JOURNAL OF APPLIED ELECTROCHEMISTRY 22 (1992) 1175–1179

Effects of Ta, La and Nd additions on the corrosion behaviour of aluminium bronze in mineral acids

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Received 4 December 1991; revised 17 March 1992

Corrosion studies of aluminium bronze with and without additions of Ta, La and Nd were carried out in HCl, HNO_3 and H_2SO_4 solutions, using weight loss, polarization and impedance measurements. The study showed that the addition of each of Ta, La and Nd in small quantities effectively inhibited the corrosion of the alloy in HCl solution, the inhibition effect being greatest with low content of the alloying element. The inhibition of corrosion due to alloying additions was observed to be small in H_2SO_4 solution. In HNO_3 medium, these alloying elements at low level showed slightly beneficial effects while they had adverse effects at higher concentrations.

1. Introduction

Based on cost, strength and resistance to corrosion aluminium bronze is an advantageous material for engineering applications [1]. Some alloying elements such as iron, nickel, manganese, etc. are added to improve mechanical properties [1]. Nickel and manganese additions have also been observed to increase the corrosion resistance, but the iron-addition was found to be detrimental, particularly in HCl medium [2]. Tin-addition was reported to improve both the corrosion resistance and mechanical properties of the alloy containing iron and manganese as alloying elements [3]. The beneficial effects on corrosion were also found with the addition of chromium in iron-modified aluminium bronze [4].

A survey of literature shows that the influence of common alloying elements on the corrosion of aluminium-bronzes in different corrosive environments has been investigated [5] while the addition of tantalum, misch metal and rare earths have not been evaluated for their influence on corrosion, though these newer alloying elements, in small quantities, were observed to improve machinability considerably [6].

Very recently we have found that the addition of each of lanthanum (La), cerium (Ce) and neodymium (Nd) at low level reduces the corrosion of aluminium bronze type 701B (9.5% Al, 0.2% Mn, 90.5% Cu) in HNO_3 [7], H_2SO_4 [8] and HCl [9] solutions. The effect of these additives on the corrosion behaviour of iron-modified aluminium bronze has not been investigated.

This paper describes the study of the influence of minor additions of Ta, La and Nd on the corrosion of aluminium bronze containing 2% iron as an alloying element, in dilute solutions of mineral acids.

2. Experimental details

Aluminium bronze samples type B-150 (91% Cu, 7% Al and 2% Fe) were prepared by melting the proportionate amount of Cu (99.9% purity), Al (99.5% purity) and Fe (99.9% purity) in an oil-fired furnace at 1200 °C. Ta, La, and Nd-modified aluminium bronzes were obtained by melting the alloy and then adding the required amount of the alloying element; details of the experimental procedure can be found elsewhere [7]. The actual composition of the base alloy shown by chemical analyses was 91.3% Cu, 6.9% Al and 1.8% Fe (wt %).

The weight loss study was performed at 30 °C by immersing the alloy samples in the experimental solution. These samples were in the form of disks of ~2 cm diameter and ~0.15 cm thickness and prepared for corrosion tests as described earlier [7]. The percentage inhibition efficiency for different additions was computed [7] by determining weight losses of the base and the modified alloy in the same corrosive medium and using the expression,

$$E = \frac{a - b}{a} \times 100$$

where E is the percentage inhibition efficiency, and a and b are the weight losses of the base and modified alloy in the same solution, respectively.

An electrochemical impedance system (EG & G Princeton Applied Research Corp, Model 378-3) was used to carry out polarization and impedance measurements. The electrochemical cell employed in the study was similar to that described elsewhere [10]. The potential of the test electrode was measured with respect to the saturated calomel electrode (SCE).

In the polarization study, the open-circuit potential (o.c.p.) of the test electrode was initially recorded until a stable potential was attained. The electrode was then cathodically polarized at -600 mV/SCE for 3–5 min and was then brought back to o.c.p. and the anodic polarization curve was recorded at a potential scan rate of 1 mV s^{-1}. The experiments for impedance measurements were performed at the o.c.p. of the test

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Table 1. Effect of additions of Ta, La and Nd on the weight loss of aluminium bronze type B-150 in 1 M HCl (30 °C)

Amount of additives /wt %	Weight loss/$g\,m^{-2}\,day^{-1}$						
	Immersion period/h						
	24	48	72	96	120	144	168
Base	5.90	6.35	6.07	5.90	5.62	4.92	4.27
Ta 0.1	2.30	2.75	2.43	2.05	1.74	1.90	1.88
	(61)	(57)	(60)	(65)	(69)	(61)	(56)
0.2	4.80	4.40	3.64	3.83	3.09	2.90	2.60
	(19)	(31)	(40)	(35)	(45)	(41)	(39)
La 0.1	3.90	3.25	2.30	2.25	1.90	2.02	2.08
	(34)	(49)	(62)	(62)	(66)	(59)	(51)
0.25	4.40	3.50	2.80	2.87	2.58	2.42	2.33
	(25)	(45)	(54)	(51)	(54)	(51)	(46)
Nd 0.05	5.90	3.20	2.27	1.87	1.54	1.63	1.64
		(49)	(62)	(68)	(73)	(67)	(61)

The figures in brackets represent the percentage inhibition efficiency.

Table 2. Effect of additions of Ta, La and Nd on the weight loss of aluminium bronze type B-150 in 0.175 M H_2SO_4 (30 °C)

Amount of additives /wt %	Weight loss/$g\,m^{-2}\,day^{-1}$				
	Immersion period/h				
	48	96	144	192	240
Base	2.90	1.80	1.27	1.25	1.30
Ta 0.1	2.55	1.50	1.08	1.04	0.93
	(12)	(16)	(15)	(17)	(28)
0.2	2.65	1.65	1.10	1.02	0.98
	(9)	(8)	(13)	(18)	(25)
La 0.1	1.25	1.32	0.93	0.81	0.97
	(58)	(26)	(27)	(35)	(25)
0.25	1.80	1.35	0.98	0.94	1.12
	(38)	(25)	(23)	(25)	(14)
Nd 0.05	2.70	1.57	1.08	1.02	1.10
	(7)	(13)	(15)	(18)	(15)

The figures in brackets represent the percentage inhibition efficiency.

electrode in the frequency range 5×10^{-3}–10^5 Hz. Usually ten measurements were taken for each decade of frequency with an applied a.c. voltage of 10 mV (r.m.s.).

The effect of dissolved oxygen on the corrosion of the alloy was also examined by passing pure nitrogen [11] through the electrolyte under stirred condition for 45 min before the experiment. All electrochemical studies were made in an air-conditioned room at 25 ± 1 °C and in each experiment 100 cm^3 of the test solution was employed. Bi-distilled water was used in the preparation of the test solution.

3. Results and discussion

3.1. *Weight loss measurements*

The influence of minor additions of Ta, La and Nd on the corrosion of aluminium bronze containing 2% iron was studied in 0.1 M HNO_3, 1.0 M HCl and 0.175 M H_2SO_4 at 30 °C and the results are shown in Tables 1–3. The results indicate that the addition of each of Ta, La and Nd decreases the corrosion rate of the alloy in HCl solution considerably. These additions were, however, found to be less effective for the corrosion inhibition in H_2SO_4 solution. It is noteworthy that the additives showed best performance as corrosion inhibitor when they were present at low level in the alloy. The lowest Ta, Nd and La additions reduced the rate of corrosion of the alloy in 1 M HCl to nearly 60% during 144 h immersion while in H_2SO_4 for the same immersion period, the corrosion was inhibited to only 15–27%. On the other hand, in HNO_3 medium, 0.1% Ta, 0.1% La and 0.05% Nd additions showed a beneficial effect and reduced the corrosion of the base alloy nearly 7–14% in an 120 h immersion test. 0.25% La addition, on the contrary, played an opposite role. In an 120 h immersion test in HNO_3, 0.2% Ta decreased the corrosion rate of the alloy up to 72 h and had an adverse effect thereafter.

Comparison of the results obtained in this test and with those already reported [7–9] for aluminium bronze type 701B shows that the presence of iron in the alloy produces detrimental effects on the corrosion stability in the test solutions employed. In HCl medium La and Nd have better corrosion inhibition properties in the presence of iron in the alloy than in its absence. However, in HNO_3 and H_2SO_4 solutions, no significant difference in their inhibiting actions was observed regardless of the presence of iron in the alloy.

3.2. *Open circuit potential measurements*

The study indicated that the o.c.p. of the test samples gradually became more noble and attained a steady value in 50–60 min, regardless of the nature of the corrosive medium and of alloying elements. Steady values of the o.c.p. under various conditions are shown in Table 4. In HNO_3 medium, the o.c.p. of the base alloy does not change with small additions of Nd

Table 3. Effect of additions of Ta, La and Nd on the weight loss of aluminium bronze type B-150 in 0.1 M HNO_3 (30 °C)

Amount of additives /wt %	Weight loss/$g\,m^{-2}\,day^{-1}$				
	Immersion period/h				
	24	48	72	96	120
Base	100.5	99.5	84.0	75.2	67.6
Ta 0.1	58.0	61.0	51.7	62.1	60.5
	(42)	(39)	(38)	(17)	(10)
0.2	57.8	68.2	67.7	86.7	77.6
	(42)	(31)	(19)		
La 0.1	45.0	73.5	61.0	61.7	62.5
	(55)	(26)	(27)	(18)	(07)
0.25	149.0	88.3	97.3	82.0	85.8
Nd 0.05	40.4	33.3	43.3	48.5	57.8
	(60)	(66)	(48)	(35)	(14)

Figures in brackets represent the percentage inhibition efficiency.

Table 4. Open circuit potentials of aluminium bronzes in acid solutions (25 °C)

Amount of additives /wt %	*o.c.p./mV*		
	[HNO_3] 0.1 M	*[HCl] 0.5 M*	*[H_2SO_4] 0.175 M*
Base	11	−304	−110
Ta 0.1	13	−369	−143
0.2	13	−325	−129
La 0.1	−38	−322	−137
0.25	−29	−304	−117
Nd 0.05	20	−370	−113
Base (deaerated)	−18	−351	−139

and Ta, however, it shifts negatively in the presence of La. On the other hand, with the exception of 0.25% La, other additions (La, Ta and Nd) made the o.c.p. of the alloy considerably more negative in 0.5 M HCl. In 0.175 M H_2SO_4, the o.c.p. of the base alloy also shifted towards the less noble side with each alloying addition. Similar results were obtained in the case of aluminium bronze type 701B in HNO_3 [7].

The steady open circuit potentials for the base alloy with and without additions were highly negative in HCl and H_2SO_4 solutions as compared to their values in 0.1 M HNO_3. The large negative open circuit potential may result from the modification of the alloy surface due to the adsorption of Cl^- and SO_4^{2-} ions. In order to examine the possible influence of acid anions, the o.c.p. of the base alloy was measured in different concentrations of H^+, NO_3^- and SO_4^{2-} ions; the results are given in Table 5. The H^+ ion concentration was varied keeping the ionic strength of the medium constant ($\mu = 0.5$) with the help of KNO_3. This study reveals that the change in H^+, as well as the NO_3^- ion concentration, does not change the o.c.p. of the base alloy, whereas the potential became strongly negative in the presence of each of Cl^- and SO_4^{2-} ions, the effect being greatest with Cl^- ions. Thus, the results clearly demonstrate the strong influence, particularly of Cl^-

Table 5. Effect of H^+, NO_3^- and SO_4^{2-} ions on open circuit potential of aluminium bronze type B-150 in HNO_3 solution (25 °C)

(a) $\mu = 0.5$

[HNO_3]/M			
0.05	*0.10*	*0.15*	*0.20*
10	11	13	14

(b) [HNO_3] = 0.1 M

[KNO_3]/M			*[K_2SO_4]/M*	*[KCl]/M*
0.2	*0.3*	*0.5*	*0.01*	*0.01*
11	12	15	−35	−245

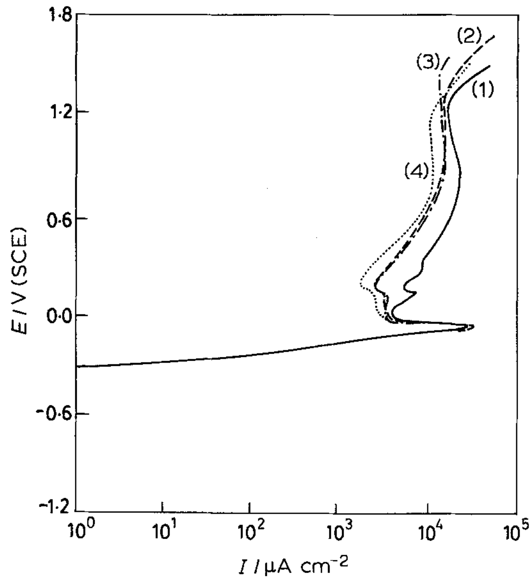

Fig. 1. Effect of Ta, La and Nd additions on the anodic polarization curve of aluminium bronze type B-150 in 0.5 M HCl (25 °C). (1) Aluminium bronze (91% Cu, 7% Al, 2% Fe), (2) 0.1% Ta, (3) 0.1% La and (4) 0.05% Nd.

ions, on the surface modification of the alloy. Further, deaeration of the medium also resulted in a negative shift of the o.c.p.

3.3. *Polarization measurements*

The anodic polarization curves were determined on aluminium bronze as well as on modified aluminium bronzes in dilute solutions of HCl, H_2SO_4 and HNO_3 at 25 °C. Small additions of Ta, La and Nd decreased the corrosion rate in 0.5 M HCl, particularly, by reducing the passivity current. The magnitude of the reduction was, however, observed to be greater with the low content of the alloying addition. Similar effects of La-addition on the passivity of the alloy were also found in 0.175 M H_2SO_4. On the other hand, 0.1% Ta addition slightly reduced the passivity current, while higher addition had no influence on the anodic dissolution of the alloy in 0.175 M H_2SO_4. Nd-addition was found to slightly enhance the corrosion rate. Typical anodic Tafel plots for the alloy in the case of HCl and H_2SO_4 solutions are shown in Figs 1 and 2. Only curves for the base alloy and the alloy treated with the lowest amount of La, Ta and Nd are shown.

In HNO_3 medium, Ta, La and Nd additions at low level did not show any noticeable beneficial effects on the anodic corrosion behaviour of the alloy, on the contrary, the higher additions showed harmful effects. Dissolved oxygen was also found to be harmful.

It is known [1] that the high resistance to corrosion of aluminium bronzes is due to the formation of a stable surface oxide film, essentially of alumina. In the presence of the alloying additions the stability of this is somewhat enhanced, possibly due to the formation of mixed oxides. The reduced effectiveness of the additives at higher levels can be attributed to their large

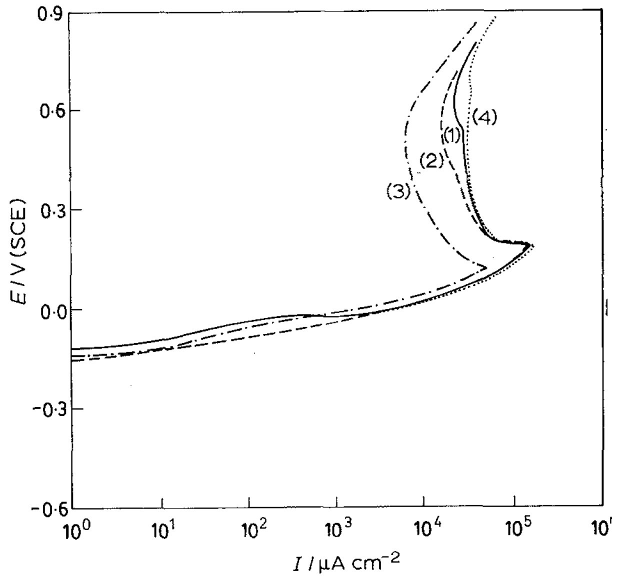

Fig. 2. Effect of Ta, La and Nd additions on the anodic polarization curve of aluminium bronze type B-150 in 0.175 M H_2SO_4 (25 °C). Key: as for Fig. 1.

atomic volumes, causing inhomogeneity in the alloy system.

3.4. *Impedance measurements*

Figures 3–5 show impedance diagrams for aluminium bronze and 0.1% Ta, 0.1% La and 0.05% Nd-modified aluminium bronzes in HNO_3, HCl and H_2SO_4 solutions. These diagrams indicate only one capacitive semicircle, showing distortion at the lower frequency end, particularly in HCl and HNO_3. The observed distortion may be due to a contribution of the Warburg impedance. Values of the charge transfer resistance (R_t), as shown in Table 6, were determined by constructing the Bode plot and using the expression,

$$R_t = 2|z| \tan \phi_{max}$$

where, $|z|$ is the magnitude of the total impedance corresponding to maximum phase shift, ϕ_{max}.

As the charge transfer resistance is inversely proportional to the corrosion rate, an increase in the R_t value implies a decrease in the corrosion rate. Thus, each additive improves the corrosion resistance of the alloy greatly in HCl solution. Of these, 0.1% Ta and 0.05% Nd displayed outstanding performance with regard to corrosion inhibition. However, these additions were less effective in HNO_3 and H_2SO_4 solutions. The higher additions of Ta and La showed deleterious effects on the corrosion behaviour of the alloy in HNO_3. Nd-addition also exhibited harmful effects on the corrosion process in H_2SO_4 solution. The removal of dissolved oxygen from the electrolyte greatly enhanced the corrosion resistance of the alloy.

Thus, weight loss, polarization and impedance measurements gave similar results.

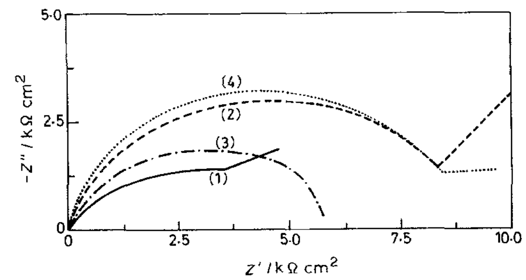

Fig. 3. Impedance plots for aluminium bronze type B-150 and Ta, La and Nd-modified bronzes in 0.5 M HCl (25 °C). Key: as for Fig. 1.

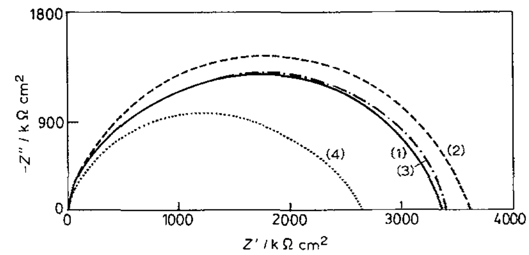

Fig. 4. Impedance plots for aluminium bronze type B-150 and Ta, La and Nd-modified bronzes in 0.175 M H_2SO_4 (25 °C). Key: as for Fig. 1.

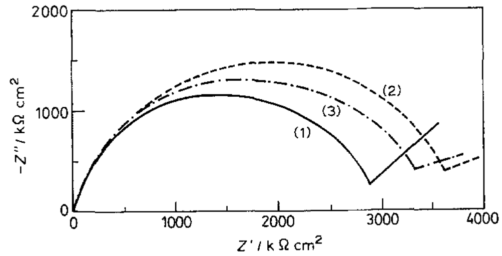

Fig. 5. Impedance plots for aluminium bronze type B-150 and La and Nd modified bronzes in 0.1 M HNO_3 (25 °C). (1) Aluminium bronze (91% Cu, 7% Al, 2% Fe), (2) 0.1% La and (3) 0.05% Nd.

4. Conclusion

This study has shown that Ta, La and Nd additives work better as the corrosion inhibitor when they are at low concentration in aluminium bronze alloys. Further, the additives are highly effective in reducing corrosion in HCl, however, the beneficial effects are small in H_2SO_4. Ta, La and Nd additions are not beneficial in HNO_3 medium.

Acknowledgement

The authors wish to thank Professor R. Sharan, Head

Table 6. Values of R_t *for aluminium bronzes in acid solutions (25 °C)*

Amount of additives /wt %	$R_t/K\Omega\,cm^2$		
	[HCl] 0.5 M	*[H_2SO_4] 0.175 M*	*[HNO_3] 0.1 M*
Base	4.7	3.6	2.5
Ta 0.1	10.0	3.9	2.8
0.2	6.5	3.6	2.0
La 0.1	5.5	4.5	3.4
0.25	4.7	3.7	2.0
Nd 0.05	9.5	2.7	3.1
Base (deaerated)	15.2	7.2	16.6

Acknowledgement

The authors wish to thank Professor R. Sharan, Head of the Forge Technology Department, Ranchi, India, for providing alloy samples for the present study.

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