International Refereed Journal of Engineering and Science (IRJES)
ISSN (Online) 2319-183X, (Print) 2319-1821
Volume 14, Issue 3 (May - June 2025), PP. 56-64

Influence of Varying Tin Content on the Corrosion Resistance of Nickel-Aluminium-Bronze Alloy

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Abstract

This research investigates the effects of varying tin content on the corrosion resistance property of nickel aluminium bronze (NAB) alloy. The study employed a systematic approach by preparing NAB specimens with different tin contents ranging from 0 to 10% and performing corrosion test on them. Corrosion resistance was evaluated through immersion method, in which the samples were immersed in acid (0.1 M H_2SO_4), base (0.2 M NaOH) and salt (0.3 M NaCl) solutions for a testing period of 60 days. During this period, observations and mass loss were recorded accurately every 48 hours. It was revealed that the corrosion rate of NAB alloy increases progressively and it was highest in acidic medium and lowest in salt medium. As the percentage of tin in NAB increases the corrosion resistance decreases. For the acidic medium which is the most corrosive medium, the mass loss and corrosion rate of specimen A (without tin) are 0.05 g and 0.50 g/mm^2/year respectively while that of specimen E (with 8% of tin) are 0.045 g and 0.4 mg/mm^2/yr. For the specimen with the highest tin content, the mass loss and corrosion rate are 0.15 g and 2.25 mg/mm^2/year. From the experimental results, specimen E gives the optimal tin content required to improve corrosion resistance of the NAB alloy. The experimental results show that reducing the quantity of copper with a small increase in amount of tin in NAB alloy decreases the corrosion resistance of the alloy in acidic medium until 8% of tin addition (i.e. specimen E) where the corrosion resistance increases. Further increase in the quantity of tin in the alloy adversely affects the corrosion resistance of the alloy in acidic medium. This clearly shows that there is an optimum amount of tin that can be added to the alloy to improve its corrosion resistance in acidic medium.

Keywords: *Corrosion rate, mass loss, tin, corrosive media, nickel-aluminium-bronze alloy*

Date of Submission: 26-05-2025 Date of acceptance: 07-06-2025

I. INTRODUCTION

Tins are micro-alloyed precipitates that cannot dissolve in the heat affected zone of the weld and decrease grain growth [1]. Additionally, tins are frequently used for wear prevention and have a high- temperature resistance. Unalloyed bronze is made of copper and tin as main alloying metal while aluminium bronze has aluminium as the primary alloying metal added to copper. Aluminium bronze is a copper-based alloy with an aluminum content ranging from 4 to 14%, with minor additions of elements such as iron, nickel, or manganese. The aluminium both strengthens the copper matrix and gives it better corrosion resistance by forming an adherent aluminium oxide layer on the surface. Additions of iron and nickel further strengthen aluminum bronze, and the nickel provides additional corrosion resistance. Aluminium bronzes in the higher range of aluminium content can rival the strength of medium-carbon steel while being more corrosion-resistant. The additional advantage is that aluminium bronze properties also include corrosion resistance [2]. It is that strength and corrosion resistance that gave rise to the early use of aluminium bronze. There are two major groups in the Aluminium Bronze family namely Aluminium Bronze and Nickel Aluminium Bronze. Aluminium Bronze contains approximately 9-14% aluminium and 4% iron while Nickel Aluminium Bronze contains approximately 9-11% aluminium, 4% iron, and 5% nickel. That addition of nickel in the latter further improves the corrosion resistance of a material with high strength. The corrosion behaviour of alpha phase aluminium bronze was studied by Balogun *et al* [3]. The alloys were produced by casting method in acidic, alkaline and marine environmnets. The results show that there is a selective phase attack in the alloys which is more obvious in hydrochloric acid. This is due to intense attack on the protective film formed on the surface of the aluminium bronze.

Nickel-aluminum bronze (NAB) is a copper-based alloy that is widely used for ship valves and propellers, among other marine applications [4]. While displaying a good combination of corrosion resistance and strength, NAB is still prone to different forms of corrosion, such as stagnant sea water corrosion, selective phase corrosion, and cavitation erosion. Surface treatments to reduce the severity of the corrosion attack of NAB have been investigated, including laser cladding, friction stir welding, and laser melting [5]. Wharton et al. described the corrosion behaviour of cast and wrought NAB alloys through a range of electrochemical techniques. They stated that NAB alloys show good corrosion resistance under marine condition [6]. The electrochemical corrosion rates of NAB in synthetic sea water and sodium hydroxide solution was measured by Schussler et al [7]. They studied the process of layer formation under flow conditions and the reaction kinetics in freshly prepared condition. It was discovered that the protective layer consists mainly of aluminium oxide acting as a barrier for ionic transport across the layer. Zheng *et al*. studied the selective corrosion behaviour of cast NAB based on failure analysis of cut-off valves. Immersion corrosion test method was utilized and the explanation was done using energy dispersive spectroscopy and microanalysis [8]. The results show that galvanic corrosion cells are formed at the phase boundary while cracks and corrosion occur at the grain boundary. The electrochemical corrosion rates of NAB alloys were investigated in synthetic sea water with and without sulphide solution [9]. They stated that the high corrosion rates resulting from exposure of sulphide were strongly influenced by the flow velocity.

While nickel-aluminum bronze alloys offer several advantages, they do have limitations, particularly in their wear and corrosion resistance. The amount of tin present in nickel-aluminum-bronze alloys has a significant impact on both wear and corrosion resistance. Higher levels of tin have been found to improve the wear resistance of these alloys, making them suitable for applications in harsh environments or high-stress conditions. However, an increase in tin content may also lead to a decrease in corrosion resistance, as tin can create intermetallic compounds that are susceptible to corrosion. Therefore, the optimal tin content in nickel-aluminum-bronze alloys must be carefully determined to balance the desired wear and corrosion properties for a specific application. The main aim of this study is to investigate the effect of varying tin content on the corrosion resistance of NAB in order to determine the optimal tin content.

II. MATERIALS AND METHOD

The methodology adopted in this research essentially involved alloy preparation by melting and casting techniques. The constituent elements of the nickel-aluminum-bronze alloy were provided, prepared and cast in the Department of Mechanical Engineering at Obafemi Awolowo University of Ife, Osun State, Nigeria. Machining of the test specimens and the tests were carried out in the Department of Mechanical Engineering, Ekiti State University, Ado-Ekiti, Ekiti State, Nigeria.

The casting process involves sand preparation, pattern and mould making, melting, pouring the molten alloy into the prepared mould, and shake-out of the solidified alloy. Bentonite and a little quantity of water was added to prepared moulding sand to give it more compatibility and make it stickier. The flat rammer was used to level and compact the sand together (ramming process) as shown in Fig 1. Six moulds were prepared and labelled A to F for the casting, and the pattern used for the cast is not a split pattern, three cylindrical rod patterns of 200 mm length and 15 mm diameter were inserted vertically into each moulding box which means each mould will have three pieces of the same specimen and a total number of 18 pieces will be cast. The patterns were removed after few minutes and the mould was left to dry and also for further casting processes.

Figure 1. Ramming process with the use of flat rammer

The compositions of the intended alloys by weight were prepared as shown in Table 1. Pit-type furnace with graphite crucible pot was pre-heated for about 10 minutes. Nickel with melting point of 1455 °C was first charged into the crucible at 1500°C and heated till it melted. Copper with a melting point of 1085 °C was then added, followed Aluminum was then added and allowed to dissolve in the molten and stirred manually properly to ensure homogeneity. The alloying element (tin) was finally introduced into the molten mixture after the control sample had been cast. The melt was stirred for 6 minutes in order to ensure homogeneity and then poured into the mould cavities and allowed to solidify for about 30 minutes before removal from the mould. Table 1 shows that the total weight composition of each specimen is 500 g. The percentage of Aluminium and Nickel in the composition of the specimens were constant at 10% and 4%, respectively, the alloying element (tin) was added separately in a concentration of 0-10% by weight to molten 76-86% Copper, stirred and sand cast. Subsequently, specimens obtained from the casting were subjected to corrosion test.

Table 1: Weight and percentage composition ratio of each specimen

Specimen	Cu	Sn (Tin)	Al	Ni
A	86% (430g)	0%(0g)	10%(50g)	4%(20g)
B	84%(420g)	2%(10g)	10%(50g)	4%(20g)
C	82%(410g)	4%(20g)	10%(50g)	4%(20g)
D	80%(400g)	6%(30g)	10%(50g)	4%(20g)
E	78%(390g)	8%(40g)	10%(50g)	4%(20g)
F	76%(380g)	10%(50g)	10%(50g)	4%(20g)

Corrosion Test

Total immersion was carried out for all the experimental specimens. The experiment was carried out under closed atmospheric condition according to the ASTM practice standard G-31 [22]. The aluminium bronze alloy samples for the corrosion test were cut into 10 mm length with approximate surface area of 824.7 mm^2 and descaled by wire brushing, polished progressively using a series of silicon emery papers to obtain a smooth surface. Thereafter, cleaned thoroughly in distilled water, degreased with ethanol, dipped into acetone, dried in air and kept in desiccators until needed for corrosion test.

Each sample of the dry NAB was weighed and then completely immersed in uniquely labeled containers separately containing prepared 0.1 M, 0.2 M and 0.3 M concentrated solutions of H_2SO_4, NaOH and NaCl respectively, as shown in Fig. 2. The containers of the corrosive solution were then sealed with a lid to minimize evaporation and contamination. At every 48 hours (2 days) of exposure, the samples were removed, washed to remove the corrosion product, rinsed with distilled water, acetone and dried in air. The corroded samples were then reweighed and recorded to determine the weight loss and corrosion rate in the corrosive media. Visual changes in specimen appearance and solution colour were also noted. The experiment was run progressively for 60 days.

The corrosion rate was obtained using the relation:

$$R = \frac{W}{A}\left(\frac{T}{365}\right) \quad (1)$$

where, R = Corrosion rate (mg/mm^2/year); W = weight loss/gain (i.e. weight difference);
A = Area of the specimen; T/365 = Exposure time in days extrapolated to year.

Figure 2. Corrosion test specimens

Microstructural Examination

Cut specimens for the microstructural examination were grinded progressively to obtain a smooth and flat surface, polished with emery cloth in decreasing coarseness and polished using polishing cloth and paste with alumina particles to obtain a mirror-like surface. The specimens were then etched in NITAL (2% Nitric acid and 98% Ethyl alcohol) to reveal the microstructure of the surface layer. The phases of the specimens were then photographically recorded at 420 magnification using electron microscope.

III. RESULTS AND DISCUSSION

Mass Loss

Figure 3 shows the various mass loss in specimens A to F in acid, base and salt. It is shows that all samples initially show a negative mass loss which implies there was increase in mass of the samples in the first 4 days. This can be attributed to formation of protective layer on the surfaces of the specimens when in contact with the corrosive medium as reported in [7]. In the next eight days, the specimens showed rapid mass loss, in most case, before exhibiting gradual loss of mass. It shows that towards the end of the test, there is no significant change in mass loss for all the samples in three corrosive media, especially from day 40 to 60. For all the specimens, mass loss was highest in acidic medium (sulphuric acid).

There is a progressive increase in mass loss for all specimens over time as shown in Fig. 3, which indicates that the corrosion of the protective layer has started. It can also be noted in the figure that attacked on the protective layer and corrosion of the alloys started as early as day 2 in the acidic medium whereas in most cases, it was in day 4 that positive mass loss was observed in the alkaline and salt media. Specimen F shows the highest mass loss of about 0.15 g in H_2SO_4 solution by day 60. Specimens A and E shows the least mass loss, staying below 0.05 g throughout the experiment. The other specimens (B, C and D) fall in between, with mass losses around 0.10 g by day 60.

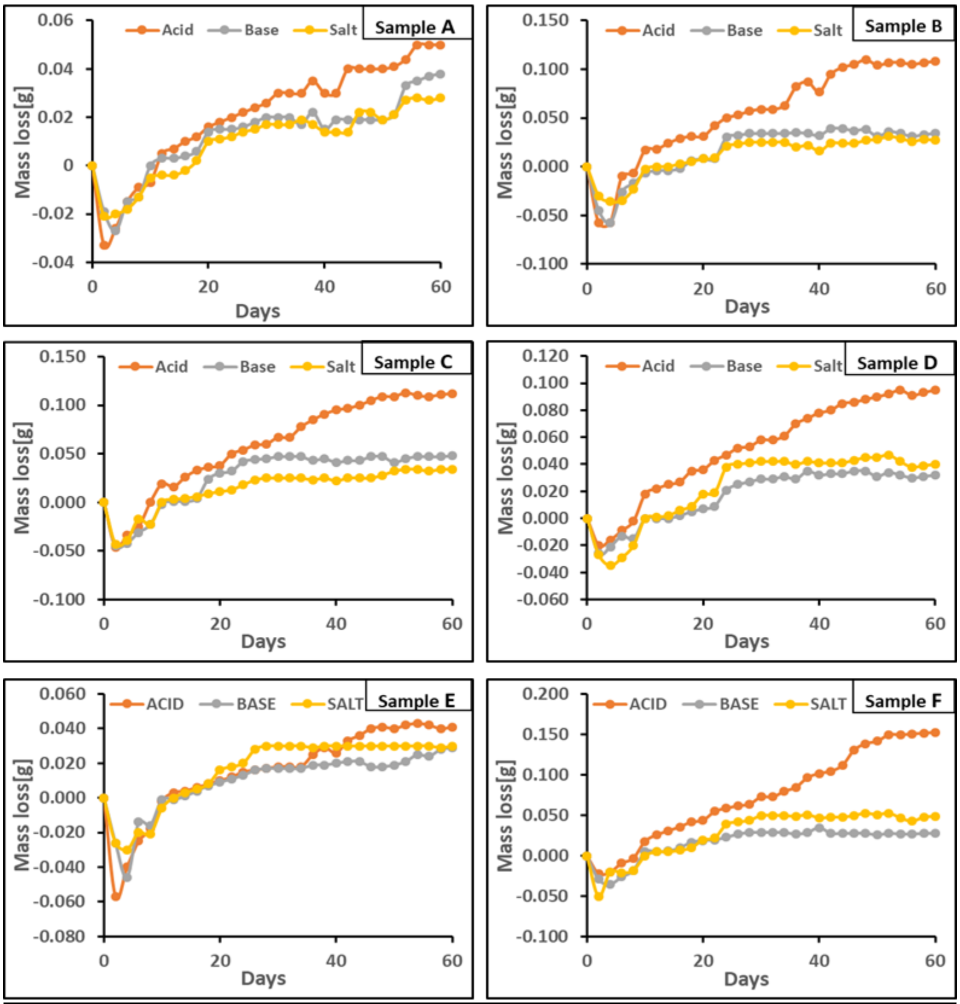


Figure 3. Mass loss of each specimen in acid, base and salt solutions

Figure 4 shows the comparison between the mass losses of the specimens in the corrosive media. There is a significant difference in the graphs of samples in alkaline and salt solutions when compared to the graph of the specimens in acidic medium. All the specimen show an initial drop in mass within the first 4 days which is the due to the formation of oxide layer on the specimens as mentioned earlier. From day 5 to about day 35, mass losses of all specimens are increasing. After day 35, the mass losses remain relatively stable with little fluctuation in some of the specimens showing gains and losses in their masses. Specimens A (the control specimen), B and C (with lower percentage of tin) show least mass loss in salt solution whereas specimens D, E and F (with higher percentage of tin) exhibit least mass loss in sodium hydroxide. This implies that specimens without and little percentage of tin have better corrosion resistance in salt while specimen with higher percentage of tin have better corrosion resistance in sodium hydroxide. Specifically, the mass loss of specimen E is 0.025 g and 0.028 in both the acidic and basic media respectively. These values are the least mass losses in bot corrosive media. Therefore, specimen E has the highest corrosion resistance in both acidic and basic media while specimens A, B and E have the highest corrosion resistance in salt at 60 days because they have the same mass loss of about 0.025 g. It is obvious that specimen E (with 8 % tin) has the best corrosion resistance among all the specimen.

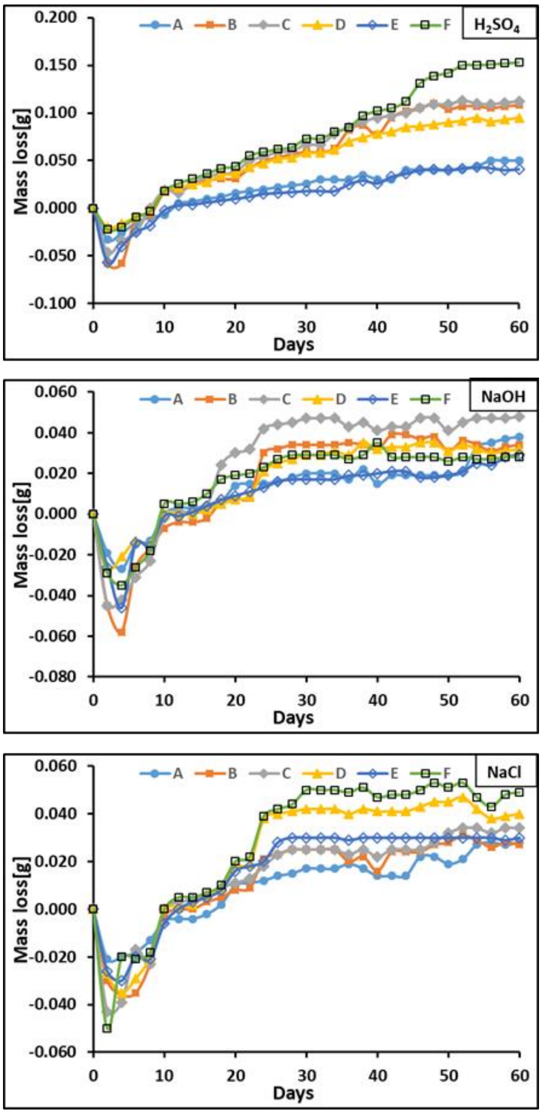


Figure 4. Comparison between mass loss of specimens in acid, base and salt for a period of 60 days

Corrosion rate

The results of corrosion rates of the specimens are shown in Fig. 5 for each of the specimen in acid, base and salt. All specimens initially show a slight negative corrosion rate up to approximately day 8 before displaying positive increase in corrosion rate over time. However, for all the specimens, corrosion rates of specimens in the acidic medium is the highest when compared to basic and salt media. For instance, at day 60, corrosion rates of specimens B and D in acidic medium are 1.57 and 1.38 mg/mm^2/yr respectively whereas in basic medium, their corrosion rates are 0.40 and 0.47 mg/mm/yr respectively. For salt as the corrosive medium, the corrosion rates of specimens B and D are 0.39 and 0.55 mg/mm^2/yr respectively.

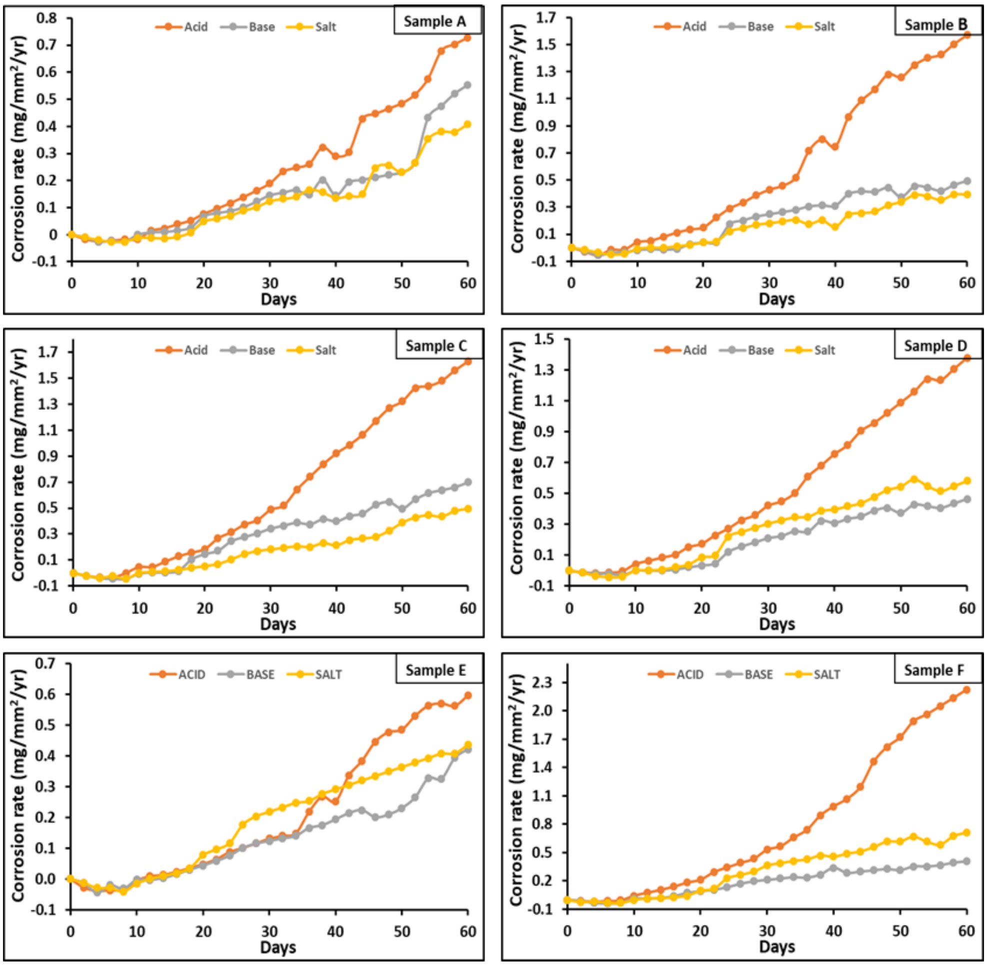


Figure 5. Corrosion rate of each specimen in acid, base and salt

The corrosion rates of all the specimens in the three corrosive media are compared and shown in Fig. 6. In the acidic medium, specimen F exhibits the highest corrosion rate of about 2.25 mg/mm^2/year at day 60. This was followed by specimens C and B with a corrosion rate of 1.50 and 1.62 mg/mm^2/year. Specimen D show moderate corrosion rates of about 1.38 mg/mm^2/year at the end of the experiment. Specimens A and E have the lowest corrosion rates, staying below 0.72 g/mm^2/year and 0.59 mg/mm^2/year throughout the experiment. The corrosion rates increase more rapidly after about day 30 for most samples.

The corrosion rate of the specimens in the basic medium shows that all samples demonstrate an initial slight negative corrosion rate in the first few days (Fig. 6). From day 10 to about day 35, there is a general increase in corrosion rates for all specimens. After day 35, the corrosion rates fluctuate, with some samples showing positive and negative rates. Specimen F shows the highest corrosion rate of about 0.00038 g/mm^2/year at day 60. Specimens A and E exhibited the lowest corrosion rates in the alkaline environment, mostly staying below 0.00050 g/mm^2/year throughout the experiment. Specimens C, D and B, respectively, displayed moderately higher corrosion rate than Specimens A and E.

These results indicate that replacing the quantity of copper with a small amount of tin in NAB alloy reduces the corrosion resistance of the composite in acidic medium until 8% of tin addition (i.e. sample E) where the corrosion resistance increases. Further increase in the quantity of tin in the alloy adversely affects the corrosion resistance of the alloy in acidic medium. It further shows that there is an optimum amount of tin that can be added to the alloy to benefit its corrosion in acidic medium.

Corrosion rate of the specimens in salt solution are almost similar to that of the base medium, with an initial dip into negative corrosion rates for all specimens within the first 10 days. From day 10 to about day 35, there's been a steady increase in corrosion rates, and after day 35, the most of the corrosion rates of the samples fluctuate. As observed in the acidic and alkaline environments, Sample F also shows the highest corrosion rate whereas Sample A exhibited the least corrosion rate throughout the duration of the test. Furthermore, it was noted that samples A and B exhibit least corrosion rate (0.35 mg/mm^2/yr) in salt solution whereas samples D, E and F experienced least corrosion rate of about 0.35 mg/mm^2/yr) in base medium. In general, Aluminium bronze has been observed to be more susceptible to corrosion in acidic environment when compared with that of alkaline environment. For this study, specimen E has the lowest corrosion rate in acidic medium. An alkaline environment creates more protective oxide layer on the surface of the bronze alloy, reducing the rate of corrosion [10].

In general, the addition of Tin to the Nickel-Aluminum-bronze alloy make the alloy generally more susceptible to corrosion in corrosive media considered. Only specimen E has corrosion approximately close to the alloy without Tin addition. This is in agreement with literature that bronze alloy containing tin is more susceptible to corrosion (especially galvanic corrosion) than one without tin in acidic and alkaline environments [10], [11]. The formation of α- and Sn- rich solid solution at the grain boundaries impact positively on the strength and hardness of the alloy. However, the α- and Sn- rich solid solution at the grain boundaries are more susceptible to corrosion in acidic and alkaline environments than the matrix of β-solid solution.

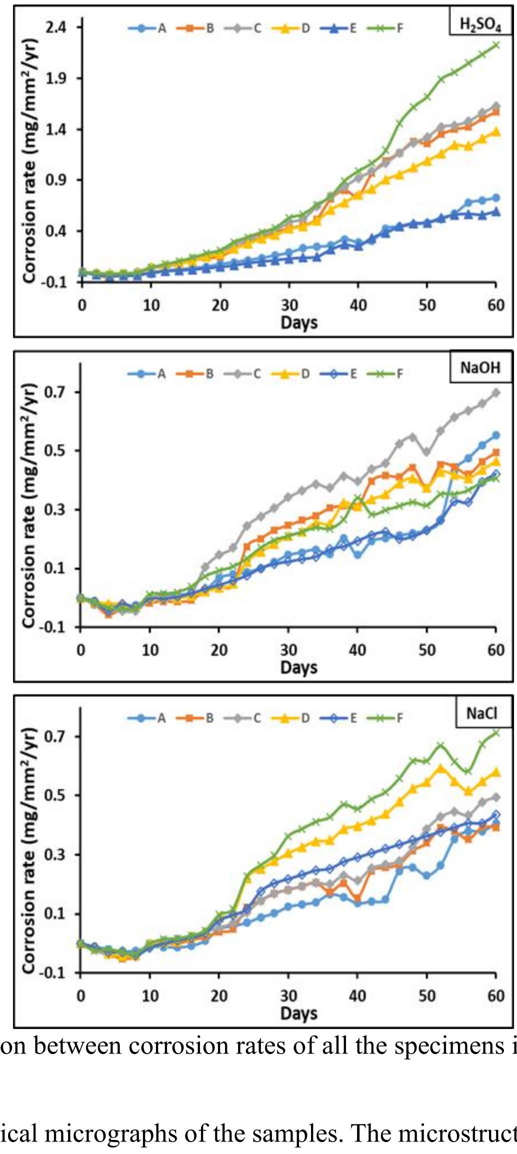
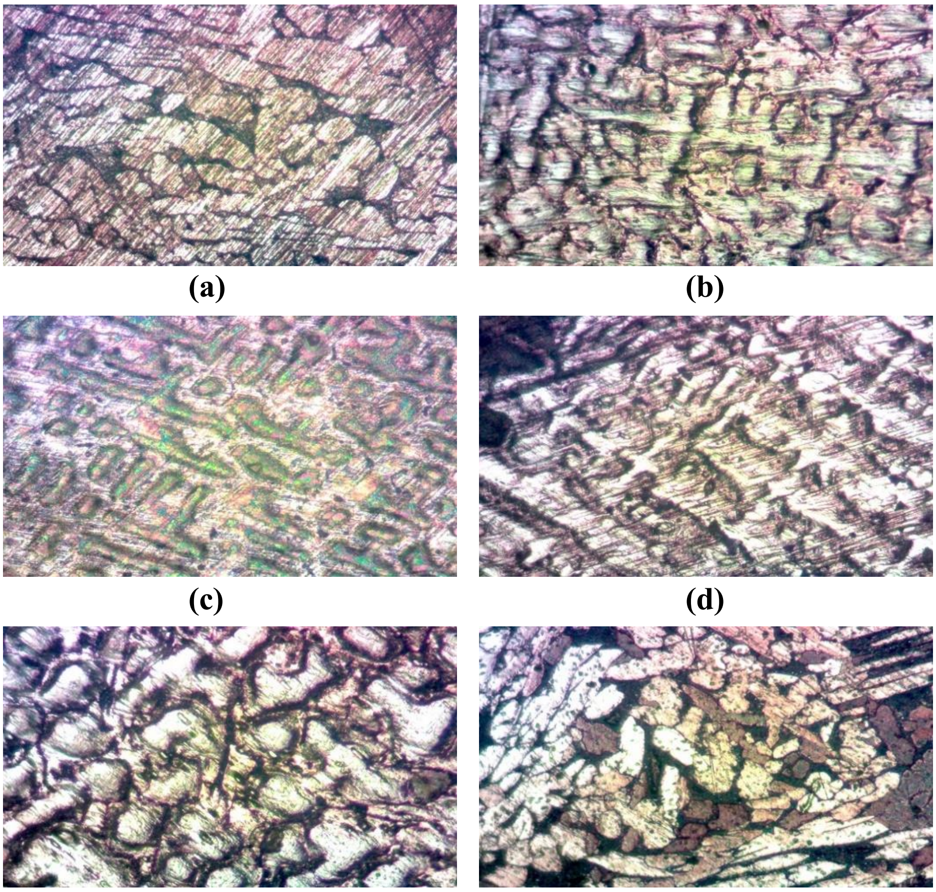


Figure 6. Comparison between corrosion rates of all the specimens in acid, base and salt

Microstructural Evaluation

Figure 7 shows the optical micrographs of the samples. The microstructure of the specimen without Tin, 4% of Nickel and 10% of Aluminium in the Cu-Ni-Al alloy (Figure 7 (a)) showed large grains of rosette-shaped β-phase uniformly distributed around α-phase which is the white background, as also reported by Oluwadare et al [1]. Consequently, the microstructure of sample A can be described as having an α-β solid phase.



(a) **(b)**

(c) **(d)**

(c) **(d)**

Figure 7. Micrograph showing (a) 0% of Tin (b) 2% of Tin (c) 4% of Tin (d) 6% of Tin (e) 8% of Tin (f) 10% of Tin microstructures (× 420 magnifications).

Addition of 2% of Tin to the Cu-Ni-Al alloy (Figure 7 (b)) resulted into formation light background of α-solid solution in a dark matrix of β-solid solution with some dendritic structure α-δ eutectoid as also reported by Poojary et al [12]. Fig. 7 (c) shows optical micrograph of Cu-Ni- Al-Sn alloy with 4% of Tin. Light α-solid solution in a dark matrix of β- solid solution is observed with some dendritic structure α-δ eutectoid. It can be observed that that increasing Tin contents in the Cu-Ni- Al-Sn alloy gives a lighter coloured microstructure of α + β multi-phase. This is evident in the figures with Tin content. (i.e. Fig. 7 (d, e and f).

Figs.7 (d) and (e) show the optical micrographs by adding 6% and 8% of Tin to the aluminium bronze alloy. The alpha phase is more pronounced in these samples than in Figs (b) and (c). The observed structures are due increasing tin content as they grow composition gradient in the cored dendrites. According to Cu-Sn binary alloy phase diagram, the solid solubility of the Sn element in the α-Cu matrix steadily declines as temperature rises. At normal temperature, tin is not very soluble in copper but it can acts as a solid solution strengthener copper alloy. In addition, specimen (f) with the highest tin percentage Tin content gives a better lighter coloured microstructures of alpha plus beta multi- phase.

Overall, the change in structure observed in Cu-Ni-Al alloy with tin which has been reported to be altered from a columnar to an equiaxed structure can be attributed to the influence of tin on cooling rate, nucleation temperatures, and undercooling intensity. This impact the properties of the alloy due to formation of high temperature α- and Sn- rich solid solution at the grain boundaries[1], [13].

IV. Conclusions

This study investigated the effect of tin content on corrosion resistance of NAB alloy and at the major conclusions are summarized below:

- There is a significant difference in the mass loss and corrosion resistance of samples in alkaline and salt solutions compared to those specimens in acidic medium. The acid is the most corrosive among the corrosive media.

- For tin addition to NAB alloy, there was initial mass increase for all specimens in all the corrosive media which was as a result of the creation of a stable and protective oxide layer on the surface of the NAB alloy when in contact with the corrosive medium. However, the protective layer later gave way to corrosion and mass reduction was observed for all specimens in all the corrosive media.

- The study shows that replacing the quantity of copper with a small amount of tin in NAB alloy reduces the corrosion resistance of the composite in acidic medium until 8% of tin addition (i.e. sample E) where the corrosion resistance increases. Further increase in the quantity of tin in the alloy (i.e. 10 % tin) reduces the corrosion resistance of the alloy in acidic medium. It further shows that there is an optimum amount of tin that can be added to the alloy in order to achieve better corrosion resistance in acidic medium.

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