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The Effect of Chromium and Manganese Addition on the Corrosion of As-cast Al-Si-Fe-Cu Alloy System in Caustic Soda

S.A. Yaro and V.S. Aigbodion*

Department of Metallurgical and Materials Engineering, Ahmadu Bello University, Zaria P.M.B 1045, Zaria, Nigeria

Abstract

The effect of chromium and manganese addition on the corrosion of Al-Si-Fe-Cu alloy system in caustic soda (NaOH) at room temperature (28°C) was investigated using weight loss method. The alloys containing 0.1 to 0.3% Cr and Mn were produced and sand cast into cylindrical test bars at the foundry shop of the National Metallurgical Development Center, Jos. After casting the microstructures of the as- cast alloys were determined. The as-cast test bars were machined to corrosion coupons and immersed into 0.5M NaOH solution and their rate of corrosion determined using the weight loss method. It was observed that simultaneous addition of chromium and manganese to the alloy system imparted the highest corrosion resistance to the alloy due to the formation of hard and passive phases which acted as strong protective barriers to corrosion. While addition of chromium alone to the alloy gave a better corrosion resistance than the addition of manganese alone due to the formation of passive oxide layer of chromium oxide.

Introduction

Aluminium is a very important metal because of its low density and excellent mechanical properties which stem largely from its face centered cubic crystal structure. It is alloyed with elements like Mg, Si, Cu, Mn, Fe *etc.* to produce a variety of wrought products from beverage cans to aircraft structural parts, to cast product like engine blocks and steering knuckles for automobiles [1]. Aluminium alloys are characterized by light weights, corrosion resistance and excellent resistance against corrosive elements in the atmosphere and water [2]. Aluminium based alloys also have high thermal conductivity and low coefficient of linear expansion values and based on these two properties, they can be forged to the desired shapes at elevated temperatures and then solution treated and aged hardened to obtain desired microstructures and excellent mechanical properties [3].

The Al-Si-Fe-Cu alloy system represents the largest volume of aluminium alloys produced by sand casting methods [4]. The alloy provides good combination of cost, strength, together with high fluidity and freedom from hot shortness [5]. The compositional specification of these alloys rests mainly on the iron, silicon and copper contents, while addition of copper alone imparts to the alloy the ability to be sand cast. Copper also increases strength, fatigue properties and make the alloys more responsive to heat treatments and reduces the corrosion resistance of these alloys [6]. While iron increases strength and hardness, reduces tendency to hot cracking and Silicon improves the fluidity of the molten metal as well as its castability and mechanical properties. Chromium and manganese are normally added to increase the strengths for high temperature applications [7]. Based on these properties these alloys have found wide applications as manifolds, valve bodies, automotive cylinders heads and pistons [8-10].

The presence of Si, Cu, Fe, Cr and Mn in aluminium alloys causes various precipitates to be formed during solidification of the alloys [11]. During the solidification of the alloys system, development of dendritic network, precipitation of AlFe-containing phase, eutectic reaction involving precipitation of Si and Fe containing phases and formation of complex eutectic phases containing $CuAl_2$ and $(FeCu)_3SiAl_{12}$,

*corresponding authors. E-mail: aigbodionv@yahoo.com

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$(FeMn)_3SiAl_{12}$, $(FeCr)_3SiAl_{12}$, $(FeMnCr)_3SiAl_{12}$ and $Cu_2Mn_3Al_{20}$ do occur [3]. The phases formed depend on the composition and cooling rates of the alloy system. Usually the formed phases reveal the presence of eutectic Si structure dispersed in copper aluminium complexes [12]. The copper complexes are easily visible under optical microscope because of their distinct pink colour but the iron phases seem to be present in both needle (β) and Chinese script form (α), [8].

Aluminium based alloys usually posses good corrosion resistance to atmosphere and in mild acid solutions [9]. It has also been observed and reported by Idenyi *et al.* [10] that aluminium based alloys have low corrosion resistance in alkaline media. Hence, the objective of this work which is to look at the possibility of increasing the corrosion resistance of this aluminium based alloys by addition of chromium and manganese.

Experimental Procedures

Materials and Methods

Materials

The various alloys with compositions shown in Table 1 used for the purpose of this research were produced at the foundry shop of the National Metallurgical Development Center, Jos using high purity aluminium and copper electrical wires obtained from Northern Cable Company NOCACO (Kaduna), Ferro-silicon, Ferro-chromium and Ferro-manganese of known chemical composition.

Methods

The alloys were cast into bars of diameter 20 mm and 300 mm length, cut and machined to corrosion test coupons of dimension 15×15×15 mm. A total of seventy coupons were used for the investigation. All the coupons were cleaned, dried, weighed and stored in desiccators. Three sets of 0.5M NaOH solutions were prepared and the coupons suspended in these solution at room temperature (28°C) with the aid of threads.

The weight losses of the coupons were taken at intervals of 24 hours over a period of 168 hours, the surface was scrubbed with brush in distilled water, cleaned in 0.5% HCl pickling solution and rinsed in ethanol to remove the corrosion product and then air-dried to constant weight.

Table 1

The composition of the alloys produced

Sample	Si, %	Fe, %	Cu, %	Cr, %	Mn, %	Al, %
Alloy 1	2.8	0.8	5.5	----	----	Bal
Alloy 2	2.8	0.8	5.5	0.1	----	Bal
Alloy 3	2.8	0.8	5.5	0.2	----	Bal
Alloy 4	2.8	0.8	5.5	0.3	----	Bal
Alloy 5	2.8	0.8	5.5	----	0.1	Bal
Alloy 6	2.8	0.8	5.5	----	0.2	Bal
Alloy 7	2.8	0.8	5.5	----	0.3	Bal
Alloy 8	2.8	0.8	5.5	0.1	0.1	Bal
Alloy 9	2.8	0.8	5.5	0.2	0.2	Bal
Alloy 10	2.8	0.8	5.5	0.3	0.3	Bal

Weight Loss and Corrosion Rate Determination

The weight loss was determined by finding the difference between the initial and final weight of the coupon after 24 hours interval using the following relationship:

$$W = W_0 - W_F \tag{1}$$

were W – weight loss (mg), W_0 – original weight of coupon, W_f – new weight of the coupons.

While the corrosion rate (R_{corr}) was determined in millimeters per year (mpy) using the relationship [2]:

$$R_{corr} = \frac{534W}{DAT} \tag{2}$$

where D – density of the materials (g/cm^3), A – total surface area of the materials (In^2), T – time of exposure (hours).

Results and Discussions

Results

Micrographs 1-10 are the microstructures of the as-cast alloys from which the coupons used in this work were cut. While the variation of corrosion rates with time of exposure for the three categories of coupons are given in Tables 2 and Fig. 1-3.

Table 2
The corrosion rate (mpy) against time of exposure (hours) for the various alloys

	24 hrs	48 hrs	72 hrs	96 hrs	120 hrs	144 hrs	168 hrs
Control Sample	7241.4	4157.0	2903.1	2226.3	1857.0	1640.8	1499.2
0.1 Cr	6540.7	3804.1	2691.5	2189.1	1826.4	1559.6	1431.7
0.2 Cr	5103.7	2986.4	2279.3	1868.0	1548.4	1366.7	1216.2
0.3 Cr	4816.0	2623.4	2025.5	1642.4	1342.9	1169.3	1062.7
0.1 Mn	6574.4	3929.2	2737.9	2197.3	1862.0	1614.3	1472.8
0.2 Mn	6555.6	3903.3	2646.9	1991.3	1599.9	1398.5	1435.1
0.3 Mn	6311.3	3489.2	2490.5	1812.1	1559.3	1375.1	1254.6
0.1 Cr - 0.1 Mn	6264.4	3875.4	2685.3	2038.5	1685.6	1441.8	1305.2
0.2 Cr - 0.2 Mn	5213.7	2687.1	2015.8	1616.6	1398.2	1242.1	1137.4
0.3 Cr - 0.3 Mn	47776.9	2585.5	2012.4	1616.8	1329.8	1155.4	1059.7

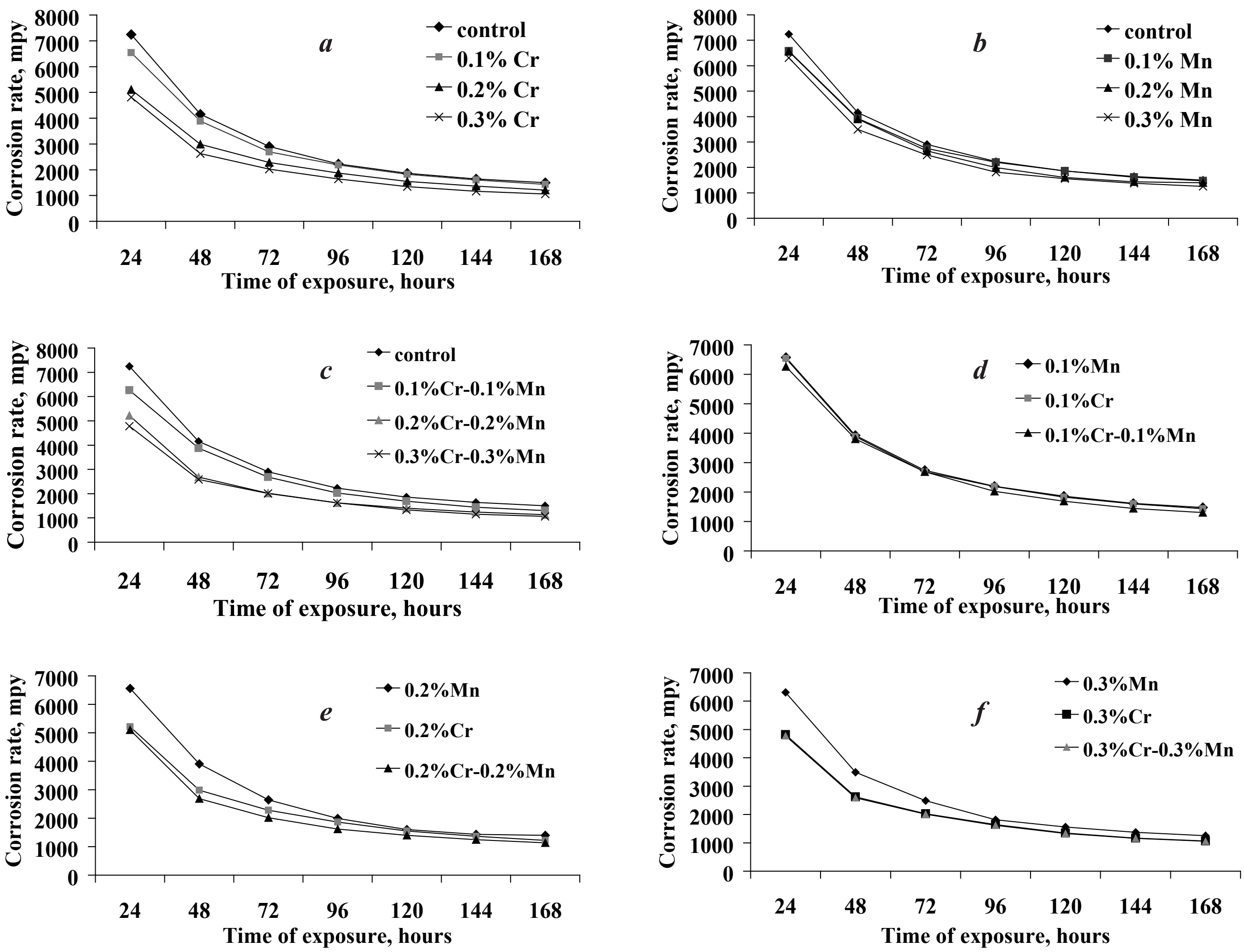

Fig. 1. Variation of corrosion rate with time of exposure for various additions: *a* – for chromium addition; *b* – for manganese addition; *c* – for combine addition of manganese and chromium; *d* – at 0.1% addition of chromium and manganese; *e* – at 0.2% addition of chromium and manganese; *f* – at 0.3% addition of chromium and manganese.

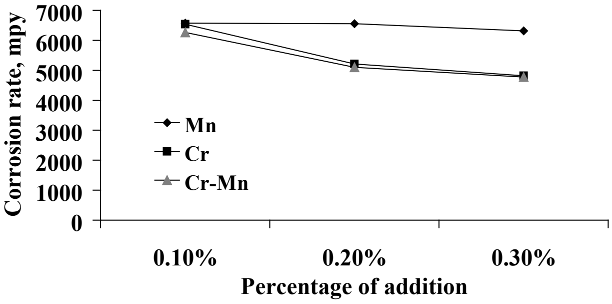

Fig. 2. Variation of corrosion rate with percentage addition of chromium and manganese at 24 hours

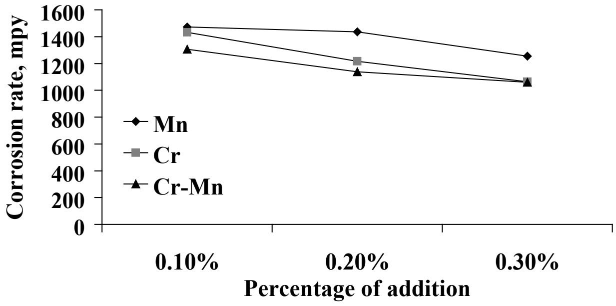

Fig. 3. Variation of corrosion rate with percentage addition of chromium and manganese at 168 hours.

Discussions

Visual Observations of the Coupons During Corrosion Test

Visual observation of the coupons at the end of the first day revealed a progressive change in colour of the coupons from bright surfaces to dull ones while the colour of the solutions had already turned to dark brown. However, by the 2-nd day, all the coupons had dull surfaces. Also traces of micro cracks and pits were observed here and there on the coupons indicating mild attack by the solution and the attack was more pronounced on the coupon without Cr or Mn addition (controlled test bar).

Corrosion Cate of the Coupons

From the results obtained Table 2, it could be observed that, simultaneous addition of chromium and manganese to the alloy system imparted the highest corrosion resistance to the alloy due to the formation of inter-metallic and complex compounds of $(FeMn)_3SiAl_{12}$, $(FeCr)_3SiAl_{12}$ and $(FeMnCr)_3SiAl_{12}$ (Micrographs 2-10) that formed hard and passive phases once the alloy starts corroding and these phases served as strong protective barriers to further corrosion attacked as depicted in Figs. 2, 3 [3,11]. From these Figures 2, 3, while addition of chromium alone to the alloy gave a better corrosion resistance than the addition of manganese alone due to the formation of passive oxide layer of chromium oxide (Figs. 1 *a*, *b*).

Also from the results obtained in this work it is clear, that the controlled coupons have the highest corrosion rate compared to those with either chromium, manganese or a combination of the two. However, the rate of corrosion is decreasing with increase in the amount of Cr and Mn added to the alloy system in the following sequence: Chromium & manganese > chromium > manganese respectively.

The observed high corrosion rates of the controlled coupons, may be probably due to the high percentage of copper in the alloy as the presence of copper leads to the formation of copper rich phase $CuAl_2$ (Fig. 4). This eutectic phase creates galvanic cell with the matrix thus setting up a corrosion cell [10]. The addition of chromium and manganese help to suppress the formation of the copper rich phase of $CuAl_2$ in favour of hard and corrosion resistance phases of $(FeMn)_3SiAl_{12}$, $(FeCr)_3SiAl_{12}$, $(FeMnCr)_3SiAl_{12}$ (Figs. 5-13) [3,11]. The resistances of these phases to corrosion in this medium followed the following sequence, $(FeMnCr)_3SiAl_{12}$ > $(FeCr)_3SiAl_{12}$ > $(FeMn)_3SiAl_{12}$, with the resistance increasing as the amount of Cr and Mn addition to the alloy increased. This is because an increase in Cr and Mn addition results in the formation of more of these phases in the alloy system [1,3]. However, the observed decrease in the corrosion rate for all the alloys in respective of either Mn or Cr addition with increasing numbers of days of exposure in this medium may be probably due to the deposition of corrosion products which tends to shield the corroding surface from further corrosion attack, there by depressing the rate of corrosion [2,9].

Fig. 4. Microstructure of Al-Si-Fe-Cu alloy system (×200).

Fig. 5. Microstructure of Al-Si-Fe-Cu Alloy containing 0.1% Cr (×200).

Fig. 6. Microstructure of Al-Si-Fe-Cu Alloy containing 0.2% Cr (×200).

Fig. 7. Microstructure of Al-Si-Fe-Cu Alloy containing 0.3% Cr (×200).

Fig. 8. Microstructure of Al-Si-Fe-Cu Alloy containing 0.1% Mn (×200).

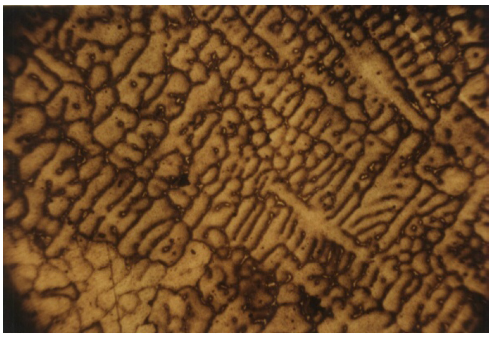

Fig. 9. Microstructure of Al-Si-Fe-Cu Alloy (0.2% Mn) (×200).

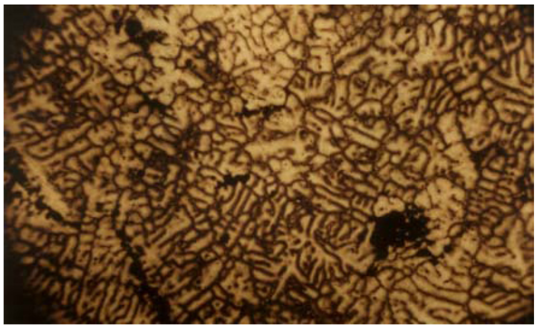

Fig. 10. Microstructure of Al-Si-Fe-Cu Alloy (0.3% Mn) (×200).

Fig. 11. Microstructure of Al-Si-Fe-Cu Alloy (0.1% Cr - 0.1% Mn) (×200).

Fig. 12. Microstructure of Al-Si-Fe-Cu Alloy (0.2% Cr - 0.2% Mn) (×200).

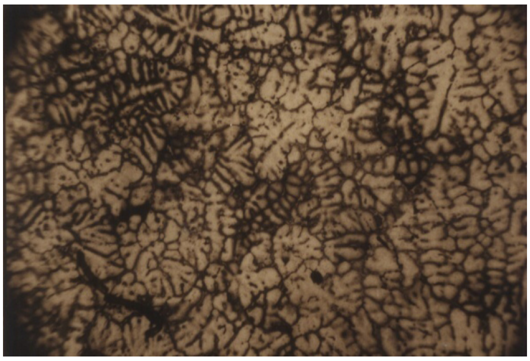

Fig. 13. Microstructure of Al-Si-Fe-Cu Alloy (0.3% Cr - 0.3% Mn) (×200).

Conclusions

From the results of this study, it can be concluded that addition of chromium and manganese to the alloy system (Al-Si-Fe-Cu) significantly increased its corrosion resistance. The corrosion resistance of the resulting alloy is dependent on the phases that are formed after chromium and manganese addition. Also the corrosion products resulting from the corrosion of the formed alloy after the addition of chromium and manganese have some shielding effect and helped to retard further corrosion attack. Therefore it can be concluded that, addition of chromium and manganese to the alloy system (Al-Si-Fe-Cu) significantly improves the corrosion resistance of the resulting alloy.

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