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Effect Of Copper And Zinc Additives On The Corrosion Rate Of Aluminium alloys In Aqueous Solutions

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ABSTRACT

The corrosion behavior of five Al-alloys containing different amounts of copper (0-4%) or zinc (0-6%) was investigated in aqueous solutions of ammonium chloride, ammonium nitrate, sodium chloride, sodium hydroxide, and sodium silicate using weight loss measurements and eletrochemical methods, namely corrosion potential, polarization and cyclic polarization techniques. The results show that copper (or zinc) has an accelerating effect on the corrosion rate of the investigated alloys in all previous solutions except sodium hydroxide solution, where it has an inhibiting effect. The accelerating effect is explained by an anodic (in sodium chloride, sodium silicate, and ammonium chloride solutions) and cathodic (in ammonium nitrate solution) depolarization mechanism.The inhibiting effect is explained by an anodic polarization mechanism.

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INTRODUCTION

The corrosion rate measurements and pitting of different aluminium alloys were investigated by many authors [1-7]. Galvanic coupling of copper alloys with aluminium in (0.01 - 1N) sodium chloride solution showed that the increase in the dissolution rates of aluminium in different concentrations of sodium chloride was cathodically controlled and proportional to the average galvanic current density [8]. Chaudhary and others[9] showed that tungstate ions stimulate the corrosion of aluminium by acting as a cathodic depolarizer while morpholine polarizes local cathodic sites, acting as an inhibitor. A four-steps model was proposed for the localized corrosion of Al-alloys by Foley [10]. In 3.5% sodium chloride solution, the Al-alloy 2024 exhibited considerable corrosion attack, attributed to a cathodic control mechanism [11].

Although the corrosion of Al-alloys has been studied in a large variety of aqueous solutions, the specific role of some additives ,e.g. copper and zinc , has not been fully clarified. The aim of the present work is to investigate the individual effect of copper and zinc additions on the corrosion behaviour of Al-alloys in certain aqueous solutions.

EXPERIMENTAL

1. Material :

Five Al-alloys of different compositions, Table 1., were casted in metallurgy laboratories, M.T.C., Cairo, Egypt. Rectangular sheets of 40x30x3 mm and 10x10x3 mm were prepared as testing specimens for weight loss and polarization measurements, respectively. Samples were polished, degreased, washed and finally dried, according to sample preparation standards [12].

2. Solutions :

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Aqueous solutions of ammonium chloride, ammonium nitrate, sodium chloride, sodium hydroxide, and sodium silicate, of one molar concentration each, were prepared from reagent grade chemicals using distilled water. Lower concentrations of sodium chloride and sodium hydroxide solutions were prepared, by successive dilution, whenever needed.

3. Techniques and Apparatus :

Weight loss measurements were conducted using Sartorius analytical balance (Germany) of maximal sensitivity 0.1 mg and

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accuracy ± 0.2 mg. The electrochemical tests (corrosion potential, polarization, and cyclic polarization measurements) were conducted by an electronic potentiostat, model Tacussel PRT 10-05L, equipped with a pilot scanner, electronic millivoltmeter, and an X-Y recorder, magufactured by Tacussel Electronique.The working electrode, one cm² area, was fixed in a cylinder of cold setting resin, while electric contact was realized by using a copper wire immersed in mercury.The samples were scanned from cathodic to anodic region in the potential range of ± 250 mV w.r.t. the predetermined corrosion potential, at a scan rate of 20 mV/min, in stirred aqueous solutions. A scan rate of 60 mV/min was used for cyclic polarization experiments.

RESULTS

1. Weight Loss Results :

The effect , of copper additions on the weight loss of Al-alloys in the investigated aqueous solutions, is shown in Table 2. The corrosion rate increased with the copper content increase in all solutions except sodium hydroxide where corrosion rate decreased. Similarly, the corrosion rate of Al-alloys decreased in NaOH but increased in other solutions with the increase of Zn-content, Table 3.

2. Corrosion Potential Results :

The steady state corrosion potentials of Al- alloys in the investigated aqueous solutions are shown in Table 4. Al alloys were found the least noble in NaOH and the most noble in NH_4NO_3 solution. Also, alloy 120 was the most noble in all solutions except NaOH and NH_4NO_3 . The change of corrosion potential with time for Al-alloys in Na_2SiO_3 and NH_4Cl solutions is shown in Fig.1 and Fig.2. Similar curves were obtained in other solutions.

3. Determination of Electrochemical Parameters From Tafel Plots:

The corrosion potential , E cor, and corrosion current, i cor, of Al-alloys were determined graphically from polarization curves of these alloys in the investigated aqueous solutions. Due to the severe corrosion of Al-alloys in 1M NaOH solution noticed during the weight loss tests, a more dilute solution, namely 1x10 M, was used in polarization experiments. for the same reason, sodium chloride solution of 0.1 M was used. The polarization curves in 1x10 M NaOH solution is shown in Fig.3 and Fig.4. Similar curves were obtained in ther solutions. The numerical values are summarized in Table 5. It is clear that in 1x10 M NaOH, Al-alloy 120 has the largest corrosion current value, while in

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all other solutions, it has the lowest value of corrosion current.

4. Cyclic Polarization Results :

The cyclic polarization results of Al-alloys in the investigated solutions are classified into two groups. The curves of the first group are characterized by the following features:

- a. The reversed anodic current is higher than the corrosion current (measured at the corrosion potential) by, at least, one decade.
- b. The corrosion potential, extracted from the reverse scan, occurs at less noble potential than the original one.

The curves of the second group miss one (or all) of the previous features. The results show that the first group includes Al-alloys 121 and 122 in aqueous solutions of NH_4Cl and NaCl. All other combinations are included in the second group. Examples of cyclic polarization results are shown in Fig.5 and Fig.6 for Al-alloy 120 in 1 M NH_4NO_3 (second group) and Al-alloy 121 in 0.1 M NaCl solution (first group), respectively.

DISCUSSION

The results of weight loss show that the corrosion rates of all Al-alloys in sodium chloride, sodium silicate and ammonium chloride solutions were small (not remarkable). The most probable reaction in these solutions is :

$$A1 + 3H_20$$
 ----- $A1(0H)_3 + 3H^+ + 3e$ (1)

In ammonium nitrate solution, where corrosion rates were moderate, the corrosion action may be attributed to the formation of nitric acid with low concentrations which has a corrosive effect and the more favored reaction is :

Al _____ Al⁺³ + 3e

In sodium hydroxide solution, the remarkably high corrosion rates can be explained by the amphoteric property of aluminium and formation of soluble aluminates.

In solutions where corrosion rate was low or moderate, the general effect of Cu or Zn addition was found to increase the Alalloy corrosion with increase of Cu or Zn percentage, Tables 2. and 3. For example, in NH₂Cl solution (corrosion is little), the corrosion increases with the increase of Zn%; and this effect is

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prominent in NH₄NO₃ solution, where corrosion rate is moderate, Table 3. However, in NaOH solution, where corrosion rate is very high, it is clear that Cu or Zn has an inhibiting effect on the corrosion behavior of Al-alloys.

The corrosion potential results, Table 4., show that all the tested alloys have their noble potentials in $\rm NH_4NO_3$ solution, and their basic potentials in NaOH solution, while the potentials in the other three solutions are inbetween. Relating the weight loss results to the corrosion potential values, it is clear that corrosion rate is low in the potential range -500 to -850 mV, moderate at -100 to -350 mV, and very severe around the potential of -1300 mV. Although the results of corrosion potential extracted from polarization curves are not exactly the same as those measured before, Table 4., yet the results have the same trend of relative nobility of different alloys in various solutions. The noticeable differences in case of NaOH solutions may be attributed to the difference in concentration. According to corrosion parameters determined from polarization curves, Table 5., it is clear that in the solutions of NaCl, NapSiO2 and NH4C1 the addition of Cu (or Zn) increases the corrosion current and shifts E to less noble potential. This can be explained on the basis of anodic depolarization, shown by Evans diagram, Fig.7.

In ammonium nitrate solution, where the corrosion reaction is different, the increase of copper (or zinc) content results in higher values of i and shifts E to more positive values, i.e. copper (or zinc) acts as cathodic depolarizer, Fig.8.

In sodium hydroxide solution, the remarkably high corrosion rate of Al-alloys is generally attributed to the formation of soluble Na-aluminate. However, the increase of Cu (or Zn) content decreases the corrosion rate and shifts corrosion potential to more noble values, suggesting that Cu (or Zn) may act as anodic polarizer, Fig.7.

The cyclic polarization curves at constant scan rate were used to predict pit formation [13,14]. The pit formation may be predicted when the cyclic polarization curve has the following features :

- a. The reversed anodic current is higher than the corrosion current (measured at the corrosion potential) by, at least, one decade.
- b. The corrosion potential, extracted from the reverse scan, occurs at less noble potential than the original one.

The present results show that pit formation can be predicted only in aqueous solutions of NaCl, and NH_4Cl , and only for alloys 121 and 122. These results are in accordance with the visual inspection of samples after the immersion for 24 hours. So, in NH_4NO_3 and NaOH solutions, where corrosion is moderate or extensive and no chloride ions are present, the anodic

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dissolution occurs on the whole surface and no pits are formed. In addition to the known effect of chloride ions on pit formation, the present results reveal the role of copper which increases the probability of pit formation on Al-alloys in NaCl and NH₄Cl solutions. In absence of copper, the corrosion rate of Al-alloy 120 is very low in these solutions. However, the addition of copper (Al-alloys 121 and 122) increases the corrosion rate and accordingly the probability of pit formation. This is confirmed by the fact that pitting is greatly increased if traces of copper are present in the aqueous medium. The copper may slowly deposit by cathodic reaction providing a cathodic surface which increases the corrosion rate of aluminium.

CONCLUSIONS

- 1- The corrosion rate, of Al-alloys with (or without) copper or zinc, was low in aqueous solutions of ammonium chloride, sodium silicate and sodium chloride, moderate in ammonium nitrate, and very high in sodium hydroxide solution.
- 2- In all solutions (except sodium hydroxide) copper (or zinc) acts as an accelerator of Al-alloys corrosion.
- 3- In sodium hydroxide solution, copper (or zinc) acts as an inhibitor of Al-alloys corrosion.
- 4- The accelerating effect of copper or zinc is explained by anodic (or cathodic) depolarization, while the inhibiting effect is explained by anodic polarization mechanism.
- 5- Pitting corrosion can be predicted in case of Al-alloys containing copper immersed in sodium or ammonium chloride solutions.

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Alloy No.	Mg	Cu	Zn
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120	2.36		
121	2.47	1.93	No
122	2.55	4.12	are an 4m
123	2.60		2.55
124	2.40		6.00

Table 1 The Chemical Composition of the Al- alloys tested (% wt)

* The remainder is Al

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Table 2 Effect of Copper Additions on Weight Loss Results for Al- alloys in Several Aqueous Solutions (1M concentration) at 25°C

Alloy	Cu%		Wt. loss in aqueous solutions $\mu g/m^2 S$				
e S		NaCl	Na ₂ SiO ₃	NH ₄ Cl	NH4NO3	NaOH	
120	0.00	0.34	0.64	1.36	0.00	4105.51	
21	1.93	5.28	3.70	6.30	23.67	2121.96	
22	4.12	7.47	9.98	12.55	26.77	1874.10	

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Alloy Z	Zn%	W٤.	loss in aqu	ieous solutions, µg/m ² S			
		NaCl	Na2SiO3	NH4CI	NH4NO3	NaOH	
20	0.00	0.00	0.64	1.36	0.00	4105.51	
23	2.55	0.34	1.13	1.87	6.22	1524.52	
124	6.00	0.44	1.77	2.75	12.30	1435.67	

Table 3 Effect of Zinc Additions on Weight Loss Results for Al-alloys in Several Aqueous Solutions (1M concentration) at 25°C

Table 4 Measured Corrosion Potential (open circuit potential) of Al-alloys in Aqueous Solutions (1M concentration) at 25°C by Compensation Method

lloy	ŀ	Measured Corrosion Potential, mVSHE						
	NaCl	Na2SiO3	NH4CI	NH4NO3	NaOH			
120	-558	-518	-543	-333	-1348			
121	-608	-858	-588	-173	-1228			
122	-623	-683	-603	-133	-1198			
123	-618	-833	-708	-298	-1288			
124	-678	-723	-778	-183	-1228			

:24 Ecor		123 Ecol	122 Ecor	121 Ecor	120 Ecor Icor		Alloy Corr Par
	-753.0 r -2.5 x	-733.5 r 1.9 X	-599.0 7.0 X	-590.0 r 5.5 X	т – 540.5 т 9.5 Х	NaCl	rosion ameter
	10-51	10-5	-1 10 ⁻⁵ 3.	10-5	10-6 -5	(10 ⁻¹ M) Na	
	114.8 5 x 10 ⁻⁶	012.5 8X 10 ⁻⁶	166.0 5 X 10 ⁻⁵	025.5 9 X 10 ⁻⁵	365.0 5 X 10 ⁻⁷	¹ 2 ^{SiO} 3 ^(IM) 1	Aqueous So
	-798.0 3.5 X 10 ⁻⁵	-788.0 3.0 X 10 ⁻⁵	-616.0 6.1 X 10 ⁻⁵	-596.0 1.5 X 10 ⁻⁵	-590.5 3.5 X 10-6	NH ₄ CI (IM)	lutions
	-312.5 1.9 X 10 ⁻⁴	-395.0 1.5 X 10 ⁻⁴	-127.0 4.6 × 10 ⁻⁴	-167.0 4.4 X 10 ⁻⁴	-421.4 5.5 X 10 ⁻⁵	NH4NO3(1M)	
والمحافظ المحافظ والمحافظ والمحافظ والمحافظ والمحافظ والمحافظ والمحافظ والمحافظ والمحافظ والمحافظ والمحاف	-555.6 4.7 X 10 ⁻⁷	-706.0 5.6 X 10 ⁻⁷	-18.0 3.7 X 10-7	-56.4 7.3 X 10 ⁻⁷	-798.8 1.7 X 10 ⁻⁶	NaOH(10 ⁻⁴ M)	

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Fig. 1 Corrosion potential vs time curves for Al-alloys in 1M sodium silicate solution at 25°C.





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Fig. 3 Polarization curves for the tested Al-alloys (120, 123 and 124) in 1×10⁻⁴ M sodium hydroxide solution at 25°C. 金属

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Fig. 5 Cyclic polarization curve for the tested Al-alloy 120 in 1M ammonium nitrate solution at 25°C.



Fig. 6 Cyclic polarization curve for the tested Al-alloy 121 in 1×10^{-4} M sodium chloride solution at 25°C.



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Fig. 7 Anodic depolarizer. Fig. 8 Cathodic depolarizer. 1