SYNERGISTIC CORROSION INHIBITION OF ZINC -ALUMINIUM ALLOY

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Abstract

The Chemical composition of superplastic Zinc-Aluminium alloy used in the present study is as follows: 29.5-23.9% Al, 0.3-0.6% Cu, 0.001% Mg, 0.1% Fe, 0.03% Si,0.003% Pb, 0.0003% Cd, 0.0001% Sn, 0.0001 Th, 0.005% others and the remainder is Zn. The density of the alloy was reported as $6.25g/cm^3$. The alloy was manufactured by ISC alloys Limited, Bristol, England.

Introduction

Zinc is one of the major tools of the corrosion engineer due to its faculty of galvanically protecting steel and other metals while having good resistance to attack by corrosive atmospheres, natural water and seawater [1]. In aqueous solutions it galvanically protects iron, nickel, tin, lead and copper. Ordinarily found zinc is impure. The impurities normally present in zinc are lead, cadmium, and iron. The impurities in pine change corrosion behaviour of zinc. It is generally believed that the corrosion resistance of metal increases with increasing purity. Zinc is anodic to iron and most of common metals. It is cathodic to magnesium and is protected by magnesium while to aluminium it can be either cathodic or anodic. Depending upon the nature of environment, alloys of aluminium, magnesium or zinc are used as galvanic anodes. Hull plates for the protection of steel ships is the best known application of zinc [2]. Zine is also utilised in the form of bars or slabs as sacrificial anodes to protect pipelines and other structures. Zinc alloy parts are made by die-casting because of their low melting points. Many automobile components such as grilles and door handles are die-cast but are usually plated with corrosion-resistant metals. Zinc is more corrosion resistant than steel in most natural atmospheres, the exceptions being ventilated.

Indoor atmospheres where the corrosion of both steel and zinc is extremely low and certain highly corrosive industrial atmospheres. For example, in seacoast atmospheres, the corrosion rate of zine is about that of steel. Is usually not considered to be a useful metal in the acidic or strongly alkaline chemical environments. Historically zinc was one of the Zinc very first metals to be used as a galvanic anode; early in the 19th century. Zinc is an ideal metal for cathodic protection in seawater because it does not subject the adjacent painted surfaces of the hull to high potentials, which are injurious to many commonly used paints. Zinc and zinc coated steel are definitely useful in the chemical industry.

Zinc owes its high degree of resistance to atmospheric corrosion to the formation of insoluble basic carbonate films. Sea water deposits protective scales on zinc and is less corrosive then soft water. Softer waters, with their higher content of dissolved oxygen and CO_2, generally attack Zinc more vigorously than the fairly hard waters. River waters have been found to deposit scale more easily than well waters. The normal corrosion product on zinc in water is $ZnCO_3$. The presence of oxygen in the water accelerates the corrosion of zinc by depolarisation of the cathodic areas. In distilled water the rate of corrosion is controlled by diffusion of oxygen through the film of $Zn(OH)_2$ corrosion products. At the temperatures of maximum corrosion, the film is granular and non-adherent, but at the lower temperature, it is gelatinous and adherent. At higher temperatures, it is compact and adherent. From this it might be concluded that the granular coating is more permeable to oxygen, which would account for the increased corrosion.

It was found that pure aluminium and most of its commercial alloys can not be considered as good sacrificial anodes, because of the properties of their oxide film, which is prone to passivation. In most environments when aluminium is alloyed with zinc, zinc has only a small influence on corrosion resistance. The alloy, used in the present study was a superplastic zinc-aluminium eutectoid alloy. Attention to this unusual eutectoid alloy in the

Zn-Al system was first drawn by Rosenhain et al [3]. It is sometimes therefore called as Rosehain's alloy. This alloy has not attracted industrial application owing to its high transformation rate and inadequate mechanical properties, but it is splendid for demonstrating isothermal transformation [4]. However, the relation between microstructure and the superplastic behaviour of the Zn-Al alloy has been so characterised in the last decade that the commercial development and exploitation of the alloy has been considered [5]. The limitation of binary alloys has been overcome to some extent by the commercial development of a number of alloys based on the eutectoid composition of 78% Zn-22% Al (weight percent) [6].

The chemical composition of superplastic zinc-aluminium alloy, used in the present study was as follows: 20.5-23.0% Al, 0.3-0.6% Cu, 0.001% Mg, 0.1% Fe, 0.03% Si, 0.003% Pb, 0.0003% Cd, 0.0001% Sn,0.0001% Th, 0.005% others and the remainder is 20. The density of the alloy was reported as 6,25 g/em", The alloy was manufactured by ISC alloys Limited, Bristol, England.

Weight-loss Experiments

Square specimens (20mm x 20 mm x 2mm) of the zinc-aluminium alloy were cut from the sheet and a small hole of 1.5 mm diameter was drilled near the upper edge in each specimen for mounting the specimen into the corrosive medium. The specimens were prepared, cleaned and evaluated as per ASTM G1-81 [7]. The specimens were not stored in the desiccator and were immersed in the corrosive media just after the preparation. The surface area and mass of the test specimens were 9.00-10.00 cm and 4.00-5.00 g respectively. The corrosive medium (test solation) for the static immersion studies was 0.5N H_2SO_4. The test solution was prepared by proper dilution of AR grade sulphuric acid 17664-93-9] in deionised water. The inhibitors used were of AR grade Aniline [62-53-3] and potassium iodide [7681-11-01]. The concentrations of inhibitors studied ranged from 0.01-0.10 M/L of aniline and 0.004-0.070 M/L of potassium iodide. Five specimens were used for each corrosive medium for studying the corrosion rate at five different time intervals. The testing periods were 48, 54,60, 66 and 72 hours. The temperature, throughout the experiment was maintained at 30 ± 2 °C. The specimens were cleaned by the following method after the test:

The specimens were dipped in:

Ammonium hydroxide (NH₄OH, sp gr 0.90)	150 ml
Water to make	1 litre
Temperature	Room
Time	5-7 minutes

Potentiostatic Polarisation Measurement

Cut from the sheet of zinc-aluminium alloy. Within one hour of the experiment the working electrodes (test electrodes) were prepared. Each working electrode was drilled, tapped and mounted onto the electrode holder. The back and sides of the working electrode were coated with a mixture of perspex and wax from chloroform solution, leaving only the 1 cm² portion of the working electrode exposed to the test solution (0.5N H_2SO_4). The volume of the test solution was 300 ml in the polarisation cell (test cell or corrosion cell). The auxiliary electrode (platinum electrode) salt-bridge probe and other components were placed in the test cell and the salt-bridge was filled with the test solution (0.5N H_2SO_4). The working electrode was transferred to the test cell and the salt-bridge probe tip was adjusted in the manner that it was about 2 mm away from the test electrode. The open circuit potential E_{corr} (corrosion potential) of the test specimen, after 5 and 55 min immersion was recorded and E_{corr} was suppressed. After this the potentiostatic potential scan was started at a constant step rate of 10 mV/min and the corresponding current densities were recorded. The cathodic polarisation scan was performed first and after one minute the anodic polarisation scan was performed. The polarisation curve was plotted as a linear potential- current density curve and the cathodic and anodic potentiostatic polarisation data were plotted on semilogarithmic paper in accordance with practice G3-74 [7], (potential- ordinate, current density-abscissa). The polarisation resistance, Rp has been determined graphically as the tangent of the linear polarisation curve at the origin of the plot (AE=0) and b. Be (anodic and cathodic Tafel slopes) were obtained from Evan's diagram. Each step was performed as per ASTM G3-74, GS-87 and G59-78 [7].
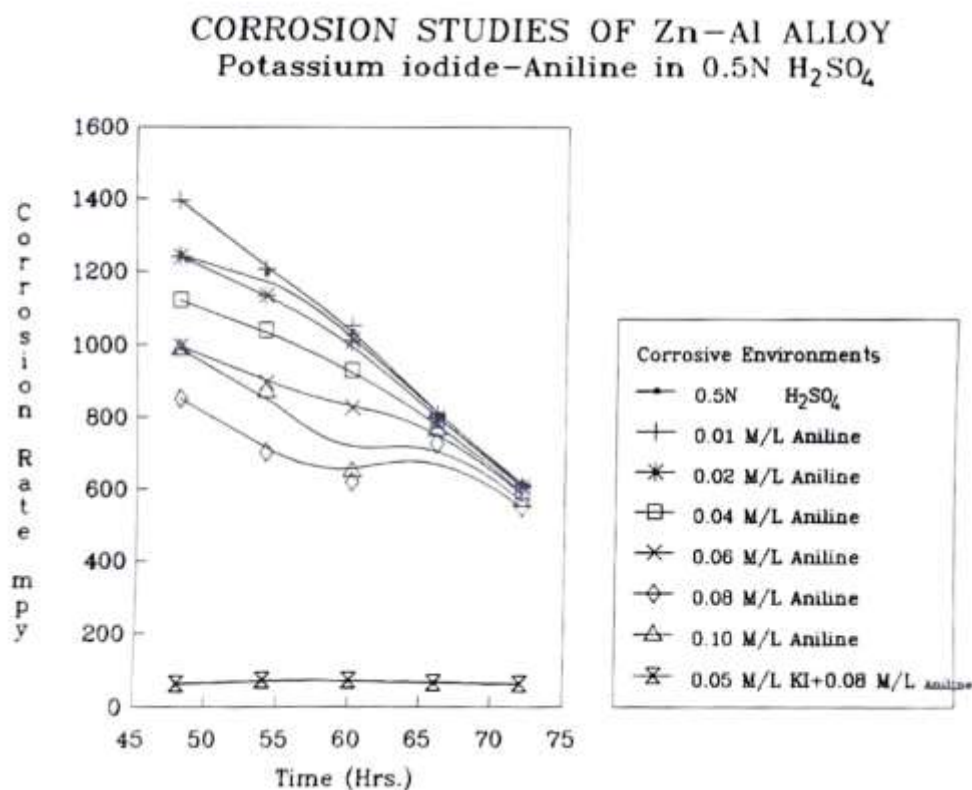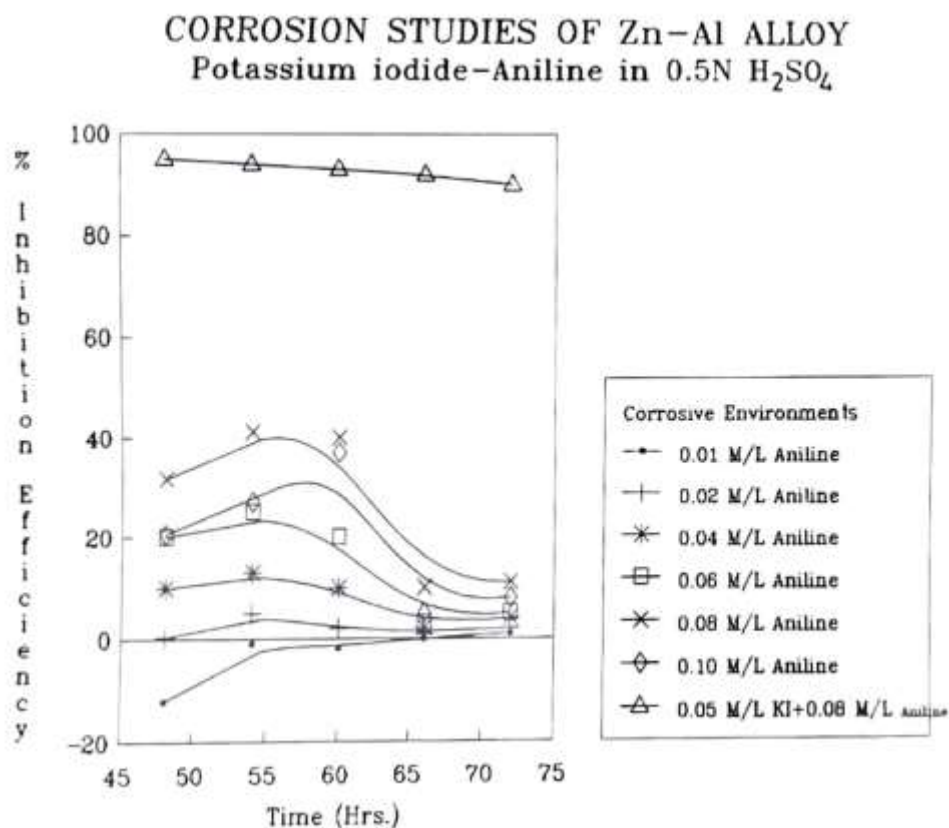
Figure 1. Corrosion studied (Corrosion rate) of Zn-Al Alloy Potassium Iodide-Aniline in 0.5N H₂SO₄.

Results and Discussions

Weight-loss Kinetics

The results of my investigations on corrosion of Zn-Al alloy in 0.5N H_2SO_4, with and without inhibitor(s) are presented in Figures 1-3. It will be seen that the corrosion rate of the alloy is very high in 0.5N H_2SO_4 in the absence of any inhibitor. Aniline at low concentrations (around 0.01 M/L) accelerates the corrosion rate but at higher concentrations inhibition in corrosion is observed. The corrosion rate is minimum with 0.08 M/L aniline concentration. Beyond itis concentration, the corrosion rate again increases showing stimulating effect. In general, the corrosion rate decreases with time. The maximum inhibition efficiency is obtained with 0.08 M/L aniline (about 41%) at 54 hours.

Corrosion studies of Zn-Al alloy in 0.5N H_2SO_4 in presence of potassium iodide show the same trend as observed with aniline. Potassium iodide at low concentrations (around 0.004 M/L) accelerates the corrosion of the alloy which is higher than the rate in the absence of inhibitor.
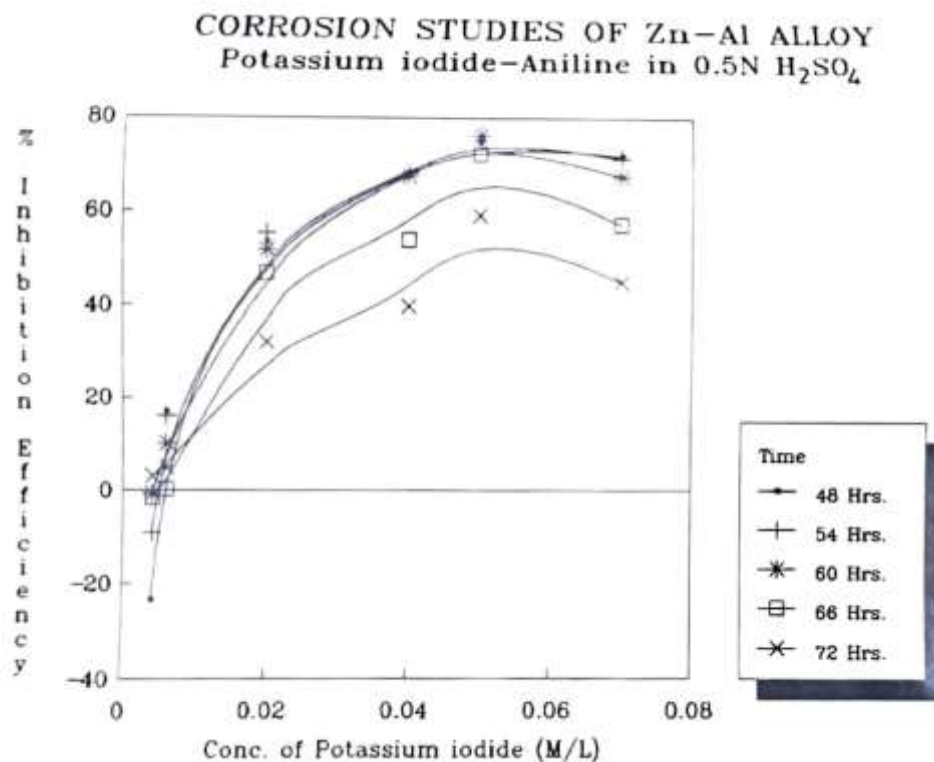
Figure 2. Corrosion studied (Inhibition Efficiency) of Zn-Al Alloy Potassium Iodide-Aniline in 0.5N H₂SO₄.

Again as the concentration of potassium iodide is increased the corrosion rate decreases and it is minimum with 0.05 M/L KI concentration. Beyond this concentration the corrosion rate again increases showing stimulating effect. As with aniline, the corrosion rate decreases with time. The maximum inhibition efficiency in this system is about 76% with 0.05 M/L KI at 54-60 hours. It is evident that considerable inhibition in corrosion rate can be achieved by such a synergistic combination. The inhibition efficiency also fairly good (90-95%).

Potentiostatic Polarisation Studies

Potentiostatic polarisation studies with the alloy in 0.5N H₂SO₄ show the corrosion process to be initially predominantly anodic but later it is under mixed control. The values of corrosion current density I_{corr} as calculated by linear polarisation and Tafel extrapolation methods are 4.65x10 and 5.00×10 A/cm². The addition of aniline (0.08 M/L) reduces the corrosion current density and shifts Ecorr slightly towards anodic direction. The corrosion process appears to be initially anodic but later it is under cathodic control. However, the corrosion process with 0.05M/L. KI in 0.5N H₂SO₄ becomes lower with shifting of E_{corr} towards anodic direction. The reaction is clearly anodically controlled. Synergistic combinations (0.05 M/L KI+0.05 M/L aniline, 0.05 M/L KI+0.06 M/L aniline, 0.08 M/L KI+0.08 M/L aniline, 0.09 M/L KI+0.08 M/L aniline) are all under anodic control and the corrosion current densities slightly increase or decrease for these combinations. These facts indicate that with Potassium iodide alone and with combinations where the concentration of potassium iodide is equal to aniline or slightly less or more than aniline, the corrosion process is under anodic control. The corrosion process with aniline alone is initially anodic but later becomes under cathodic control. For all other synergistic combinations where aniline concentration is higher and potassium iodide concentration is comparatively low, corrosion process seems to be initially under anodic control but later becomes under mixed control.

CORROSION STUDIES OF Zn−Al ALLOY
Potassium iodide−Aniline in 0.5N H₂SO₄

Figure 3. Corrosion studied (Inhibition Efficiency) of Zn-Al Alloy Potassium Iodide-Aniline in 0.5N H₂SO₄.

Conclusion

It can be concluded from my studies on weight-loss kinetics and potentiostatic polarisation measurements that both aniline and potassium iodide act as inhibitors in resolution of Zn-Al alloy in 0.5N H_2SO_4 at some suitable concentration. The synergistic effect of the two inhibitors as also obvious from the inhibition efficiency which is from 90-95%. The other observations are summarised below:

In the field of corrosion, the behaviour of solid alloy electrodes at anodic polarisation is of primary interest. In many cases steady state dissolution mode is virtually simultaneous i.e. anodic dissolution apparently proceeds without preferential dissolution processes. This holds, in particular, if alloys with similar electrochemical behaviour of the components are polarised to potentials that are anodic to the equilibrium potential of the more noble component. This means that simultaneous dissolution in the steady state may be preceded, however, by a transient period of preferential dissolution of less noble components. If, on the other hand, the nobilities of the alloy components differ considerably. And the electrode potential does not exceed the reversible potential of the more noble component significantly, steady state anodic dissolution may occur selectively, i.e. by preferential dissolution of less noble components.

Acknowledgement

References

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