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INHIBITION EFFECTS OF Co^{+2}, Ni^{+2} La^{+3} AND Ce^{+3} IONS ON THE CORROSION OF ALUMINIUM AND ALUMINIUM ALLOYS IN THE NaCl SOLUTION

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ABSTRACT

Corrosion inhibitors are widely used in aerated neutral sodium cloride solution. In this study, the effect of metal cations (Co^{+2}, Ni^{+2}, La^{+3} and Ce^{+3}) on the corrosion of aluminium and its alloys in an aerated 1 M NaCl solution were investigated by polarisation measurements. The inhibition efficiencies of metal cations were investigated by obtaining current-potential curves in 1M NaCl solution and by calculating corrosion characteristics from current-potential curves. Electrochemical studies showed these cations to axhibit inhibitive effect on the corrosion of aluminium alloys in the studied solution.

KEYWORDS: Aluminium alloys; Inhibition, Corrosion resistance; Metal cations

INTRODUCTION

Aluminium is more active compared with many other metals, but it shows good resistance to atmospheric corrosion other corrosive media. The main aim of the study is to obtain better mechanical and physical properties with small alloying elements. If it is alloyed with small amounts of other metals, the copper-containing alloys are the least resistant to corrosion, but in the form of sheet can be protected by being clad on both sides by a thin layer of pure aluminium. The aluminium alloys recommended for building purposes have good resistance.

Inhibition of corrosion is of high technological importance **[1]** and progress made in this field has been phenomenal in last few decades **[2-3].** Most of the early studies on the inhibition of corrosion of metals in neutral media have been related to the studies of organic compounds having π bonds and or containing N, O and S donor atoms. Chemical treatment in solutions containing cerium compounds has been widely studied for the prevention of localized corrosion of aluminium and its alloys**[4-7].** Cerium (III) compounds are enviromentally acceptable and effective inhibitors for corrosion of metals like aluminium and zinc **[8-16].**

It is well known that lanthanide ions form insoluble hydroxides **[17]** which enable them to be used as inhibitors. Lanthanides have a low toxicity and their ingestion or inhalation has not been considered harmful to health **[18]** The toxic effects of their oxides are similar to sodium chloride **[19].** Furthermore, lanthanides can be considered as economically competitive products **[20].**
Some studies have been carried out on the effect of metal cations on the corrosion behaviour of aluminium and aluminium alloys in neutral media. Drazic and Vorkapic studied the inhibition effects of manganese, cadmium and zinc ions on hydrogen evolution reaction during corrosion of iron in 0.25 M sulphuric acid solution and explained the inhibition by metal cations due to under potential deposition of ad atoms of these metals on iron **[21].** In the present study, inhibition effect of metal cations such as Co^{+2}, Ni^{+2}, La^{+3} and Ce^{+3} cations on aluminium and its alloys were studied in 1 M NaCl solution.

Additions of Co^{+2}, Ni^{+2} La^{+2} and Ce^{+2} metal cations into the corrosive media have proved to increase the corrosion resistance of aluminium alloys. This paper is devoted to the comparison of the inhibiting effect of some cations on pure aluminium, Al-8%Si-3%Cu, Al-4%Cu, Al-12%Cu and Al-22%Cu-4%Fe alloys in NaCl solution by using potentiostatic technique.

2. EXPERIMENTAL DETAILS

The inorganic salts solutions were prepared by dissolving of $CoCl_2$, $NiCl_2$, $LaCl_3$, and $CeCl_3$ in water. The electrodes were abraded with sand paper, washed with bidistilled water, and immersed in studied solutions. High grade reagent of $CoCl_2$, $NiCl_2$, $LaCl_3$ and $CeCl_3$ were used for experiments.

Pure aluminium and its alloys electrode were polished with emery paper 1200 grit then, the electrodes were cleaned with double distilled water and at the and electrodes were plunged into the aerated cell solution obtaining current-potential curves.

A high purity (99,99 %) aluminium and aluminium alloy rods (5mm diameter) were fixed with an adhesive in teflon. Chemical composition of aluminium alloys are given in **Table 1.** A saturated Hg/Hg_2Cl_2 as reference and a platinium wire as counter electrode was used experiments were performed on a Wenking potentiostat with an electrochemical Workstation computer programe. Experiments were obtained in aerated aqueous solutions at 25°C. Corrosion rates and polarisation resistances were calculated from Tafel extrapolation equation.

Table 1. Chemical compositon of aluminium alloys

Elements	Alloys			
	Al-8%Si-3%Cu	Al-4%Cu	Al-12%Cu	Al-22%Cu-4%Fe
Si	8.2828	0.8098	0.0086	0.17
Fe	0.7246	0.4400	0.1240	3.93
Cu	3.1938	4.0219	12.25	21.85
Mn	0.0999	0.6413	< 0.001	-
Mg	0.1448	0.4218	< 0.0005	-
Zn	0.3594	0.1199	0.0026	0.10
Ti	0.0142	0.0255	< 0.0020	-
Cr	0.0148	0.0331	< 0.0005	-
Ni	0.0236	0.0089	< 0.0020	-
Pb	0.1148	0.0220	0.0075	0.77
Sn	0.0249	0.0063	0.0095	-

3. RESULTS AND DISCUSSION

These current-potential curve show that Co^{+2} and Ni^{+2} ions were reduced on the aluminium alloys, but La^{+3} and Ce^{+3} ions were not reduced on the aluminium alloys in the same conditions (Figure 2). Co^{+2} and Ni^{+2} ions reduced approximetly -1.0 V (SCE) on the aluminium alloys. These results agreement with literature **[1-6].** The height of reduction peak on current-potential curves is related with the amount of adsorbed ions on the electrode surface (Fig. 1-2). Addition metal cations into in the neutral solutions is more effective on the corrosion of aluminium alloys formed barrier film and the corrosion rate should be low after asteady states surface condition was reached.

Fig 1 shows polarisation curves of the Al-8%Si-3%Cu, Al-4%Cu, Al-12%Cu and Al-22%Cu-4%Fe alloys in 1 M NaCl solution containing 10^{-2}M Co^{+2}, Ni^{+2}, La^{+3} and Ce^{+3} ions at 25°C.

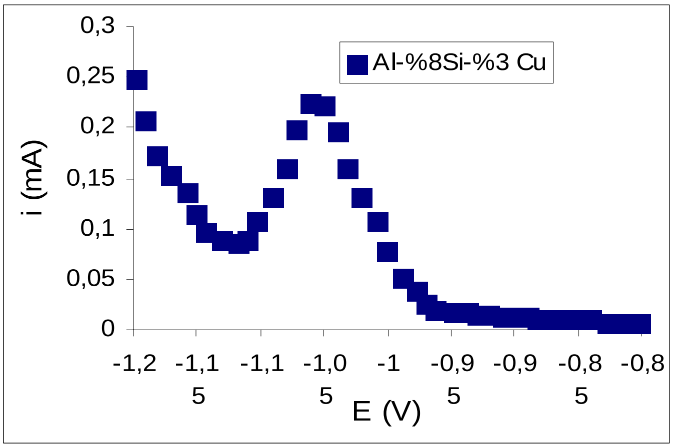
The corrosion characteristics of aluminium and aluminium alloys obtained form current potential curves were given in Table(2-7). The inhibition efficiency of cations, μ (%) was calculated by an equation,

$$\mu\ (\%) = 100\ (1 - i_{corr} / i^{\circ}_{corr})$$

where i°_{corr} and i_{corr} refer to the corrosion current densities of bare and coated electrodes with cations, in corrosive media respectively.

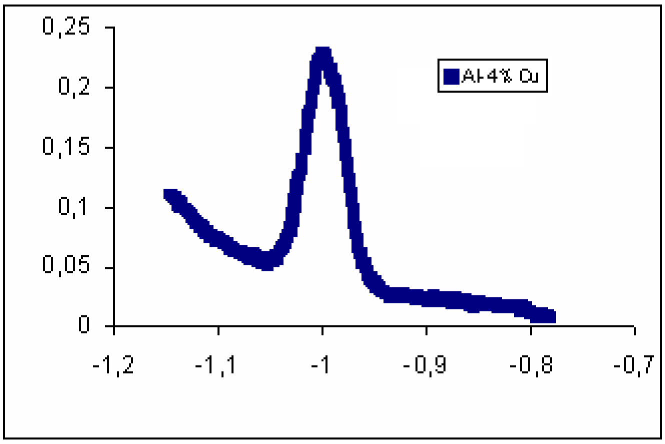
The obtained i_{cor} and the calculated protection eficiency, μ (%) values of cations from polarization curves are listed Table (1-7). The values of cathodic (β_c) and anodic Tafel slope (β_a) of metal cations and corrosion potentials are also given in the same Tables. Inhibition efficiency value of cations on the pure aluminium are 26%, 30%, 43 % and 55 % in 1 M NaCl solution containing 10^{-2} M cations respectively (Table 2).

The highest μ values were obtained for 10^{-2} M Co^{+2}, Ni^{+2}, La^{+3} and Ce^{+3} metal cations. The inhibition efficiency for Al-8%Si-3%Cu specimen are 50 %, 62 %, 65 % and 75 % respectively in studied solution (Table 3).



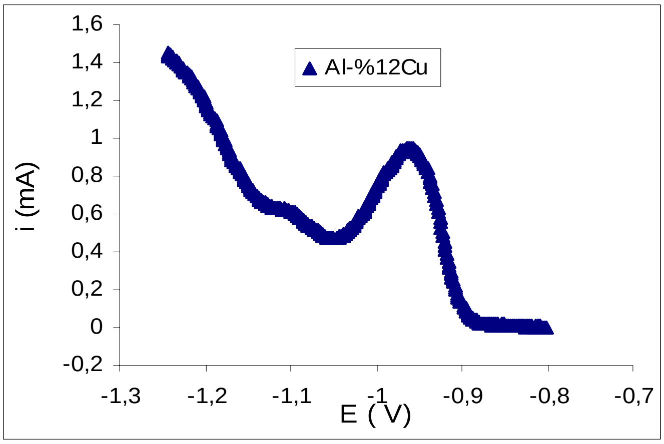
a)

Fig 1. a) Potentiodynamic polarisation curves of the Al-Si 8 %-Cu %alloy in aerated 1 M NaCl containing 10^{-2}M Co^{+2} ion.



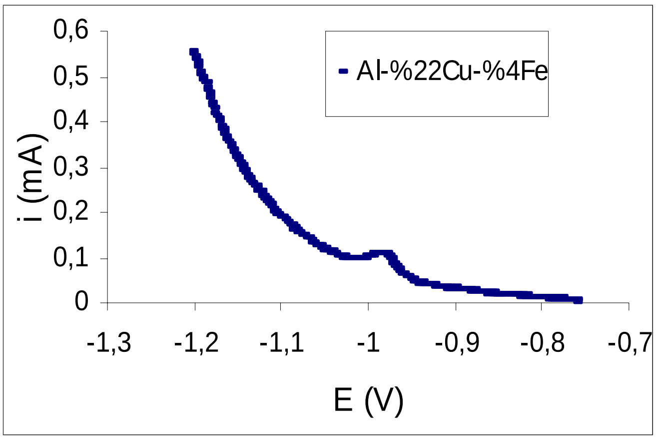
b)

Fig 1. b) Potentiodynamic polarisation curves of the Al-Cu % 4 alloy in aerated 1 M NaCl containing 10^{-2}M Co^{+2} ion.



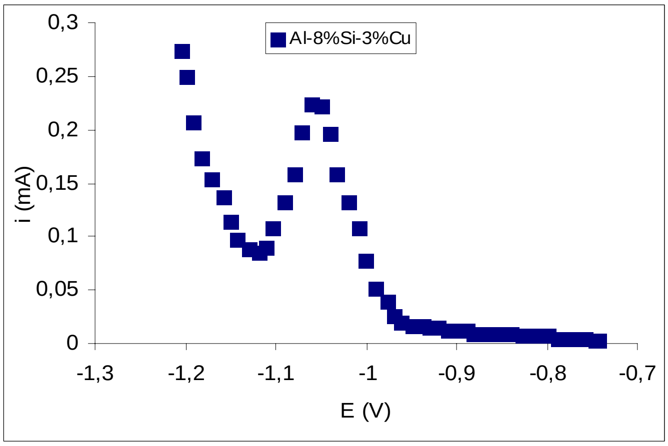
c)

Fig 1. c) Potentiodynamic polarisation curves of the Al-Cu % 12 alloy in aerated 1 M NaCl containing 10^{-2}M Co^{+2} ion.



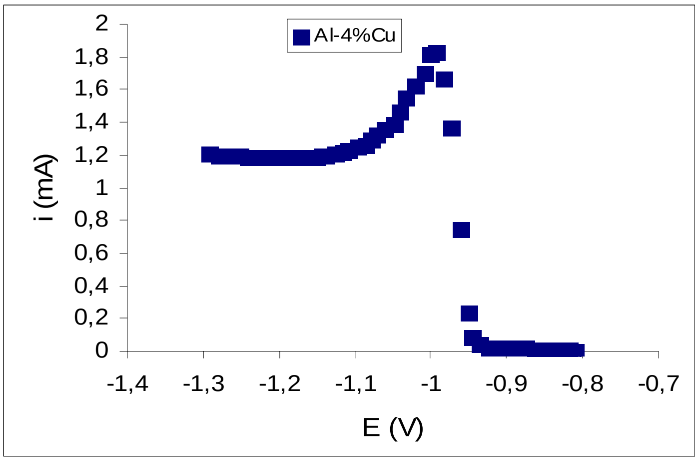
d)

Fig 1. d) Potentiodynamic polarisation curves of the Al-Cu 22 % -Fe % 4 alloy in aerated 1 M NaCl containing 10^{-2}M Co^{+2} ion.



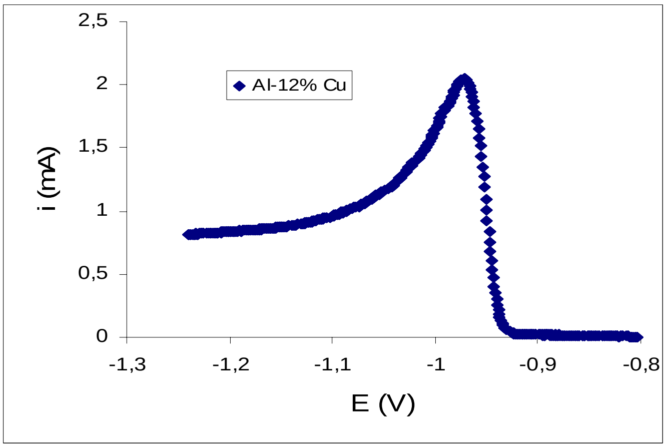
a)

Fig 2. a) Potentiodynamic polarisation curves of the Al-Si 8 %-Cu %3 alloy in aerated 1 M NaCl containing 10^{-2}M Ni^{+2} ion.



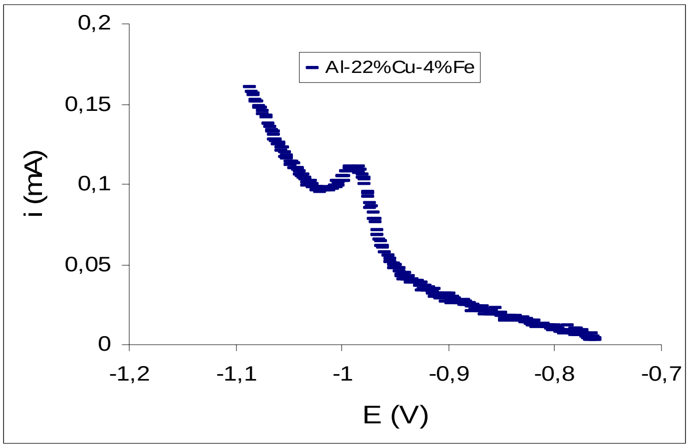
b)

Fig 2. b) Potentiodynamic polarisation curves of the Al-Cu % 4 alloy in aerated 1 M NaCl containing 10^{-2}M Ni^{+2} ion.



c)

Fig 2. c) Potentiodynamic polarisation curves of the Al-Cu % 12 alloy in aerated 1 M NaCl containing 10^{-2}M Ni^{+2} ion.



d)

Fig 2. d) Potentiodynamic polarisation curves of the Al-Cu 22 % -Fe % 4 alloy in aerated 1 M NaCl containing 10^{-2}M Ni^{+2} ion.

Table 2. Corrosion characteristics of pure aluminium obtained in 1 M NaCl solution containing $CoCl_2$, $NiCl_2$, $LaCl_3$ and $CeCl_3$ respectively.

1 M NaCl	$-E_{corr}$ *(mV)*	β_a *(mV)*	β_c *(mV)*	$R_p (\Omega)$	i_{corr} *(A/cm²)*	*% μ*
Blank	840	35	400	4500	10	-
$CoCl_2$						
0,1 mM	850	75	330	13250	6,5	35
10 mM	840	50	420	10500	5,7	43
$NiCl_2$						
0,1 mM	850	120	290	15750	7,5	25
10 mM	820	70	250	11250	7	30
$LaCl_3$						
0,1 mM	850	120	300	17000	8	20
10 mM	860	55	500	9250	4,5	55
$CeCl_3$						
0,1 mM	820	40	730	12000	7,8	22
10 mM	820	90	485	18750	7,4	26

Table 3. Corrosion characteristics of Al-8%Si-3%Cu alloy obtained in 1 M NaCl solution containing $CoCl_2$, $NiCl_2$, $LaCl_3$ and $CeCl_3$ respectively.

1 M NaCl	$-E_{corr}$ (mV)	β_a (mV)	β_c (mV)	$R_p (\Omega)$	i_{corr} (A/cm^2)	% μ
Blank	740	65	175	14720	11	-
$CoCl_2$						
0,1 mM	730	85	580	36480	8,6	22
10 mM	750	90	350	67200	3,8	65
$NiCl_2$						
0,1 mM	720	65	800	12160	14	-
10 mM	740	95	275	81280	4,2	62
$LaCl_3$						
0,1 mM	720	60	540	30720	6	45
10 mM	750	80	500	64000	5,4	50
$CeCl_3$						
0,1 mM	720	10	400	56008	5	55
10 mM	760	60	1150	73600	2,7	75

Table 4. Corrosion characteristics of Al-4%Cu alloy obtained in 1 M NaCl solution containing $CoCl_2$, $NiCl_2$, $LaCl_3$ and $CeCl_3$ respectively.

1 M NaCl	$-E_{corr}$ (mV)	β_a (mV)	β_c (mV)	$R_p (\Omega)$	i_{corr} (A/cm^2)	% μ
Blank	780	55	580	28800	8,0	-
$CoCl_2$						
0,1 mM	780	70	600	73600	6,0	25
10 mM	780	35	230	51200	3,1	60
NiCl2						
0,1 mM	780	100	560	35840	12	-
10 mM	780	30	330	66600	4,2	47
$LaCl_3$						
0,1 mM	720	40	520	40320	7,0	13
10 mM	750	50	450	11200	3,3	60
$CeCl_3$						
0,1 mM	770	130	400	131200	3,5	56
10 mM	790	155	350	192000	3,0	63

Table 5. Corrosion characteristics of Al-12%Cu alloy obtained in 1 M NaCl solution containing $CoCl_2$, $NiCl_2$, $LaCl_3$ and $CeCl_3$ respectively.

1 M NaCl	-E_{corr} (mV)	β_a (mV)	β_c (mV)	R_p (Ω)	i_{corr} (A/cm^2)	% μ
Blank	800	100	350	41600	8	-
$CoCl_2$						
0,1 mM	780	100	330	51840	7	13
10 mM	790	135	160	15625	4	50
$NiCl_2$						
0,1 mM	790	200	375	35200	11	-
10 mM	800	140	150	91520	2,7	65
$LaCl_3$						
0,1 mM	800	180	330	70400	6,8	15
10 mM	780	200	300	137600	5	37
$CeCl_3$						
0,1 mM	780	200	350	81920	5	38
10 mM	820	150	300	92800	3,8	52

Table 6. Corrosion characteristics of Al-22%Cu-4%Fe alloy obtained in 1 M NaCl solution containing $CoCl_2$, $NiCl_2$, $LaCl_3$ and $CeCl_3$ respectively

1 M NaCl	-E_{corr} (mV)	β_a (mV)	β_c (mV)	R_p (Ω)	i_{corr} (A/cm^2)	% μ
Blank	760	60	475	37120	9,1	-
$CoCl_2$						
0,1 mM	760	100	37	60800	8	32
10 mM	760	75	200	62720	6,8	25
$NiCl_2$						
0,1 mM	720	85	700	30720	18	-
10 mM	760	70	230	67200	4,6	50
$LaCl_3$						
0,1 mM	760	55	410	56320	7,2	20
10 mM	760	75	330	60800	6,1	32
$CeCl_3$						
0,1 mM	760	130	375	172800	7,8	15
10 mM	770	135	350	89600	6	35

Table 7. Corrosion characteristics of pure copper alloy obtained in 1 M NaCl solution containing $CoCl_2$, $NiCl_2$, $LaCl_3$ and $CeCl_3$ respectively

1 M NaCl	$-E_{corr}$ (mV)	β_a (mV)	β_c (mV)	R_p (Ω)	i_{corr} (A/cm^2)	% μ
Blank	290	65	530	33160	38	-
$CoCl_2$						
0,1 mM	290	60	500	47040	35	7,8
10 mM	290	70	700	68600	28	26
$NiCl_2$						
0,1 mM	290	65	450	54880	33	13
10 mM	290	60	450	47040	25	35
$LaCl_3$						
0,1 mM	300	65	500	52920	30	20
10 mM	300	70	500	50960	28	26
$CeCl_3$						
0,1 mM	300	70	500	60760	20	47
10 mM	300	65	700	58800	22	42

4. CONCLUSIONS

The addition of metal cations into 1 M NaCl electrolyte decreased the corrosion rates of pure aluminium, pure copper and aluminium-copper alloys. The Ni^{+2} and Co^{+2} cations adsorbed on the metal surface were reduced in the cathodic zone. The corrosion rate of aluminium alloys are dependent on the alloying material and solution composition.

Height of the current peaks and observed inhibition effect in the cathodic region are in agrement with each other. As the adsorbed Ni^{+2} and Co^{+2} amounts increased higer inhibition is observed. Average current peaks of the Ni^{+2} and Co^{+2} in 1M NaCl solution containing 10^{-2} M metal cations are given below.

Alloys	Co (mA)	Ni (mA)
Al-8%Si-3%Cu	1,4	0,29
Al-4%Cu	1,8	0,23
Al-12%Cu	1,2	0,53
Al-12%Cu-4%Fe	0,7	0,13

The observed inhibition effect of cations depend on chemical composition of aluminium alloys and concentration of cations.

Standart reduction potential of the Co^{+2} and Ni^{+2} metal cations are $E^{o}_{Co^{+2}/Co} = -0,28$ V (SHE) $=-0,53$ V (SCE), $E^{o}_{Ni^{+2}/Ni} = -0,23$ V (SHE) $= -0,48$ V (SCE) respectively. This observation clearly shows that reduction potential of the Co^{+2} and Ni^{+2} metal cations are near to the each other. Ni^{+2} and Co^{+2} metal cations are reduced at more negative potentials with overgrowth and lower cation concentration on the aluminium alloys. It was show that low ion concentration of nickel cation acts as a catalyst. The corrosion rate decreased with increasing concentration of metal cations.

ÖZET

Korozyon inhibitörleri havaya açık sodyum klorür çözeltisinde metal yüzeyinde kapatıcı katman oluşturarak etkimektedir. Bu çalışmada da Co^{+2}, Ni^{+2}, La^{+3} ve Ce^{+3} metal katyonlarının atmosfere açık 1 M NaCl çözeltisinde alüminyum ve alüminyum alaşımlarının korozyonuna etkisi polarizasyon ölçümleri ile araştırıldı. Metal katyonlarının inhibitör etkisi 1 M NaCl de elde edilen akım-potansiyel eğrilerinden belirlenmiş olan korozyon karakteristikleriyle incelendi. Elektrokimyasal veriler metal katyonlarının alüminyum ve alüminyum alaşımlarının korozyonu azatlığını gösterdi.

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