, for inhibited systems are higher than those of uninhibited system indicating that the inhibitor retards the dissolution of aluminium making it more difficult for corrosion reaction to proceed based on equation of reaction in eqn (4).

$$Al \longrightarrow Al^{3+} + 3e^- \qquad (4)$$

The forward reaction is a corrosion process indicating anodic, while the reverse reaction is inhibiting action. The presence of inhibitor retards the dissolution of the Al thereby increasing the inhibiting action (Madugu and Abdulwahab, 2007; Aku *et al*, 2005). The negative values of free energy of adsorption obtained means that the adsorption process was spontaneous (Metal Handbook, 1979). The activation energy increases as the inhibitor concentration increases as shown in Tables 8.

Table 8: Activation energy, Eads, (KJ/mol) of Al-Cu-Ni alloy at 1 and 5 hrs respectively.

Inhibitor concentration (M)	Ea, 1hr 30-50°C	Ea, 1hr 50-70°C	Ea, 1hr 30-70°C	Ea, 5hrs 30-50°C	Ea, 5hrs 50-70°C	Ea, 5hrs 30-70°C
0.25	-451	144	-263	-443	1441	152
0.5	-462	008	-314	-506	1031	-21
1.0	-520	-222	-426	-443	1986	324
1.5	-571	-733	-622	-617	1634	93
2.0	-701	-920	-770	-754	776	-271

D. Effect of Inhibitor Concentration on free Energy

The free energy was calculated and the values obtained in this work were all negatives suggesting that the adsorption of the inhibitor (Na_2CrO_4) on to the surface of the alloy was a spontaneous process. The low negative values of free energy as shown in Table 9 indicated spontaneous adsorption of the inhibitor of molecules (Madugu and Abdulwahab, 2007) and the negative values also suggest a strong interaction of the inhibitor molecules on the alloy surface (Aku *et al*, 2005; Metal handbook, 1979).

E. Effect of Inhibitor Concentration on Heat of Adsorption

The heat of adsorption was calculated and the negative values obtained indicate inhibitor adsorption. From Table 10

Table 9: Free energy of Al-Cu-Ni alloy at 1hr and 5hrs, and at various temperatures.

Inhibitor concentration (M)	$\Delta G_{ads.}$ 1hr, 30°C	$\Delta G_{ads.}$ 5hrs, 30°C	$\Delta G_{ads.}$ 1hr, 50°C	$\Delta G_{ads.}$ 5hrs, 50°C	$\Delta G_{ads.}$ 1hr, 70°C	$\Delta G_{ads.}$ 5hrs, 70°C
0.25	-129.27	-40.42	-126.62	-32.54	-62.43	-15.23
0.5	-20.21	-3.00	-15.18	-5.00	-7.32	-37.73
1.0	-8.09	-1.50	-4.75	-1.42	-1.49	-2.64
1.5	-4.10	-0.85	-1.53	-0.57	-0.58	-0.42
2.0	-4.50	-1.42	-1.95	-4.07	-0.49	-0.75

the heat of adsorption decreases with increase in inhibitor concentration (Aku *et al*, 2005). Thermodynamic models can be used to explain the corrosion inhibition of sodium chromate on the alloy. The nature of adsorption depends on the values of ΔH_{ads}. Thus if $\Delta H_{ads} < -10kJ/mol.$, the adsorption is probably physical adsorption and if $\Delta H_{ads} > -10kJ/mol.$, the adsorption is chemical (Asuke, 2008). The values obtained in this work were all less than -10KJ/Mol. which supports the assertion that physical adsorption is proposed.

Table 10: Heat of adsorption, Hads, (kJ/mol) of Al-Cu-Ni alloy at 1 and 5 hrs.

Inhibitor concentration (M)	$H_{ads.}$, 1hr 30-50°C	$H_{ads.}$, 1hr 50-70°C	$H_{ads.}$, 1hr 30-70°C	$H_{ads.}$, 5hrs 30-50°C	$H_{ads.}$, 5hrs 50-70°C	$H_{ads.}$, 5hrs 30-70°C
0.25	-332	-1519	-456	-454	-1595	-796
0.5	-497	-1432	-430	-612	2453	307
1.0	-652	-2173	-652	-353	408	125
1.5	-930	-1917	-575	-564	-963	-684
2.0	-842	-2460	-740	-337	-2959	-457

F. Effect of Temperature on Corrosion Rate

The analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies in the presence of inhibitor gives some insight into the possible mechanism of inhibitor adsorption (Nnanna *et al*, 2005). The effect of temperature on the corrosion rate of cast Al-Cu-Ni alloy with and without inhibitor addition was studied in the temperature range of 30°C, 50°C and 70°C. From Table 11, it can be deduced that the corrosion rates decrease with increase in inhibitor concentration. This means

that the adsorption process took place easily and the protective film becomes stable on the cast Al-Cu-Ni alloy. This is similar to the claim by Chetouani (2004).

G. Effect of Temperature on Inhibition Efficiency and Activation Energy

The inhibitory efficiency was found to increase with rise in temperature. This can be as a result of increase in the rate of chemical reaction with rise in temperature as suggested by (ASM, 1990). This also indicates that at higher temperature, there is likely desorption of the inhibitor from the surface (Tang. et al, 2003). The corrosion inhibition of sodium chromate could also be attributed to the presence of multiple bonds in inhibitor molecular structure as suggested by (Rahim and Kassim, 2008; Fontana, 1987) which enhanced adsorption of its molecules on the surface of the alloy.

The activation energy increases with increase in temperature as shown in Table 8 earlier discussed. This means that the mechanism of inhibition of the inhibitor is of physical adsorption on to the alloy surface (Nnanna *et al*, 2010).

H. Evaluation of Adsorption Isotherm

The degree of surface coverage shown in Tables 12 varied linearly with the logarithm of inhibitor concentration at 1hr and 5hr and at various temperatures, fitting a Temkin Isotherm, since it obeys the Temkin Isotherm and the mechanism of inhibition is by adsorption (Ekuma and Idenyi, 2006).

Table 12: Surface coverage (θ) and logarithm of inhibitor concentration (log c) at various temperatures (Temkin isotherm).

Inhibitor conc. (M)	Log.C	$\theta_{1hr,}$ 30°C	$\theta_{5hrs,at}$ 30°C	$\theta_{1hr,at,}$ 50°C	$\theta_{5hrs,at}$ 50°C	$\theta_{1hr,at,}$ 70°C	$\theta_{5hrs,at}$ 70°C
0.25	-0.6021	0.0284	0.085	0.046	0.1714	0.134	0.111
0.5	-0.3010	0.0909	0.400	0.183	0.4000	0.373	0.383
1.0	0.0000	0.1051	0.400	0.258	0.5429	0.606	0.474
1.5	0.1761	0.1420	0.442	0.419	0.6571	0.730	0.787
2.0	0.3010	0.1022	0.257	0.304	0.1714	0.704	0.606

The high negative values of the activation energy in this work indicate an efficient inhibiting action of the inhibitor (Ekuma and Idenyi, 2006). This indicated that the adsorption of sodium chromate on the surface of the Al-Cu-Ni alloy followed the Temkin Isotherm (Chetouani, 2004).
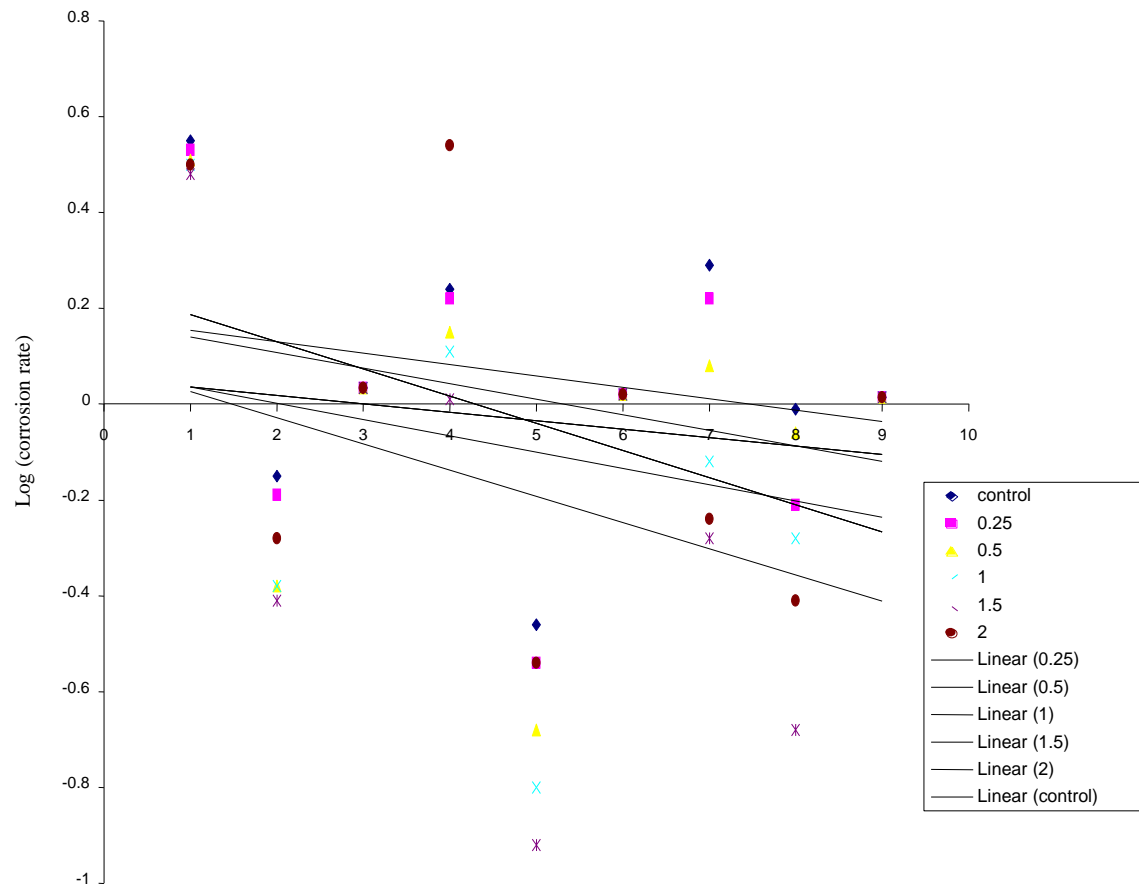
Table 11: Logarithms of corrosion rates and inverse of temperatures.

Inhibitor concentration (M)	Log. C.R at 1hr	Log. C.R at 5hrs	1/T at 30°C	Log. C.R at 1hr	Log. C.R at 5hrs	1/T at 50°C	Log. C.R at 1hr	Log. C.R at 5hrs	1/T at 70°C
0.25	0.55	-0.15	0.033	0.24	-0.46	0.02	0.29	-0.01	0.0143
0.5	0.53	-0.19	0.033	0.22	-0.54	0.02	0.22	-0.21	0.0143
1.0	0.51	-0.38	0.033	0.15	-0.68	0.02	0.08	-0.06	0.0143
1.5	0.50	-0.38	0.033	0.11	-0.80	0.02	-0.12	-0.28	0.0143
2.0	0.48	-0.41	0.033	0.01	-0.92	0.02	-0.28	-0.68	0.0143

Figure 2: Arrhenius plot for the adsorption of sodium chromate on Al-Cu-Ni alloy in 3.5wt.% sodium chloride solution.

IV. CONCLUSION

Studies on the corrosion inhibition of Al-Cu-Ni alloy in simulated sea-water environment were investigated by varying the concentrations of Sodium Chromate as inhibitor and temperature of exposure to the corrosion medium i.e. 3.5wt% sodium chloride solution. From the results obtained, it was concluded that the addition of inhibitor (sodium chromate) to the cast alloy show significant effect on the corrosion resistance of the alloy. The resistance of the alloy to corrosion increases with an increase in the concentration of the inhibitor. Secondly, the inhibitor efficiency of Al-Cu-Ni alloy in 3.5wt % sodium chloride solution at 30°C, 50°C and 70°C increases with increase in temperature and that sodium chromate is an effective corrosion inhibitor for Al-Cu-Ni alloy in the examined environment.

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