Organic Corrosion Inhibitors for TA6V Alloy in Non Oxidizing Acid Solutions

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The efficiency of the azo compounds as corrosion inhibitors for TA6V alloy in aerated 10, 15 and 25N H_2SO_4 has been investigated. It was found that these compounds are good passivators only in the presence of the naturally occuring oxide layer. A mechanism for the corrosion inhibition is proposed based on the reduction of the azo compounds on the surface of the alloy. As a result of this the corrosion potential is completely passive. Potentiostatic measurements have made it possible to establish the limits of stability of the passive state. The results of the corrosion tests agree fully with the results of the electrochemical measurements.

The inhibition of titanium corrosion has been the subject of a number of investigations. A good survey for all the type of inhibitors on titanium corrosion is reported by Petit et al[1]. Many of these investigations have studied the effect of oxidizing agents. Our studies have shown that the corrosion rate of titanium in sulfuric acid may be diminished considerably by oxidizing anions[2], as well as some azonic compounds[3]. TA6V is one of the most important titanium alloys and having high specific strength and excellent mechanical properties used widely in the industrial applications especially in the domain of the aerospace industry. So it was interesting to study effective organic corrosion inhibitors for TA6V in sulfuric acid solutions. A limited amount of work on TA5V from this standpoint has been published[4-5] as far as we are aware.

EXPERIMENTAL

The chemical composition of TA6V sample is given in Table 1.

In order to examine the inhibition efficiency of the azoic derivatives on the retardation of TA6V alloy dissolution in 10, 15 and 25N H_2SO_4, the loss in weight and the corrosion potential were followed as a function of exposure time.

Corrosion Rate by Weight Loss Technique

Experiments were performed on alloy specimens measuring 3 x 2 cm^2 and 2 mm thick. The test piece surface is treated as discussed above and the corrosion tests are carried out in 200 ml beaker, in which the specimen is suspended by means of glass hooks in the test solution. After a limited time, the specimen is removed, washed with water, dried and finally weighed. All corossion tests were carried out in aerated, unstirred solution at room temperature. All solutions are prepared from the purest available chemicals. Results are duplicated and the average was computed.

TABLE 1

CHEMICAL COMPOSITION OF TA6V ALLOY (wt.%)

Al	V	Fe	C	O	N	H
5.7	3.85	0.18	0.038	0.106	0.035	0.0053

Potentiostatic Measurements

Test electrodes of 1 cm^2 surface area are cut from the sample sheet and then annealed in vacuum at 800°C for 1 hour. A thin copper wire was tightly wrapped around one end of the electrode, which was squeezed inside a clean glass tube, and the glass was sealed over the copper wire by Araldite. Each electrode was mechanically polished with 600 emery paper under water, followed by ultra-sonic cleaning, rinsed throughly with distilled water and then dried with compressed air. Each experiment was carried out with a newly polished electrode and with a fresh portion of the test solution.

Anodic measurements are potentiostatic. The reference electrode, is a saturated calomel electrode and the counter electrode is in the form of a 1 cm^2 platinum sheet. The cell used is made of pyrex glass. Experimental details have been given elsewhere[6].

RESULTS AND DISCUSSION

Weight Loss Measurements

Weight loss was followed as a function of time in the absence and in the presence of 0.5 g/L of the different azo compounds. Table (2) shows the

TABLE 2

THE WEIGHT LOSS MEASUREMENTS (mg/cm^2) IN DIFFERENT MEDIA AND DIFFERENT PERIOD

Inhibitors 0.5 g/L	10N H_2SO_4			15N H_2SO_4			25N H_2SO_4		
Time in days	7	15	30	7	15	30	7	15	30
1. Without inhibitor	5.2	29.4	60.00	140.00	-	-	200.0	-	-
2. Azo benzene	nil	1.0	7.20	0.02	4.00	19.90	0.8	1.50	-
3. p. Oxiazo-benzene	nil	1.0	6.90	0.03	3.90	10.00	0.5	1.60	-
4. Methyl oxiazo-benzene	nil	nil	0.01	0.01	0.09	9.01	0.39	0.85	-
5. Dimethyl aminoazo benzene	nil	nil	nil	nil	0.05	9.00	0.10	0.82	-
6. Methyl orange	nil	nil	nil	nil	0.05	8.70	0.079	0.83	-
7. Methyl red	nil	nil	nil	nil	0.04	8.30	0.07	8.80	-
8. Chrysoidine	nil	nil	nil	nil	0.04	9.30	0.06	0.80	30

weight loss change expressed in mg/cm^2 during the period of 30 days. After a long period the inhibiting property decrease with increase of acid concentration in all cases. Chrysoidin for example is active in 25N H_2SO_4 over a period of 15 days, the loss in weight being 0.8 mg/cm^2 (it is 0.04 in the case of 15N and zero for 10N H_2SO_4). This means that the critical inhibitor concentration varies with acid concentration. These results suggest that the additives studied belong to the class of passivators, which added in sufficient amounts, reduce corrosion rates. It is worthy to remark that the colour of the solutions change slowly during the experiment (for example in the case of methyl red, the colour changes from red to yellow after about 19 days and finally it turned colourless after 70 days in 10N H_2SO_4). After this period, the loss in weight increases as in the absence of the inhibitors. Hence, our observations have shown that the azo compounds in an acid solution in contact with the metal surface, undergo a number of transformations. In this respect, the azo groups seem to be involved in the corrosion inhibition process like the nitro groups [5], and the film formation reaction on the electrode surface plays an important role for the attainment of the passivity.

Dissolution Rate and Stability of Protective Film

In order to examine the resistance of the film formed on the electrode surface in the presence of inhibitors after a certain period of immersion, the test electrode which has been passivated in inhibited 10N H_2SO_4 solution for 20 days, is transfered into a 10 N H_2SO_4 in the absence of inhibitors. The electrode becomes active after a period which depends on the type of the inhibitor as shown in Table (3). From the experimental results obtained, we can therefore assume that the surface alloy is oxidized in presence of the inhibitors, and that when the concentration of the inhibitor is decreased or in the absence of inhibitors as decribed above, the oxides are dissolved and, consequently the inhibitive action of the oxide film decreases with the immersion time till the oxide film is completely dissolved. This process

TABLE 3

LOSS IN WEIGHT IN 10N H_2SO_4 IN PRESENCE OF A PROTECTIVE FILM FORMED IN DIFFERENT INHIBITORS

Inhibitors 0.5 g/L	Loss in weight mg/cm^2						
Time in days	1	3	5	8	10	12	15
- Azo benezene	3.2	4.5	5.09	9.20	12.00	15.00	-
- Methyl oxiazo-benzene	nil	nil	nil	0.09	0.300	1.00	2.30
- Methyl orange	nil	nil	nil	nil	0.020	0.08	0.12
- Methyl red	nil	nil	nil	nil	0.030	0.10	0.12
- Chrysoidine	nil	nil	nil	nil	nil	nil	0.01

TABLE 4

VARIATION OF TA6V ELECTRODE POTENTIAL WITH EXPOSURE TIME IN SULFURIC ACID SOLUTIONS CONTAINING THE DIFFERENTNT AZO COMPOUNDS (in mv)

Inhibitors / Expos. time	10N H_2SO_4				15N H_2SO_4				25N H_2SO_4			
	1 min.	7 days	15 days	30 days	1 min.	7 days	15 days	30 days	1 min.	7 days	15 days	30 days
1. Without inhibitor	-610	-640	-640	-610	-600	-640	-640	-640	-600	-630	-620	-620
2. Azobenzen	-100	+75	-480	-600	-180	-400	-610	-610	-170	-360	-600	-600
3. P.Oxiazo benzene	-80	-10	-420	-610	-170	-400	-600	-600	-100	-380	-610	-600
4. Methyl-oxiazo-benzene	-10	+30	-100	+10	-70	+10	-420	-620	-10	-410	-600	-590
5. Diame-thyl amino-azo benzene	+20	+80	+100	+100	-15	-10	-390	-600	-10	-380	-600	-
6. Methyl orange	+50	+100	+120	+120	-10	-10	-380	-600	-15	-360	-600	-
7. Methyl red	+100	+120	+120	+125	+15	+20	-390	-610	+10	-380	-610	-
8. Chryso-idine	+100	+110	+120	+110	+20	+20	-390	-600	+90	-360	-600	-

is essentially chemical in nature, and the dissolution of the oxide is apparently the reduction of TiO_2 to oxides of a lower valency, which are more readily soluble in the acid medium. From all the above tests, it seems that the azoic derivatives have only a low oxidizing capacity which depends not only on the -N=N- group but also on the functional groups for each compound. These views were confirmed by the electrochemical measurments.

Corrosion Potential

The open circuit potentials of the TA6V electrode were followed as a function of time in sulfuric acid solutions containing the different azo compounds until steady state values were attained. The results (Table 4) show that the potential values at the moment of immersion are positive. This suggests that these compounds promote the resistance of the air formed pre-immersion oxide film against acid attack.

After certain time, dependent on the type of inhibitor, a sudden drop in the potential was observed; which indicates that the electrode comes to the active state. The shift of potential to the active range (~-600 mV), when no current is supplied, shows that only the active state is then stable. After that, when adding the same amount of the inhibitor (0.5 g/L), the potential remains active. This confirms that the azo compounds maintain the passive state of the alloy only in the presence of the film formed naturally in air, and the shift of the potential from passive to active values denotes the reduction of azo compounds.

Potentiostatic Measurements

Potentiostatic current density-potential curves I = f(E) were determined for TA6V alloy in 10 and 25 N H_2SO_4 solutions in the presence and absence of inhibitors starting from the corrosion potential. Some representative curves are shown in Figs. (1&2). In the absence of inhibitors an active to passive transititon is observed, each value of the potential on the anodic curves has a corresponding steady current density; the maximum current density value I_M is 0.56 mA/cm^2 for 10 M H_2SO_4 and 2.65 mA/cm^2 for 25N H_2SO_4 . In the presence of the different inhibitors corrosion potential shifts to a value at which the alloy is completely passivated and there is no anodic dissolution section on the curve as shown in Figs. (1&2 curves 2-8); and the current density in the passive state I remains unchanged, being 0.02mA/cm^2 in 10N H_2SO_4 and 0.03 mA/cm^2 in 25 N H_2SO_4 . The curves for this alloy resemble those for the unalloyed titanium metals corrode faster in 25N H SO . The above results suggests that the mechanism of the azo compounds inhibiton is based on its capability of achieving a more noble potential than the critical potential of passivity of TA6V.

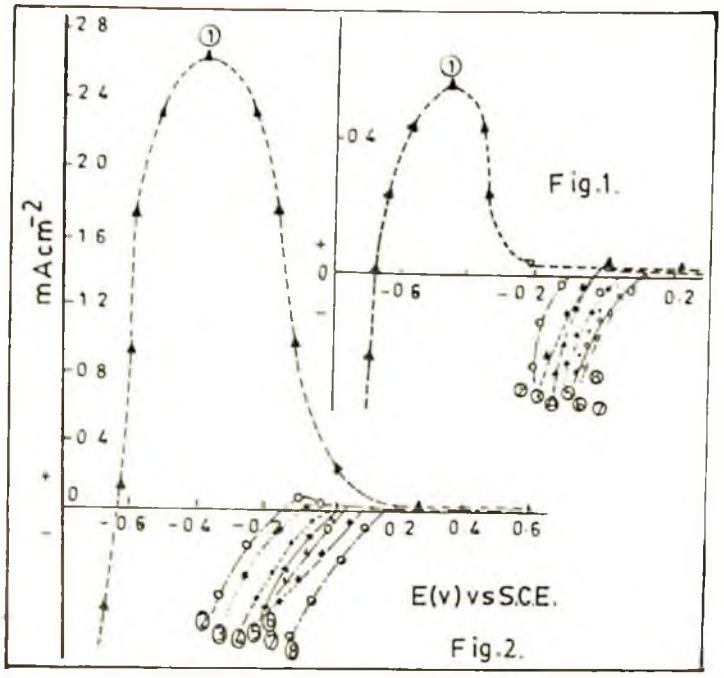


Fig.1.

Fig.2.

Fig.1 Polarization curves in 10 NH SO
Fig.2 Polarization curve in 25 N H SO with 0.5g/L inhibitor
1.Without inhibitor 2. Azobenzene
3.p-oxi azobenzene 4. Methyl oxi azobenzene
5.Dimethyl amino azobenzene 6.Methyl red
7.Methyl orange 8. Crysoidine

of passivity of TA6V.

Effect of Cathodic Reduction

In order to find more about the stability of the protective film and the mechanism by which these organic inhibitors reduce corrosion rates of TA6V alloy, the test electrode is activated by holding at a cathodic potential of -1 V/S.C.E. for 15 minutes without inhibitors; after that the inhibitor is added and the electrode is anodically polarized as described before. The results obtained in the presence of crysoidine is shown in Fig. (3). It is clean that an active to passive transition is still observed even in the presence of 0.5 g/L of inhibitor indicating that the electrode is in the active state. The presence of the inhibitor is manifested by the decrease in the maximum current density I_M, the appearence of a small cathodic loop as shown in Fig. (3 curve 2), and the corrosion potential becomes slightly more noble. Such behaviour is due to the reduction of the organic compound according to reactions of the type [7].

Ph-N=N-Ph + 2H + 2e ----- Ph-NH-NH-Ph
Ph-NH-NH-Ph + 2H + 2e ----- 2PhNH

The above experiment confirms that the azo compounds are effective inhibitor only if the alloy is previously protected by a naturally air formed film, the inhibitor can maintain the passive state of the metal and the inhibition of the metal dissolution occurs through the reduction of the azo compounds on the alloy surface which leads to passivation of the alloy.

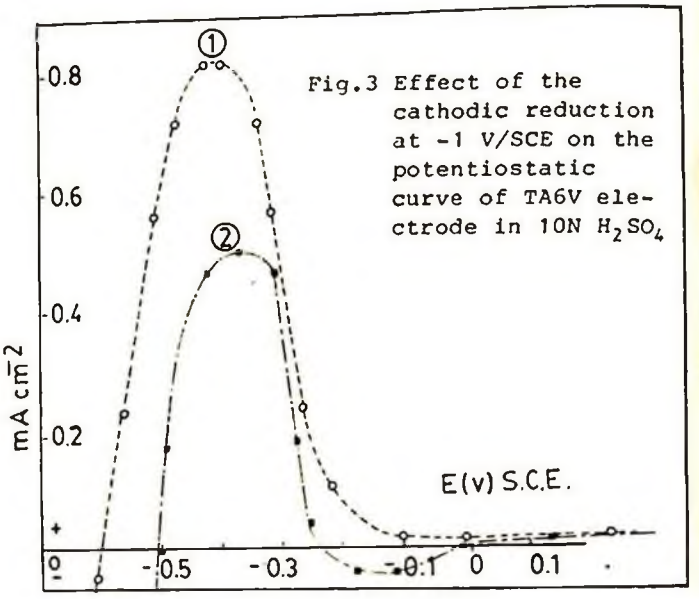


Fig.3 Effect of the cathodic reduction at -1 V/SCE on the potentiostatic curve of TA6V electrode in 10N H_2SO_4

The chemical composition of the protective films formed was not investigated in this study but from our results on pure titanium using Auger electron spectroscopy analysis [8], it was found that the passive layers formed are of TiO_2 only and the inhibitor does not seem to participate in the building of the passive film.

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