Effect of Nickel and Heat Treatment on Corrosion Behaviour of Modified ZA27 Nickel Alloy

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***Abstract* - Corrosive behaviour of the ascast and modified ZA27 alloy was investigated when exposed to acidic environment of 1Normal HCl solution. The alloy was developed by liquid metallurgy route with varying amounts of nickel and then thermally treated by T6 type heat treatment process ie., solutionizing at 320^{0}C by varying holding duration from 2 to 6hrs in steps of 2hrs followed by water quenching and then artificial ageing at 180^{0}C. Rate of corrosion of ascast and heat treated ZA27 Nickel alloy was determined in 1Normal HCl solution through static immersion test by weight loss technique. The duration of the test was 12 to 72 hours. In each test, the corrosion rate of the developed ZA27 Nickel alloy was found to decrease with time. This is due to the presence of some intermetallics and also the presence of higher percentage of aluminium in the alloy would have led to the formation Al_2O_3, which acts as a corrosion inhabitating element. Heat-treatment was found to improve the corrosion resistance in every specimen tested. Duration of heat treatment played a significant role in improving corrosion resistance. Heat treatment for a 6hrs. caused significant drop in the weight loss of the specimen. This may be due to the change in the morphology of the developed ZA27 nickel alloy during heat treatment Hence selected heat treatment is beneficial in increasing corrosion resistance..**

Keywords— Ascast; 1N-HCL; ZA27Nickel; Corrosion rate

I. INTRODUCTION

Zinc die casting alloys are specified by ASTMB86 for No.2, No.3, No.5and No.7 and ASTM B791 for ZA8, ZA12, ZA27. All the seven zinc alloys are zinc aluminium combinations. The alloys under B86 are hypoeutectic when aluminium content is considered. Those alloys under B791 are hyper eutectic as aluminium content is more than eutectic composition[1]. All of the zinc die cast alloys have dendrtitc and eutectic compositions. Though, the hypoeutectic alloy freezes with zinc rich dendrites, whereas hyper eutectic alloys solidify by aluminium rich dendrites. The physical and mechanical properties of any castings depend on the type of alloy casting process, yield of the casting produced and amount of impurities. Alloying elements such as copper and magnesium in ZA alloys increases the strength, reduces ductility and prevent intergrannular corrosion. All zinc die cast alloys have good corrosion resistance to different environments. Presence of aluminium in the zinc based alloys boosts corrosion resistance, which is main alloying element in all zinc based alloys. Aluminium content up to 12 % in zinc based alloys perform better than pure zinc. Zinc based alloy with aluminium content of 27% behaves like aluminium alloy because of high aluminium content.

Out of all the seven zinc alloys ZA27 have high strength and hardness, good machinability with excellent bearing properties, high wear resistance at lower temperatures.. Aluminium in the ZA27alloy helps to improve corrosion resistance of the alloy [1.2] ZA27 alloy exhibits high corrosion resistance in natural atmospheres, natural waters, because zinc is able to form protective layer on the surface, which is of two layers, upper layer consists of zinc hydroxi sulphate and white zinc oxide and lower layer consists of black compact zinc oxide which exhibits good corrosive resistance [3]. ZA alloys will corrode in a uniform manner, unlike aluminium alloys are susceptible to pitting corrosion.

In mild acidic environment ie., pH value ranging from 4 to 7 the ZA27 alloy perform better than other zinc based alloys due to high aluminium content. In alkaline environment the ZA27 alloy will corrode significantly as pH value rises to 12. The corrosion attack on zinc rich phase occurs in acidic solutions while in the alkaline solutions the corrosion attack is on aluminium rich phase. The optimum pH range of applications for zinc based alloys lies between 5 and 11.5.

The different approaches have been adopted to improve the mechanical and tribological properties of ZA 27 alloy at room temperature. Out of which one is addition of high strength metal such as Ni, Ti [5] and second one is thermal treatment. From literature survey many researchers have studied the mechanical and wear properties of ZA27 alloy, however, unlike most physical and mechanical properties, corrosion property is not an intrinsic and one value, but rather depends on the exposure environment. However, for certain application the corrosive behaviour is equally important as other properties [12].

As there is no much information regarding corrosive behaviour of modified ZA27 Nickel alloy when it is subjected to T6 type heat treatment. so the present work aims to investigate the effect of nickel(1 to 3% by wt.) and T6 heat treatment on the corrosive behaviour of ZA27 alloy when exposed to acidic environment.

II. EXPERIMENTAL PROCEDURE

A. *Materials*

The Alloys were prepared by liquid metallurgy route. The molten metal from electric resistance furnace at 700^{0}C is poured into cast iron metallic mould which is preheated up to 200^{0}C. The castings of 20 x 150mm were prepared from which samples are machined out (according to ASTM G68, 80) to 20mm diameter and 10mm thick. Samples were exposed to T6 heat treatment in muffle furnace for varying solutionizing durations from 2hrs to 6hrs in steps of 2hrs.

B. *Corrosion Test*

Immersion tests are the fastest and cost-effective for providing a primary selection of best suited materials for any application. Weight loss measurements following exposure or immersion in a corrodent is standard method used for assessing corrosion resistance. So in this study immersion corrosion test were used to access corrosive behaviour of ZA27 Nickel alloy in ascast and heat treated condition.

The tests were carried out at room temperature. The corrodent used was 1Normal HCl. The samples were ground using different grade emery papers (360,620,800) to obtain fine surface finish. The samples were then rinsed with distilled water, cleaned with acetone and dried in atmospheric air. Each sample was initially weighed before it is immersed in the corrodent. Later, the samples are vertically immersed in stagnant 1N, HCl solution for a period varying from 12 to 72 hours in steps of 12hrs. Different samples were used for each test condition. By each time, the corrosion products formed on the corroded samples were removed by scouring the samples with wire brush. The scoured specimens were dried and weighed. The weight loss measurements were made and weight loss values were calculated taking initial weight as reference.

C. *Corrosion Rate*

After the completion of the tests, the adherent corrosion product and salt deposit were removed by scrubbing with a wire brush under running tap water and dried thoroughly. The samples are reweighed and the difference in weight was measured. The graphs were plotted for Weight loss (g) versus Exposure Time (hr.), and the effect of nickel content and acidic medium on the weight loss is analyzed.

Weight loss can be expressed in the form of corrosion rate which can be calculated by the following expression

$$Cr = \frac{KW}{ATD}$$

Where

'Cr' corrosion rate in mm/year, 'K' is a constant 'W' is sample mass loss (mg), 'A' is surface area of sample exposed to corrodent (cm^2), 'T' is time of exposure(hrs.), 'D' is density of ZA27 nickel alloy (g/cm^3).

III. RESULTS AND DISCUSSIONS

A. *Acidic Corrosion Behaviour*

When ZA27 nickel alloy was immersed in the acidic medium, the colour of acid turned to white. This is due to the formation of Ni Chloride which has a pungent odour. The surface of the sample becomes dull and grey, due to oxidation of the surface, this does not affect the properties of the alloy. The surface of the sample is covered with aluminium oxide layer. This layer helps to reduce the corrosion penetration into the substrate of the alloy which delays the dissolution of zinc phases. Increase in corrosion resistance of the developed ZA27 nickel alloy is due to the distribution of intermetallic compounds of aluminium and nickel formed during mechanical alloying and aluminium oxide formed on the surface. Weight loss of the ZA27alloy without nickel is greater than the ZA27 alloy with nickel.

Corrosive behaviour of developed alloy in the acidic medium [1N HCl] can be interpreted by examining the surface of the samples. After hours of exposure of the alloy to corrodent 1N HCl solution the surface of all the samples are covered with white layer as corrosion product. Results from Figure1 show that the weight loss is more noticeable during initial hours of exposure to the acidic medium. Later rate of weight loss decreases as the duration of exposure increases when compared to rate of weight loss during initial hours of exposure. This behaviour is similar for all the alloys developed. This is due to the presence of aluminium and nickel in the zinc matrix.

The percentage weight loss due to corrosion decreases monotonically with nickel content. Due to the distribution of intermetallic compounds of aluminium and nickel formed in the microstructure during mechanical alloying. In other words, the more nickel content, the greater is the corrosion resistance of the alloy. The presence of aluminium in the alloy provides corrosion resistance due to the formation of a stable aluminium oxide layer on the sample surface and intermetallic compounds of nickel and aluminium in the microstructure which are stable in most acidic solutions.

B. *Effect of Nickel Content.*

The *ZA27* alloy fall in the hypereutectoid range of the Zn–A1 phase diagram [6]. The pure, ZA27, comprises of primary α dendrites surrounded by the eutectoid α + η. In addition to the above, the Nickle-containing ZA27 alloy consist of Ni-based intermetallic particles (Ni3Al) whose morphology changes from blocky to rod-shape with increasing Ni content. The optical microstructures of all the as-cast alloys are given elsewhere.

The results of the corrosion test are presented in the form of graph in Figure 1. It tracks from the graph that the corrosion which reduced with increase in the nickel content. This is due to the simple reason that the content of nickel which is just 1% can barely resist the severity of the acid attack. Its behaviour is almost the same as the ZA27 alloy without nickel with very small improvement in corrosion resistance. But this is not the case with ZA27 alloy with 3% nickel as is clearly evident. There is evidence for just the presence of pits and not for the presence of cracks. This clearly proves the effect of nickel in improving corrosion resistance of the ZA27 alloy.

Nickel being a passive and forms intermetallic compounds with aluminium, remains unaffected by the acidic medium during the test. The nickel particles resist the severity of the acid and formation of cracks, yet there is presence of pit formation on the surface. This is due to the zinc rich phases which act as encouraging sites for formation of pits on the surface which lead to the removal of minute amount of material, there by leading to weight loss. The weight loss however is very less in comparison with the ZA27 alloy without nickel. It is clearly seen from the Figure 1 that 3% nickel in the alloy provide better corrosion resistance than all

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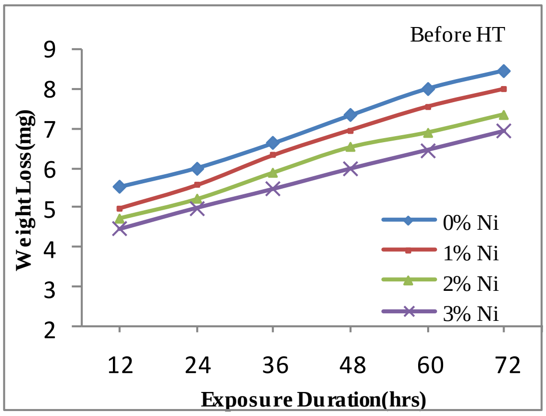
other alloys irrespective of the exposure time. Nickel being hard and strengthening element offers beneficial corrosion resistance to the alloy. Intermetallic compounds formed between nickel and aluminium during mechanical alloying improves wear resistance of the ZA27 alloy which can be used for both high and low temperature service. With previous works the addition of nickel improved wear behaviour of the ZA27 alloy. Hence this alloy can be used as machine parts in submarines.

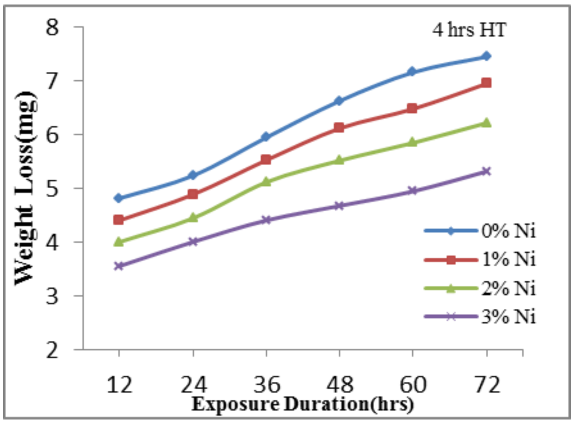
In contrast, the results observed in the present investigation, in which increasing the amount of the nickel tends to increase the corrosive resistance of the ZA27 alloy, it is believed that the different results reported by the investigators may be result of the difference in the casting methods, and the environment it is exposed to. Several investigations showed that the aforementioned factors play an important role in determining the characteristics corrosion resistance of the ZA27alloy.

C. Corrosion rate.

After each exposure of alloy samples with the corrodent, the corrosion products formed on the surface are cleaned and weighed. On the basis of weight loss the corrosion rate was calculated in mm/year. The results of the corrosion rate are presented in the form of graph in Figure 2. From the graph that the corrosion rate reduced with increase in the nickel content and duration of exposure. The results obtained infer that corrosion rate seems to decrease with the duration of corrosion test.

The calculated values of corrosion rate of alloy without nickel in as cast condition after 72 hrs exposure is 0.1138mm/yr. and the same alloy after 6 hrs heat treatment is 0.0874mm/yr. Alloy with 3% nickel in as cast condition after 72 hrs exposure is 0.0928mm/yr. and the same alloy after 6hrs heat treatment is 0.0652mm/yr.





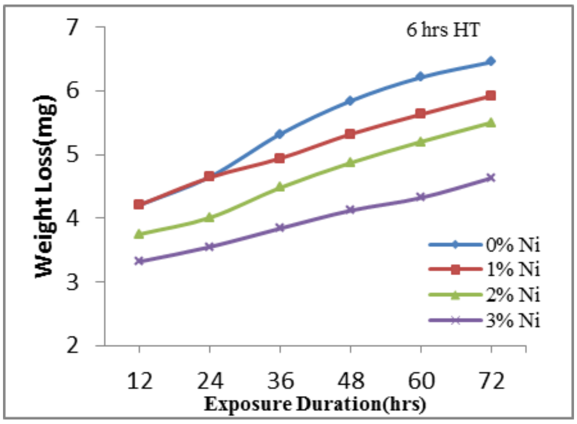
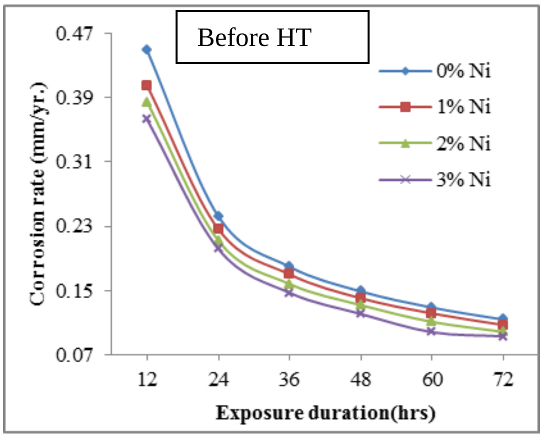


Figure 1.Weight loss due to corrosion vs. Nickel content in ZA27 alloy

Addition of nickel to alloy lead to decrease in corrosion rate with increase in duration of exposure inferring that the corrosive resistance of the alloy increases as the exposure time increased in both as cast and heat treated condition due to dispersion of intermetallics of nickel and aluminiumin in the zinc matrix and breaking of dendritic structure during heat treatment. Applied thermal treatment whether it is 2hrs or 6hrs holding time improved corrosion resistance of the modified ZA27 nickel alloy due to precipitation of phases of alloying elements and homogenization of phases.



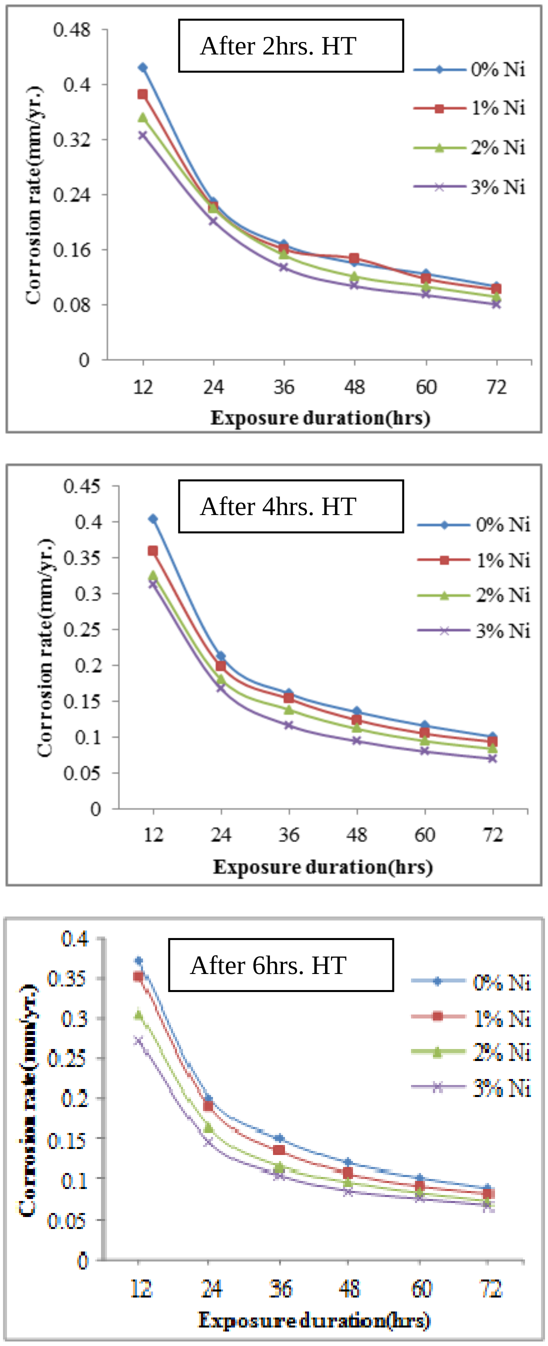


Figure 2 Corrosion rate of ZA27 Nickel alloy (mm/yr.) for varying amounts of nickel with exposure time

D. Effect of Heat Treatment

In the present work the specimens were subjected to T6 type heat treatment which includes solutionizing at 320°C between 2 to 6hrs in steps of 2hrs, and then quenched in water and ageing at an elevated temperature (180°C) for short duration. Chemical composition of the modified ZA27 nickel alloy does not change after heat treatment, Temperature were selected from Zn-Al phase diagram and also based on the experience of other researchers. solutionizing causes the breaking of dendritic structure of alpha, eutectic and eta phases, without affecting the nickel containing phases, which helps to retain its hardness to be higher when compared to ZA27 alloy without nickel.

The results of the corrosion rate after heat treatment are presented in the form of graph in figure 2. It infers from the graph that corrosion rate which reduced with increase in heat treatment duration. This is due to the simple reason that 2hrs solutionizing can barely break dendritic and interdentritic structure of the alloy. Its behavior is almost the same as ascast alloy with very small improvement in corrosion resistance. But this is not the case with alloy undergone for 6hrs. heat treatment as is clearly evident from microstructural studies.

There is evidence for breaking of dendritic and interdendritic structure of the alloy for 6hrs heat treatment. This clearly proves that corrosion resistance of the alloy improves as the heat treatment duration increases. Heat treatment substantially improves the corrosion resistance of the developed alloy, no matter what the nickel content is. Heat treatment affects only the matrix of zinc aluminium phase not the nickel phase in the alloy. The results after heat treatment infer that whether 2hrs or 6hrs heat treatment duration significantly improves the corrosion resistance of the ZA alloys when compared to as cast one. In general, it can be said that heat treatment for a few hours cause a significant drop in the weight loss of the specimen. This is due to the change in the morphology of the developed ZA27 Nickel alloy during heat treatment. One probability is that heat treatment at 320^0C has improved corrosion resistance of the zinc aluminium phases there by increasing overall corrosion resistance of the modified ZA27 alloy.

IV. CONCLUSION

• It was found from this study that the addition of nickel and T6 type heat treatment increased corrosion resistance of ZA27 Nickel alloy. Modified ZA27 alloy attained better corrosion resistance than the pure ZA27 alloy irrespective of test conditions due to the presence of nickel.

•Weight loss due to corrosion decreases as the nickel content in the alloy increases from 1to 3% by wt.

•The presence of aluminium in the alloy favours corrosion resistance by formation of aluminium oxide layer not to allow substrate zinc dissolution in the HCl solution.

•Solution Heat treatment of the alloy at 3200C helped the alloy to improve corrosion resistance significantly.

•The corrosion resistance of the heat-treated specimens for a few hours causes a significant drop in the weight loss of the specimen. This may be due to the change in the morphology of the developed ZA alloy during heat treatment.

•In each test, the corrosion rate was found to decrease with time and nickel content in the alloy developed.

•The material loss was predominantly due to the formation of pits on the surface, in the alloy without nickel, the pit formation was crack induced, while in the ZA27alloy with nickel, the pits developed without cracks.

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