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# *Anodic behaviour of titanium in concentrated sulphuric acid solutions. Influence of some oxidizing inhibitors*

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The anodic polarisation behaviour of the titanium electrode and the rate of corrosion are measured in aqueous sulphuric acid solutions as a function of the electrolyte concentration. Increasing acid concentration increases the critical current for passivity. This current passes through a maximum (4·88 mA $cm^{-2}$) at 25 N and then decreases again. Increasing temperature increases the critical current for passivity. The effect of oxidizing agents such as $K_2Cr_2O_7$, $KMnO_4$, $KIO_3$, $Na_2MoO_4$, $NaClO_3$, $HNO_3$ and $TiCl_4$ on the polarisation of titanium are also investigated. $K_2Cr_2O_7$, $HNO_3$, $TiCl_4$ are the most powerful corrosion inhibitors at room temperature and also at 80° C in 10 N $H_2SO_4$, while in more concentrated sulphuric acid solution (25 N), corrosion inhibition is observed only by $HNO_3$ for a very short period.

## 1. Introduction

Interest in the anodic behavior of titanium has grown in recent years; this interest arises from the increase in its industrial applications. It is known that titanium is highly resistant to corrosion in many aggressive, particularly oxidizing media, but it has a significant corrosion rate with mineral acids such as sulphuric and hydrochloric acids, which are widely used in the chemical process industry.

The anodic behaviour of titanium in acid media has been studied by several investigators [1–4]. Limited data have been obtained for the corrosion-inhibition of titanium in concentrated sulphuric acid solutions. The inhibitive effect of ferric and cupric ions in 10% $H_2SO_4$ was observed by Cobb and Uhlig [5], while the same effect was observed by Tomashov and Al'tovskii [6] in 15% hydrochloric acid solution. Passivation of titanium by oxidizing agents was studied in 1% $H_2SO_4$ and HCl by Milton Stern [7]. The effect of $SbCl_3$, $K_2H_2Sb_2O_7$, $NaBiO_3$ and $KNO_2$ on the corrosion and electro-chemical behaviour of titanium in 5 N $H_2SO_4$ and HCl was investigated by Anoshchenko and Zorchenko [8].

This work represents the results of experiments on the corrosion and passivation of titanium in sulphuric acid solutions. We focus our studies mainly on the point of finding a wide range of effective inorganic corrosion inhibitors in 10 N and 25 N sulphuric acid solutions.

## 2. Experimental

The test electrodes are prepared from titanium sheets, (analysis in Table 1), cut into 1 $cm^2$ surface area pieces and then annealed in vacuum at 450° C for 30 min. The sample is sealed to glass with a resin over a Ti–Cu junction, and the resistance of this junction is checked before use. Each electrode is mechanically polished with 600 emery paper, degreased with acetone, washed thoroughly with distilled water and then dried. Each experiment is carried out with a newly polished electrode and with a freshly prepared solution.

Anodic measurements are made potentiostatically, the electrode potential is continuously changed at a constant rate of 2 V $h^{-1}$. A Tacussel potentiostat is used with a motor potentiometer for automatic programming of the operating potential and the current is simultaneously recorded. The reference electrode to which all potentials are referred is a saturated calomel electrode, and the counter electrode is in the form of a 1 $cm^2$ platinum sheet; the three electrodes are mounted

*Table 1. Chemical composition of titanium (ppm)*

| *C* | *Cr* | *Ni* | *O* | *Fe* | *Al* | *V* | *Zr* | *Cu* |
|---|---|---|---|---|---|---|---|---|
| 280 | 40–60 | 50–70 | 900–1800 | 150–250 | 10–200 | 15–60 | 10–40 | 1–3 |

on a plastic support. The cell used is made of Pyrex glass. Experimental details have been given elsewhere [9].

Determination of the corrosion rate is also carried out using the weight loss technique. Experiments were performed on titanium specimens measuring 3 cm x 2 cm x 2 mm thick. The test piece surface is treated as discussed above and the corrosion tests are carried out in a 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 weighted.

At high temperatures, the measurements are made using an oil bath. All solutions are prepared from the purest available chemicals. Results are duplicated and the average computed.

## 3. Results and discussion

### 3.1. *Corrosion behaviour of titanium in sulphuric acid solutions*

For a better understanding of the process taking place on the electrode surface, anodic polarisation measurements are made potentiostatically.

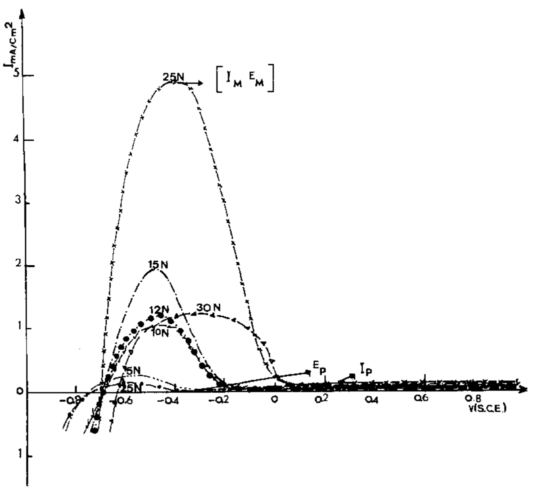

Fig. 1. Effect of concentration on anodic behaviour of Ti electrode in sulphuric acid solutions at room temperature.

*3.1.1 Effect of acid concentration.* Fig. 1 represents the potentiostatic $I = f(E)$ anodic polarisation curves of titanium electrodes in 2·5, 5, 10, 12, 25 and 30 N $H_2SO_4$. For all these concentrations, the electrode first shows an initial active region in which the current increases rapidly with increases of potential till it reaches a peak at a maximum current value $I_M$ and potential $E_M$, then drops again approaching a constant value, representative of the passive region with relatively low current value $I_P$ and potential $E_P$. Unexpected behaviour was shown in the case of 30 N, the anodic curve exhibiting a plateau between $-0{\cdot}5$ and $-0{\cdot}1$, with an approximately constant current value (0·12 mA cm$^{-2}$). After this, current decreases gradually to the passive region. The results obtained (Table 2) have shown that the resistance of titanium to sulphuric acid decreases gradually with increasing acid concentration (reduction in pH), passes through a maximum in 25 N solution, then increases again in the more concentrated solutions. There are many examples which show that the corrosion rate of titanium shows maxima and minima in certain ranges of acid concentration. Ma and Perre [10] have studied the Ti–$H_2SO_4$ system and have observed an increase in the rate of corrosion to a maximum at 40% and a fall to a minimum at 65% which is then followed by a rapid increase. They suggest that the corrosion in the low concentration region is probably due to the formation of the complex anions $[Ti(SO_4)_{2x}]^{-2x}$, and that the rate of formation of these complexes increases with acid concentration, reaching a maximum at 40%. In the range 40–65% the complex anions are supposed to break down to give $TiO_2$. The increase in the rate of corrosion at concentrations greater than 60% is explained by the formation of another complex $[TiO_2(SO_4)_x]^{-2x}$. There is, however no direct evidence of complex formation to support this view.

It is possible that the dependence of the corrosion of titanium on the concentration of sulphuric acid can be explained as follows: a maximum rate of corrosion at 25 N must be related to

*Table 2. Experimentally determined polarization parameters*

| Normality<br>*N* | $E_{Corr.}$<br>mV/S.C.E. | $E_P$<br>mV/S.C.E. | $E_M$<br>mV/S.C.E. | $I_M$<br>mA/cm² | $I_P$<br>mA/cm² |
|---|---|---|---|---|---|
| 2·5 | −750 | −350 | −570 | 0·18 | 0·01 |
| 5 | −740 | −350 | −570 | 0·25 | 0·016 |
| 10 | −710 | −220 | −450 | 1·12 | 0·02 |
| 12 | −710 | −200 | −430 | 1·20 | 0·025 |
| 15 | −710 | −200 | −430 | 1·90 | 0·025 |
| 25 | −640 | − 20 | −360 | 4·88 | 0·027 |
| 30 | −690 | + 30 | − | − | 0·1 |

$E_{corr}$ – corrosion potential; $E_P$ – passive potential; $E_M$ – potential of the peak; $I_M$ – maximum current value of the peak; $I_P$ – passive potential.

the concentration of active hydrogen ions. The dissolution of titanium in the active state can be described by the presence of one of the following reactions:

$$Ti \rightarrow Ti^{2+} + 2e \qquad (1)$$

$$Ti \rightarrow Ti^{3+} + 3e \qquad (2)$$

$$Ti \rightarrow Ti^{4+} + 4e \qquad (3)$$

Since the lower valency titanium oxides are 'unstable' in sulphuric acid media [11], and no direct passivation can take place, reactions 1 and 2 are the most probable reactions in the active state.

The reduction in the rate of corrosion of titanium in the more concentrated sulphuric acid solution 30 N is probably due to the removal of the 'originally' formed air film by the initial rapid dissolution and due to the oxidizing action of concentrated sulphuric acid solutions, a barrier amorphous layer is then formed. This layer does not prevent completely the dissolution of titanium at less positive potential values, and by shifting the potential to more positive values a much more protective invisible film is formed (probably $TiO_2$).

Direct determination of the rate of corrosion $\Delta\rho$ is measured by the loss in weight; the plots $\Delta\rho$ against the concentration are given in Fig. 2. The results obtained from anodic polarisation are in good agreement with those obtained by the weight loss procedure.

*3.1.2. Effect of temperature.* The dependence of the anodic behaviour of titanium on the temperature is shown in Fig. 3 and 4. The values shown in Table 3, indicate that the critical current density $I_M$ increases with increasing temperature, while the critical potential for passivity $E_M$ does not vary appreciably with the variation of temperature. The passive current $I_P$ increases markedly at 80° C which indicates that the passive state is less stable than at low temperature. It is clear that the higher the value of the corrosion current in the passive state, the less stable is the passive film. At lower temperatures the anodic curves were characterized by the extremely small currents required to passivate the titanium in the acid medium.

### 3.2. *Effect of oxidizing agents*

The corrosion of titanium in sulphuric acid solutions is an electrochemical process. Thus the

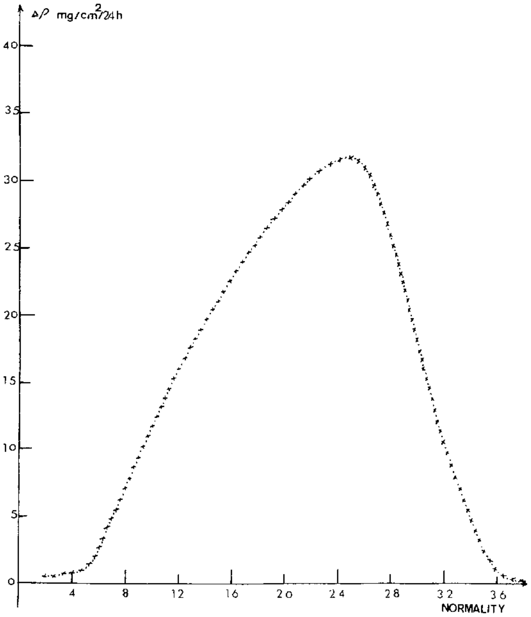

Fig. 2. Variation of loss in weight with sulphuric acid concentration.

*Table 3. Effect of temperature on the polarisation parameters*

| *Normality* *N* | *Temperature* °C | $E_M$ mV/S.C.E. | $E_P$ mV/S.C.E. | $I_M$ mA/cm² | $I_P$ mA/cm² |
|---|---|---|---|---|---|
| 10N | 20 | −450 | −220 | 1·12 | 0·02 |
| | 40 | −500 | −215 | 3·7 | 0·03 |
| | 60 | −500 | −230 | 10·3 | 0·045 |
| | 80 | −500 | −240 | 38 | 0·2 |
| 25N | 20 | −360 | −20 | 4·88 | 0·027 |
| | 40 | −425 | 0 | 15·8 | 0·11 |
| | 60 | −430 | + 5 | 34·4 | 0·2 |
| | 80 | −320 | + 20 | 100 | 0·7 |

addition of oxidizing substances raises the metal–electrolyte potential into the passive region and thus the result is the formation of a protective film. The mechanism of inhibition is based on the capability of achieving a more noble potential than the critical potential of passivity. A low corrosion rate and a noble electrode potential were observed following the addition of $HNO_3$, $K_2Cr_2O_7$, $KMnO_4$, $KIO_3$, $Na_2MoO_4$, $NaClO_3$ and $TiCl_4$.

*3.2.1. At room temperature.* $HNO_3$, $K_2Cr_2O_7$, $Na_2MoO_4$ and $TiCl_4$ are very powerful corrosion inhibitors for titanium in 10 N and 25 N $H_2SO_4$ (Table 4). The activity of these inhibitors persists over a long period. Dichromate ion, for example, is active in 25 N $H_2SO_4$ over a period of 30 days, the loss in weight being 0·7 mg cm$^{-2}$ (it is zero in 10 N $H_2SO_4$). The strong inhibiting action of dichromate ion is based on its high affinity for reduction; the dichromate ion may be regarded as an electron attractive group (an 'electrophile')

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O \qquad (4)$$

thus, when adsorbed on a bare anodic area, it leads to a local increase of the electronic density and consequently the active atoms on the metal

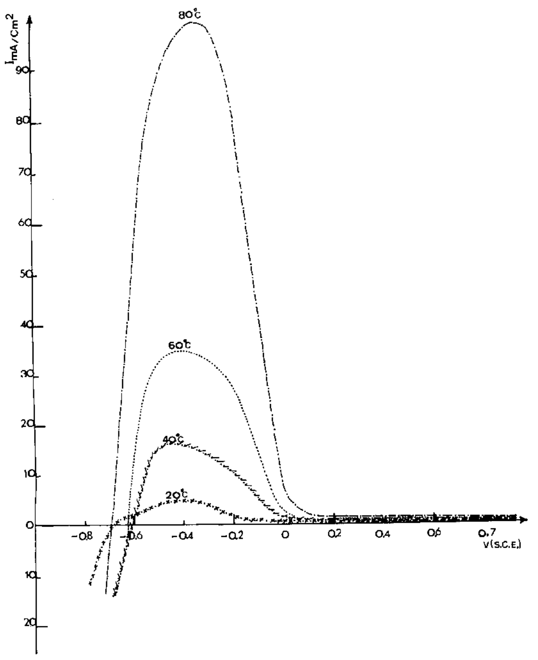

Fig. 3. Effect of temperature on anodic behaviour of Ti electrode in 25N $H_2SO_4$ solution.

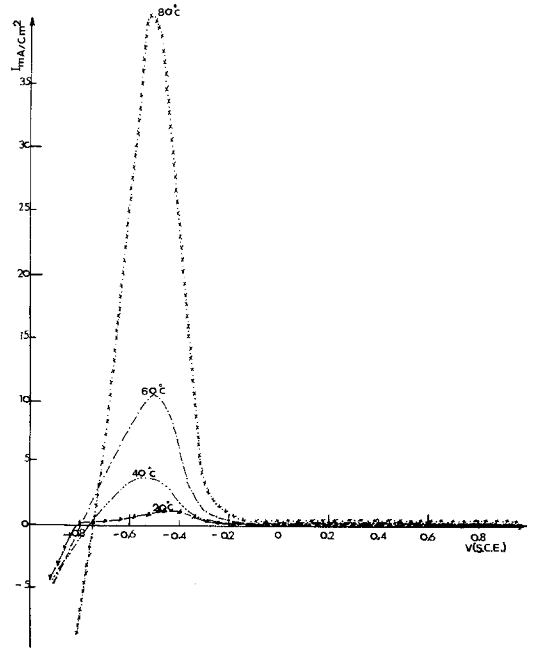

Fig. 4. Effect of temperature on anodic behaviour of Ti electrode in 10N $H_2SO_4$ solution.

*Table 4. Weight loss (mg cm$^{-2}$) measurements for Ti electrode*

| | 25N $H_2SO_4$ | | | | | 10N $H_2SO_4$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| *Inhibitors* | *E* mV/(S.C.E.) | 1 h | 24 h | 15 days | 30 days | *E* mV/(S.C.E.) | 1 h | 24 h | 15 days | 30 days |
| Without inhibitors | − 790 | 0·895 | 25 | – | – | − 660 | 0·108 | 1·39 | 33·3 | 75 |
| $HNO_3$ 2 ml l$^{-1}$ | + 575 | 0·014 | 0·025 | 0·33 | 6 | + 613 | 0 | 0 | 0·1 | 0·11 |
| $HNO_3$ 41 ml l$^{-1}$ | + 55 | 0 | 0 | 0·054 | 0·7 | + 765 | 0 | 0 | 0 | 0 |
| $K_2Cr_2O_7$ 1g l$^{-1}$ | + 430 | 0 | 0·056 | 0·116 | 0·7 | + 550 | 0 | 0 | 0 | 0·05 |
| $KIO_3$ 1g l$^{-1}$ | + 460 | 0·011 | 0·11 | 0·18 | 4 | + 525 | 0 | 0·025 | 0·15 | 0·25 |
| $KMnO_4$ 1g l$^{-1}$ | + 695 | 0 | 0·07 | 0·2 | 0·2 | + 950 | 0 | 0 | 0 | 0·08 |
| $Na_2MoO_4$ 1g l$^{-1}$ | − 570 | 0·49 | – | – | – | + 200 | 0 | 0 | 0·05 | – |
| $NaClO_4$ 1g l$^{-1}$ | − 420 | 0·05 | 0·2 | – | – | − 62 | 0·01 | 0·04 | – | – |
| $TiCl_4$ 28 ml l$^{-1}$ | + 10 | 0 | 0 | 0·02 | – | + 35 | 0 | 0 | 0 | 0 |

surface are deactivated. It seems very likely that the dichromate ion exerts a direct influence on the characteristics of the metal surface, with no visible film on the metal surface.

Nitric acid has also been found to be an effective corrosion inhibitor in $H_2SO_4$. Its inhibitive action depends on its concentration, i.e. 0·5 N, (i.e. 41 ml $l^{-1}$) is more effective than 0·02 N (i.e. 2 ml $l^{-1}$), and the potential is shifted in the noble direction (see Table 4).

Potassium permanganate which has a more positive oxidation-reduction potential than $K_2Cr_2O_7$ was found to be a less effective passivator for Ti than $K_2Cr_2O_7$. This can be explained not only by the oxidizing action but also by the specific influence of the anions in each separate case.

Potassium iodate has also been found to be an effective corrosion inhibitor in $H_2SO_4$, but only for short periods, while the potential is more noble than the critical passive potential. It is evident that the increase of potential is not necessarily an indication of corrosion inhibition.

On the basis that the iodate decomposes according to:

$$IO_3^- + 6H^+ + 5e \rightarrow 3H_2O + 1/2I_2 \qquad (5)$$

the decrease in the activity of $KIO_3$ may be due to the decrease in its concentration.

Titanium tetrachloride is a very powerful corrosion inhibitor for titanium in 10 N $H_2SO_4$. The loss in weight after four months is very small (0·1 mg $cm^{-2}$). A protective visible coloured film was found on the electrode surface.

*3.2.2. At high temperature 80° C.* Two problems are encountered at 80° C, one is connected with the instability of some oxidizing agents, such as $IO_3^-$, $Cr_2O_7^{2-}$ and $NO_3^-$ in concentrated sulphuric acid solutions (25 N). The other problem is connected with the high current value $I_P$ at 80° C (0·7 mA $cm^{-2}$) in the case of 25 N $H_2SO_4$.

It has been found that the addition of nitric acid in small quantities (0·02 N i.e. 2 ml $l^{-1}$) leads to significant corrosion inhibition at 80° C. The loss in weight after 24 h was 5·8 mg $cm^{-2}$, and the metal–electrolyte potential was shifted in the noble direction (440 mV/S.C.E). The rate of corrosion calculated by Faraday's equation gives a current value $I = 0{\cdot}6$ mA $cm^{-2}$ which is very near to the current of passivation $I_P = 0{\cdot}7$ mA $cm^{-2}$.

Increasing the nitric acid concentration (0·5 N i.e. 41 ml $l^{-1}$), decreases its inhibiting action at 80° C. The loss in weight after 24 h is 6·6 mg $cm^{-2}$, and the calculated current value obtained by Faraday's equation is $I = 0{\cdot}66$ mA $cm^{-2}$. This high current value is attributed to the decomposition of $NO_3^-$ which was indicated by the presence of red vapours.

Some of the above-mentioned oxidizing agents are stable at 80° C in 10 N $H_2SO_4$. The most characteristic example is $K_2Cr_2O_7$. No loss in weight is observed during a period of 30 days.

$TiCl_4$ is also an active corrosion inhibitor only for a short time (4 days); this may be due to its high affinity for hydrolysis.

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl \qquad (6)$$

Nitric acid has also been found to be an effective corrosion inhibitor in 10 N $H_2SO_4$ at 80° C. For the addition of 2 ml $l^{-1}$ the loss in weight after 14 h was 0·46 mg $cm^{-2}$.

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