Corrosion Behaviour of Rosenhain's Alloy in Different Corroding Media

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Attention to the unusual and eutectoid alloy in Zn - Al system was first drawn by Rosenhain et. al. [1]. This alloy has inadequate mechanical properties but it has a high transformation rate and is splendid for demonstrating isothermal transformations [2]. A review of literature reveals that most of studies of Zn - Al alloys has been carried out for cathodic protection [3] and as sacrificial anodes [4]. In aluminium - zinc alloys, zinc has only small influence on corrosion resistance in most environments. It tends to reduce the resistance of the alloy in acid medium and increase in alkaline medium [5]. Authors thought it interesting to study the corrosion behaviour of this unusual alloy in 1% NaCl, 3 % NaCl, ground water of Malaviya Nagar, Jaipur [6] and deionized water.

EXPERIMENTAL

The composition of Rosenhain's alloy is given in Table 1. A number of rectangular samples of Rosenhain's were prepared, cleaned and evaluated as per ASTM G1 [7]. Corrosion studies of this alloy was carried out by Weight Loss Method, Open Circuit Potential measurement and Tafel plots.

Weight Loss Method

Prepared samples were weighed carefully using Owa Labor single pan balance, then immersed in different corroding media. The samples were withdrawn at regular intervals, washed, dried and weighed. The corrosion rate was calculated in mpy as per ASTM G 31-72 [7]. To study the effect of mechanical treatment on corrosion, the specimen was rolled to reduce the thickness of the alloy by 10%, 20%, 30% and 40%. Weight loss experiments by static immersion test were conducted with this rolled alloy specimen in each corroding solution.

Open Circuit Potential

Positive end of a portable Toshniwal Potentiometer was connected to a platinum electrode; the test electrode (immersing in corroding medium) was connected to the negative pole of the potentiometer. Open circuit potential in each corroding medium was recorded with time.

Anodic and cathodic Tafel slopes were plotted by measuring potential and current using the three electrode corrosion cell CL - 95 supplied by M/S Elico India Ltd and Potentiostat /Galvanostat Model 551 supplied by M/S AMEL ITLY.

Table 1

% Composition of Rosenhain's alloy

Zn	Al	Cu	Mg	Fe	Si	Pb	Cd	Sn	Th	Others
76-79	20.5-23	0.3-0.6	0.001	0.1	0.03	0.003	0.0003	0.0001	0.0001	.005

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RESULTS AND DISCUSSION

It is evident from weight loss kinetic studies (Fig. 1) that the corrosion of the Zn-Al alloy is low in the various corroding solutions studied. However, the dissolution of the alloy is higher in 1% NaCl than in other corroding media. In general, the corrosion rate decreases sharply with time in all the cases, reaches a minimum value and shows a slightly increasing trend after very long exposure.

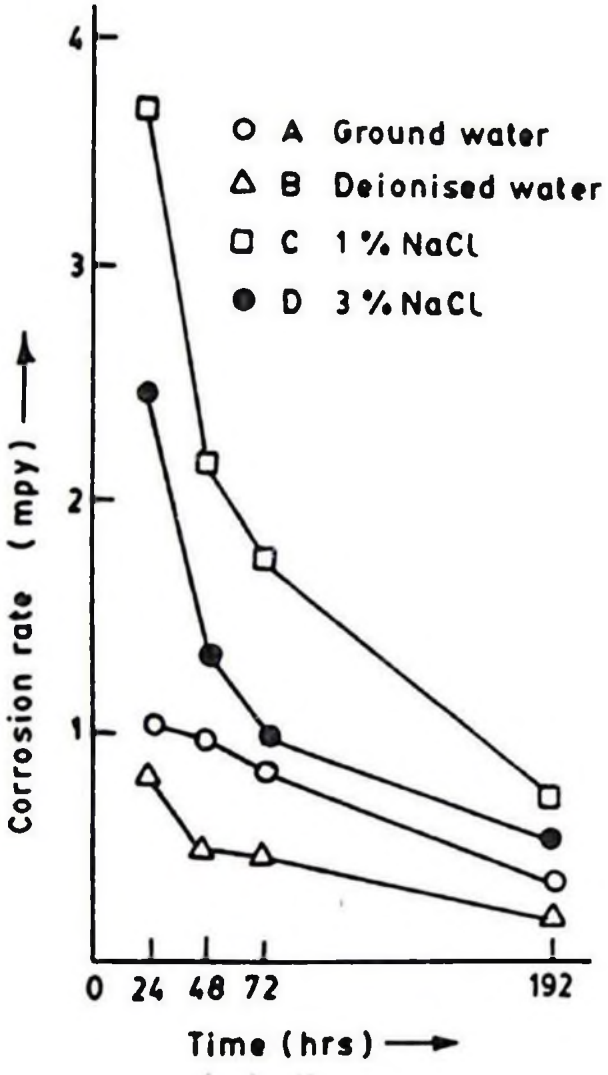


Fig 1. Kinetics of weight loss in different media

The corrosion of the alloy decreased with decrease in thickness or increased mechanical treatment. The results of investigations with 40% rolled alloy in different corroding solutions are given in Table 2.

Table 2

Corrosion Rate (MPY) of Mechanically Treated Alloy in Different Corroding Media after Different Time of Exposure (t)

Sample 40% rolled alloy

t (hrs)	Ground water	Deionized water	1%NaCl solution	3 % NaCl solution
24	0.8822	0.4671	1.7490	-
48	0.8087	0.2919	1.03613	0.1382
72	0.6862	0.2725	1.0203	-
96	0.2757	-	-	-

Mechanically treated alloy in different corroding media exhibit the same trend as observed with untreated alloy in weight loss studies. But corrosion rate is smaller for mechanically treated sample in all cases. Further, mechanically treated alloy samples show complete passivation at some stage during corrosion process. The passivation is reached earlier with 40% rolled sample (Table 2) in 3% NaCl solution.

Mechanical treatment of alloy surface causes decrease in the thickness of alloy, reduces the grain size of the particles, reduces the vacancies and makes the surface harder. This surface modification is responsible for the decrease in corrosion rate.

Table 3

OCP of the Alloy in Different Media with Time

Time hour	Ground water	Deionized water	1% NaCl solution	3 % NaCl solution
0	-0.970	-0.880	-0.980	-1.050
6	-0.977	-0.884	-0.987	-1.011
24	-0.840	-0.750	-1.05	-1.025
48	-0.874	-0.749	-1.031	-1.056
72	-0.836	-0.748	-1.026	-1.057
96	-0.840	-0.742	-1.036	-1.052

Open circuit potential (Table 3) shows higher negative values in 1% and 3% NaCl solutions than in ground water and deionized water. In the latter two cases, after an initial slight increase in negative potential, there is a shift of about 130 mV towards less active region in 24 hours. In 3% NaCl solution, the potential shifts initially to less active region but it stabilizes at its initial value with slight fluctuation. However in case of 1% NaCl, the shift is continuously in the more active direction. A negative shift in immersion potential may be attributed to the greater co-ordinating ability of OH^- and Cl^- ions on the metal surface as compared to water. It is reported [8] that the electrode potential of a couple usually becomes more negative as the co-ordinating ability of the solvent for the cation increases. However, a decrease in potential values is observed when these ions are desorbed.

The values of E_{corr} and I_{corr} obtained from the anodic and cathodic polarisation curves are given in Table 4.

Table 4

E_{corr} and I_{corr} from Tafel Extrapolation method in different media

Corroding media	I_{corr} (μA)	E_{corr} (V)
Ground water	5.623	-0.94
Deionized water	4.467	-0.87
1% NaCl solution	6.607	-0.985
3% NaCl soluton	5.370	-1.06

Mechanism

In Zn - Al alloy, both metals are amphoteric but since zinc is anodic to aluminium in galvanic series, zinc is likely to go into solution or precipitate an insoluble product $Zn(OH)_2$ in slightly alkaline or neutral solution. Mechanism of corrosion process appeares to be different in the presence and absence of chloride ions. When the alloy is immersed in water or deionised water, it appears that a protective layer is formed on Zn - Al alloy surface by the following mechanism:

$$Zn + 2\ OH \longrightarrow Zn(OH)_{2\ (surface)} + 2e^-$$

$$Zn(OH)_{2\ (surface)} \Longleftrightarrow ZnO_{\ (surface)} + H_2O$$

$$ZnO_{\ (surface)} \Longleftrightarrow ZnO_{\ (solution)}$$

There is a sharp decrease in the corrosion rate with time because of the formation of a protective layer on the alloy surface. The corrosion rate is low both in ground water and deionised water because of low hydroxyl ion concentration; However, as ground water has a higher pH (7.98), corrosion rate is also higher than in deionized water (pH=7.7). The mechanism of dissolution due to Cl^- are given below [11-12]:

$$Zn + Cl^- \Longleftrightarrow ZnCl_{ads} + e^-$$

$$ZnCl_{ads} + H^+ \Longleftrightarrow ZnClH^+$$

$$ZnClH^+ + Cl^- \Longleftrightarrow ZnCl_2 + H^+ + e^-$$

$$ZnCl_2 \Longleftrightarrow Zn^{2+} + 2\cdot Cl^-$$

Both OH^- and Cl^- are responsible for dissolution of zinc in 1% NaCl solution; however Cl^- removes more zinc. Initially both Cl^- and OH^- are adsorbed on the alloy surface faster, but the rate decreases with decrease in their concentration. Cl^- ions cover larger surface of the alloy and do not allow a protective layer to be formed. Hence, the corrosion rate in the later stages depend mainly upon the rate of adsorption of Cl^- ions. In a more concentrated solution of Cl^- (3% NaCl) the entire surface is covered by these ions and corrosion is only due to Cl^- ions. Dissolution due to Cl^- is slower than dissolution of metal by OH^-.

Thus the corrosion rate in 1% NaCl is higher than corrosion rate in ground water, deionized water and 3% NaCl solution.

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