JOURNAL OF APPLIED ELECTROCHEMISTRY **13** (1983) 807–812

Tungstate induced corrosion of some aluminium alloys in acidic chloride solution – An approach for controlling it with morpholine

R. S. CHAUDHARY, P. N. S. YADAV, C. V. AGARWAL

Applied Chemistry Section, Institute of Technology, Banaras Hindu University, Varanasi-221 005, India

Received 17 February 1982; revised 21 March 1983

The corrosion behaviour of some aluminium alloys (1060, 1100 and 3003) in acidic chloride solution ($pH = 1$) have been studied in the presence of various concentrations of tungstate ions. The alloy most vulnerable to the effects of tungstate ions is 1100 followed by 1060 and 3003 alloys. After six hours of immersion the alloys exhibit 6 to 8 times higher corrosion rates compared to that in the blank solution containing only chloride ions. The experiments suggest that the tungstate ion stimulates the corrosion of aluminium by acting as a cathodic depolarizer. Morpholine effectively arrests the dissolution of the alloys in the blank electrolyte as well as in the presence of tungstate ions. Morpholine polarizes local cathodic sites to act as an inhibitor. Tungstate ions are not adsorbed on the surface in the presence of morpholine and a synergistic effect is obtained at higher concentrations of morpholine. A Langmuir adsorption isotherm has been used to explain the data.

---

1. Introduction

Aluminium alloys commonly do not corrode because of the presence of an impervious natural oxide film on its surface. Aluminium is, however, very prone to corrosion in the presence of chloride ions. Such corrosion becomes very serious in the presence of foreign ions which have a depolarizing action on the electrochemical reactions. In our earlier publication the effect of some ions such as Cu^{2+}, Ni^{++} etc. on the corrosion of aluminium in hydrochloric acid solution has been reported [1].

Tungstate ions are used as a corrosion inhibitor in many systems. It has been observed, however, that the dissolution rate of aluminium alloys increases when tungstate ions are added at lower concentrations [2]. In the present investigation, the kinetics of dissolution of some aluminium alloys in acidic chloride solutions containing tungstate ions have been studied and an attempt has been made to control the dissolution by using morpholine.

2. Experimental details

Aluminium alloys with the following composition in sheet form (24 SWG), supplied by M/S. HINDALCO, Renukoot (Mirzapur), India, were used for the experiments:

Grade	*% alloy elements*				
	Si	Fe	Mn	Mg	Cu
1060	0.12	0.02	0.04	–	–
1100	0.13	0.52	0.068	0.021	0.01
3003	0.16	0.58	0.78	–	–

The specimens were polished with wax-coated emergy paper of grade 1/0 to 5/0 followed by cleaning with benzene, soap, tap water and finally degreased with acetone. The specimens were stored in a vacuum desiccator. All the chemicals used were of AR grade and the solutions were prepared in triply distilled water. The weight loss experiments were performed in 500 cm^3 Corning glass beakers having 300 cm^3 of the electrolyte.

Electrochemicals studies were carried out using a flag shaped specimen having 2 cm^2 working area. The stem of the specimen was covered with a thin layer of pure paraffin wax. The auxiliary electrode was a platinum foil and the experiments were carried out in a Pyrex glass cell. All the potentials

0021–891X/83 $03.00 + .12

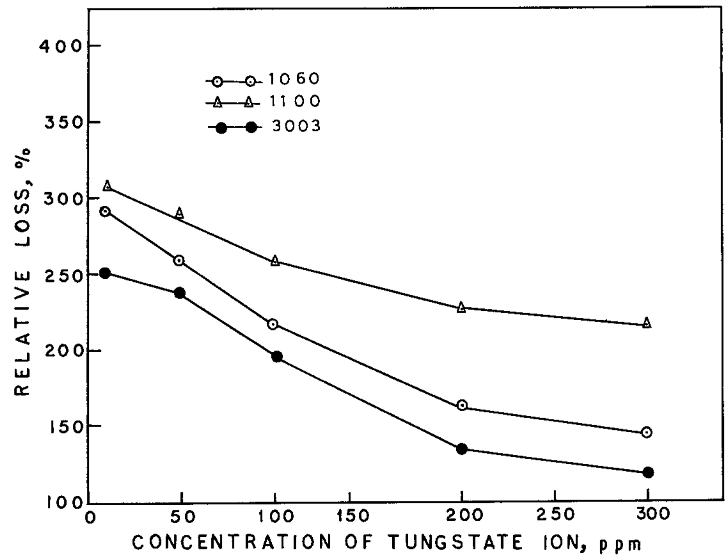

Fig. 1. Variation of relative percentage loss with concentration of tungstate ions at 45° C.

were measured against a saturated calomel electrode. The polarization studies used a Wenking potentiostat (model LB 75 M). All the experiments were performed in a thermostat at a temperature of 45° C.

3. Results and discussion

The variation of the weight loss with change in the concentration of the tungstate ions is shown in Fig. 1. The relative percentage loss, RPL, is relative to the blank solution containing only chloride ions and has been calculated using the equation

$$\mathrm{RPL} = \frac{W_\mathrm{p}}{W_\mathrm{a}} \times 100$$

where W_p is either the weight loss in the acidic chloride solution in the presence of tungstate ions or morpholine or in the presence of 10 ppm tungstate ions and morpholine; W_a is either the weight loss in acidic chloride solution or in the presence of 10 ppm tungstate ions. Tungstate ions stimulate the corrosion rate of the alloys at all concentrations but the maximum dissolution rate has been found at lower concentrations, i.e. at 10 ppm. The acceleration of the corrosion by anions at lower concentrations has been reported in the literature [3–5]. In neutral and alkaline solutions, this increase in the corrosion at lower concentrations is explained due to their depolarizing action on the oxygen reduction reaction. In the case of an acidic solution, however, the augmentation behaviour of tungstate ions is due to a depolarizing action on the hydrogen evolution reaction. The dissolution rate of 1100 alloys was found to be maximum followed by 1060 and 3003 alloys. In the blank solution the dissolution rate of the alloys was in the same order.

Fig. 2 shows a plot of relative percentage loss against time in the presence of 10 ppm of the tungstate ions. The dissolution rate of the alloys was very high in the initial stages but gradually decreased with the passage of time. After a period of 40 h, the dissolution rate becomes almost constant. On the surface of the specimen, when removed after the completion of the experiment, fine shining particles were observed adherent to it. It seems that the ions which initially get adsorbed on the surface, react with Al^{+++} to form a corrosion product which blocks the active sites of the surface.

Relative percentage loss has been plotted against concentration of morpholine in $\mathrm{cm}^3\,\mathrm{dm}^{-3}$ in Figs. 3a and b for 24 h of immersion in the absence and the presence of 10 ppm of tungstate ions, respectively. The RPL decreases with the increase in the concentration of morpholine in both cases and corrosion of the alloys completely stops at a concentration of 15 $\mathrm{cm}^3\,\mathrm{dm}^{-3}$ of morpholine. Morpholine is less effective on 3003 alloy in comparison to its effect of 1060 and 1100 alloys. At higher concentrations of morpholine a synergistic effect of tungstate ions is very clear from the plot Fig. 3b. The sharp decrease in the corrosion rate in

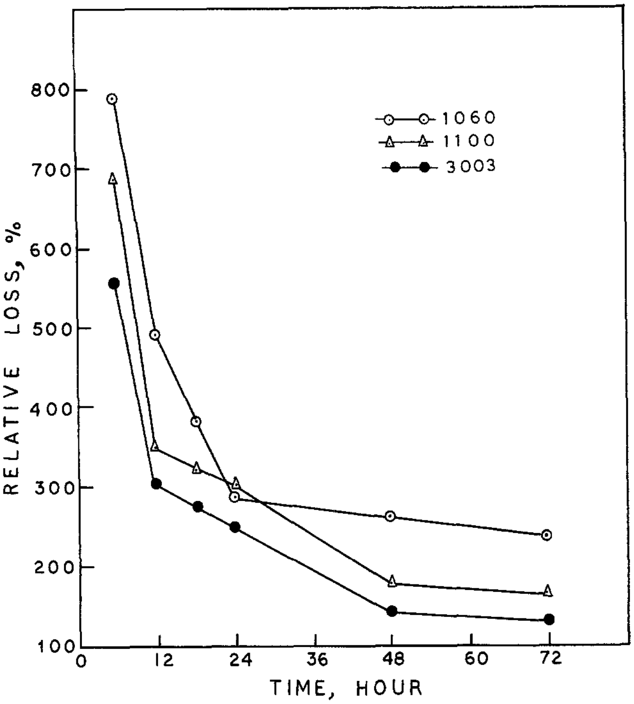

Fig. 2. Variation of relative percentage loss with immersion period at 45° C.

the presence of morpholine is due to the fact that morpholine has an electron donating capacity which is responsible for the adsorption of morpholine molecules on the metal surface through an unshared electron pair belonging to the nitrogen atom. It is, therefore, possible that the morpholine may get directly adsorbed on the metal surface and thereby retard the rate of corrosion. No shining particles were observed on the surface of the specimen after the experiment, thereby suggesting that tungstate ions were not adsorbed in the presence of morpholine.

Adsorption plays an important role in the prevention of metallic corrosion by inhibitors. The inhibitors are adsorbed on the metal surface and decrease the surface area available for cathodic or anodic reactions to take place. If the decrease in surface area is directly proportional to the decrease in corrosion rate then a Langmuir adsorption isotherm is applicable which is given by the equation

$$\log \theta/1 - \theta = \log A + \log C - Q/2.3RT$$

where θ is the surface covered by the inhibitor, A, a temperature dependent constant, C, the bulk

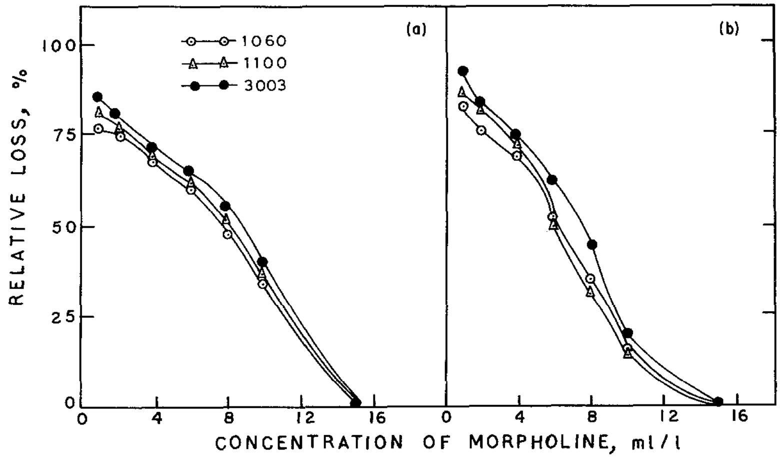

Fig. 3. Variation of relative percentage loss with concentration of morpholine at 45° C. (a) In the absence of tungstate ions. (b) In the presence of 10 pm tungstate ions.

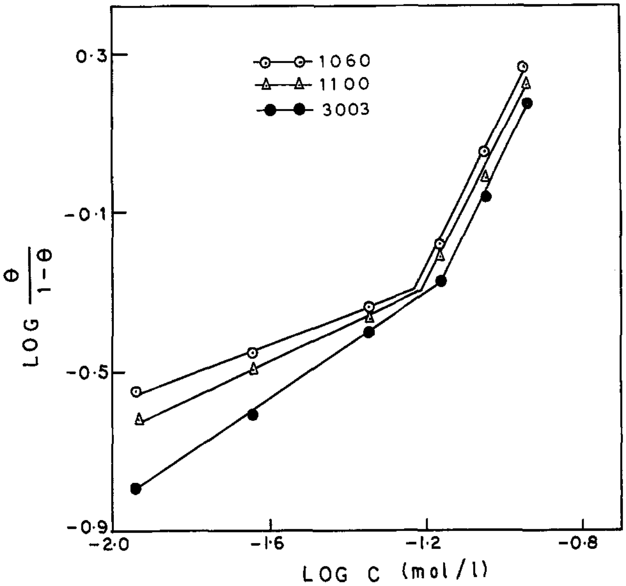

Fig. 4. Plots for the adsorption studies of morpholine in the absence of tungstate ions.

concentration of the inhibitor (mol dm^{-3}) and Q, the heat of adsorption. It is expected that the plot of log $\theta/1-\theta$ against log C should be a straight line with unit gradient. Such plots have been shown for morpholine in Figs. 4 and 5 in the absence and the presence of 10 ppm of tungstate ions respectively. $\theta/1-\theta$ values were directly calculated from the percentage inhibition efficiencies or RPL determined by the weight loss method. It is observed from the plots that there is a change in the gradient value with the increase in concentration of morpholine. At lower concentration, where the inhibitor affords lower efficiency, the slopes are almost tending to unity but at higher concentrations the slopes are far away from unity. This type of behaviour has been noted in the presence as well as in the absence of the tungstate ions. In the presence of the tungstate ions where a synergistic effect has been found and a better protection due to morpholine is achieved, the slopes are rather higher than those obtained for morpholine alone.

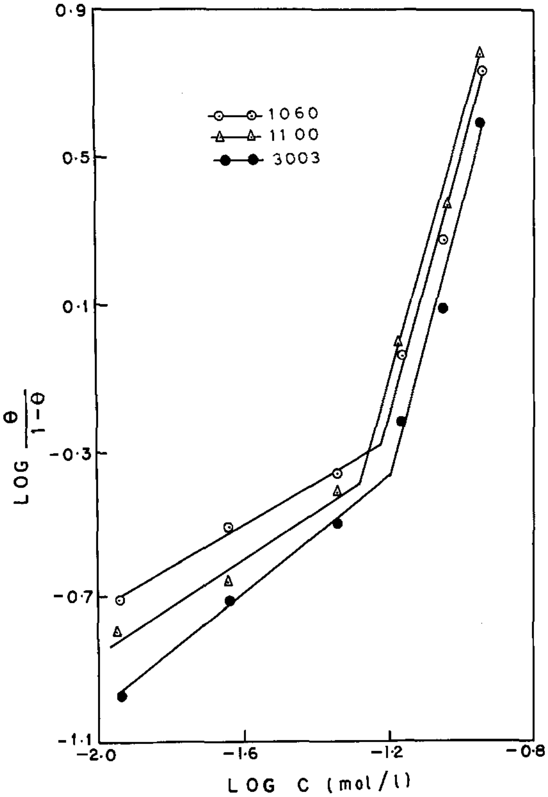

Fig. 5. Plots for the adsorption studies of morpholine in the presence of tungstate ions.

The reason for the inhibitor not obeying the adsorption isotherm may be ascribed to the interactions between the adsorbed species on the metal surface. These interaction effects, which have not been considered during the derivation of the isotherm equation, would affect the heat of adsorption of the inhibitor. If the interaction is repulsive in nature, the heat of adsorption would be negative and vice versa. This difference in the heat of adsorption could lead to deviation from the ideal type of isotherm. At lower surface coverage one would expect very little interaction among the adsorbed species and the

Table 1. Variation of steady state corrosion potential with concentration of morpholine for the various alloys

Alloys	*Steady state corrosion potential* (mV)			
	Concentration of morpholine (cm^3 dm^{-3})			
	0	4	8	15
1060	−807	−815	−893	−910
1100	−811	−814	−835	−895
3003	−805	−809	−830	−905

inhibitor should follow a Langmuir adsorption isotherm.

Variation of the steady state corrosion potential with the concentration of the morpholine, is recorded in Table 1. It is evident that the steady state corrosion potential increased in the active direction with the concentration of morpholine. This, in conjunction with the weight loss studies, indicates that the inhibitor is predominantly effective on the local cathodic corrosion sites. The maximum shift in the corrosion potential by the addition of 15 cm^3 dm^{-3} of morpholine occurs with 1060 alloy where the inhibitor also shows a maximum efficiency.

Fig. 6 shows the cathodic polarization curves for the alloys with and without morpholine. Cathodic polarization curves were substantially polarized in the presence of the inhibitor. In the presence of 10 ppm tungstate ions along with morpholine (not shown in the diagram), the curves did not show any significant change. This is compatible with the results obtained in Fig. 3 and confirms that tungstate ions are not adsorbed in the presence of morpholine. On addition of 10 ppm tungstate ions, the corrosion potential values of 1060, 1100 and 3003 alloys shifted to −644, −632 and −625 mV from −807, −811 and −805 mV, respectively in the blank solution. These results indicate that the tungstate ions depolarize the hydrogen discharge reaction taking place on the metal surface and consequently enhance the rate of the dissolution of the alloys.

Potentiostatic anodic polarization curves of alloys at various concentrations of morpholine are recorded in Fig. 7. With the increase in the concentration of the inhibitor, the curves were polarized and shifted towards the lower current density region. This suggests the presence of a very stable and impervious inhibitor film on the metal surface. The maximum polarization in the presence of the inhibitor is for 1060 alloys. This is in agreement with the results of the weight loss method where maximum inhibition efficiency has been observed for this particular alloy.

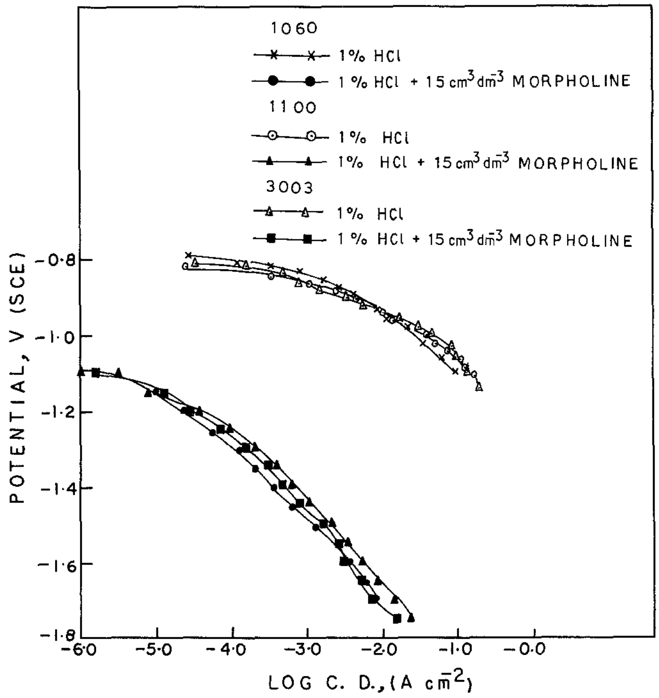

Fig. 6. Cathodic polarization of 1060, 1100 and 3003 alloys.

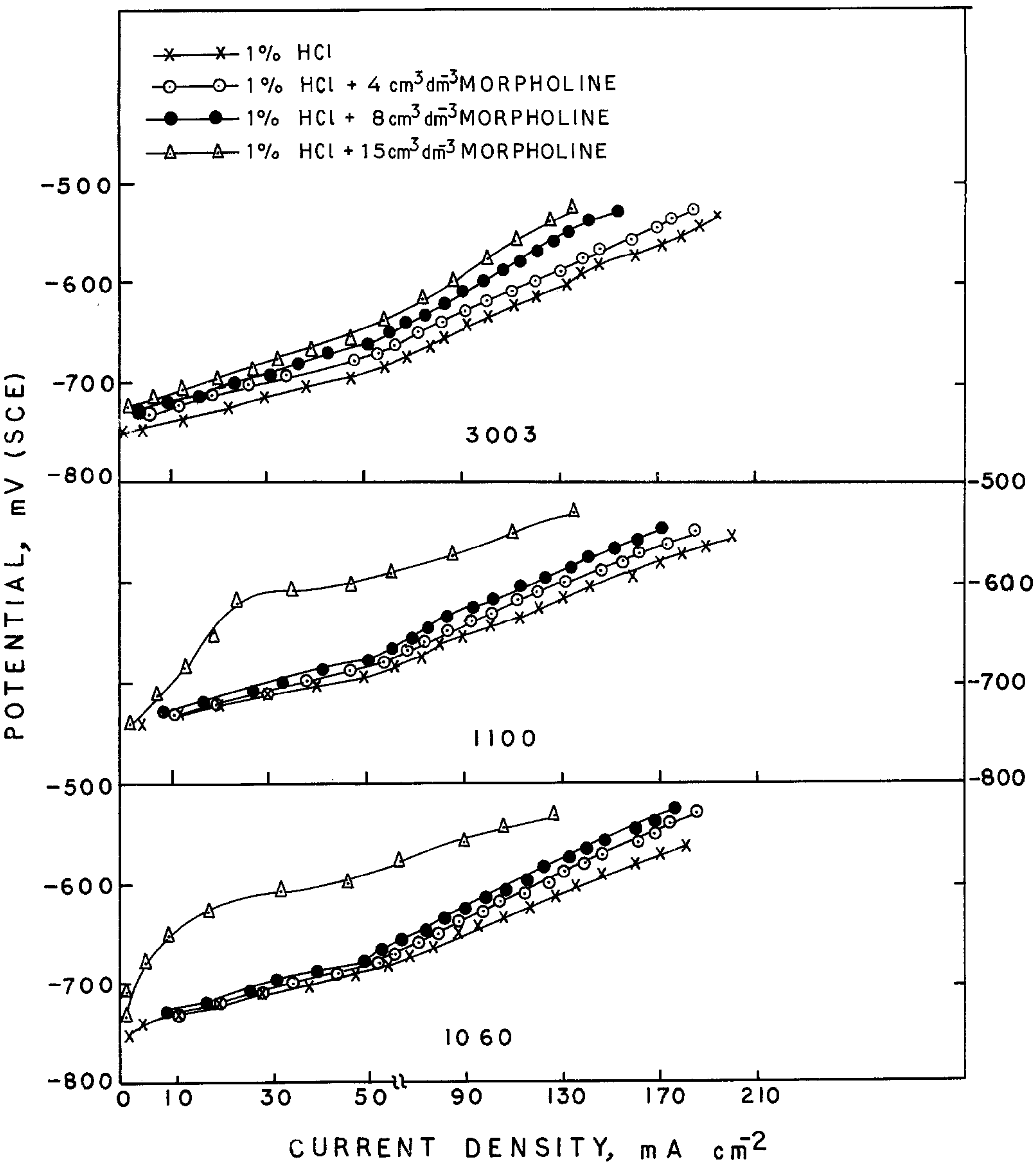

Fig. 7. Anodic polarization of 1060, 1100 and 3003 alloys.

References

[1] R. S. Chaudhary, P. N. S. Yadav, D. D. N. Singh and C. V. Agarwal, *J. Electrochem. Soc. (India)* 29 (1980) 125.

[2] P. N. S. Yadav, D. D. N. Singh, R. S. Chaudhary and C. V. Agarwal, *Ind. J. Technol.* 19 (1981) 461.

[3] D. M. Brasher, *Nature* 193 (1962) 868.

[4] T. P. Hoar and W. R. Jacob, *ibid.* 216 (1967) 1299.

[5] H. Bohni and H. H. Uhlig, *J. Electrochem. Soc.* 116 (1969) 906.