Polarization Behaviour of Titanium in Sulphuric Acid Solutions*

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When the anodic polarization properties of titanium are investigated in a solution in which the corrosion potential of titanium varies to the positive direction with time, the potential of titanium becomes constant between 1.7 and 1.9 volts (vs.S.C.E.), while the anodic current density is increased and the polarization curve has a plateau. The plateau, which shows the oxygen evolution potential, on the polarization curve can be found neither in the measurement performed in a solution in which the corrosion potential of titanium varies to the negative direction with time, nor in the measurement with the titanium surface which has been pretreated to reduce the natural oxide film cathodically or chemically. From these experiments and electron diffraction studies, it is concluded that the oxide film of titanium produced by electrochemical oxidation is different from the natural oxide film formed in air, and that the former is of the rutile type and non-conductive crystals and the latter is presumably of the rutile type but conductive crystals. An anatase type TiO_2 is formed only when titanium is oxidized in the solution using no current.

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I. Introduction

Titanium, in spite of a less noble metal in the ionization series, is one of the metals having high passi-

vity to anodic dissolution, to which the high resistance of titanium to corrosion is attributed. It is, therefore, important to study the electrochemical properties in regard to the mechanism of passivation.

This report deals with the anodic and cathodic polarization behaviour of titanium in various sulphuric acid solutions.

II. Experimental Materials and Methods

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The chemical composition of the titanium specimen used is shown in Table 1.

Table 1 Chemical composition of the titanium specimen.

C	Si	Fe	W	Cl	Mg	Remarks
0.034	0.016	0.053	0.008	0.010	—	38% cold worked

The specimens were first washed to remove grease and then coated with Picein wax except the 1 sq. cm area to be tested. The exposed area was polished with a piece of 2/0 emery paper. Each specimen was kept in air for 30 sec after polishing, and then placed in the test solutions. The measurement of polarization was started 30 min after immersion of the specimen. The current density was kept at a constant value for 5 min and was raised in steps. The potential-current density curves were determined using a saturated calomel electrode as the standard.

The solutions were naturally aerated and kept at 20°C.

III. Experimental Results

1. Polarization in sulphuric acid solutions

Fig. 1 shows the polarization curves ($E - \log D$) of titanium in sulphuric acid solutions with various concentrations.

Fig. 1 Polarization of titanium in the naturally aerated sulphuric acid solution at 20°C.

The cathodic polarization curves obtained are nearly identical, but the anodic polarization curves differ widely depending upon the concentration of sulphuric acid. As the anodic polarization increases, the potential of titanium rises eventually to a very high level exceeding 3 volts, but not in the same way by different sulphuric acid concentrations. In solutions of low sulphuric acid concentrations, a gradual change of the potential takes place at a low current density, while in those of high sulphuric acid concentrations the potential rise occurs suddenly at a high current den-

sity. The spontaneous potential of titanium in sulphuric acid solutions of the concentration below 0.2 N (Fig. 1 a) varies to the positive direction with time (in other words, the oxide film formed in air is stable), and the anodic polarization curves of titanium pass through a stage where the potential remains constant between 1.7 and 1.9 volts (vs. S.C.E.) during the increment of the current density. This potential arrest does not appear on the anodic polarization curves obtained in 2 N or more concentrated solutions of sulphuric acid. In these solutions the potential of titanium varies to the negative direction with time (viz., the oxide film formed in air dissolves).

Fig. 2 shows an example of the polarization curves obtained in an experiment in which cyclic polarization was applied from the anodic to the cathodic direction and vice versa in the sulphuric acid solution. In the diagram, the solid line and the accompanying arrows indicate the direction of the initial polarization. It was ascertained that when the oxide film formed in air was once cathodically reduced, the potential arrest did not appear even if the anodic polarization was subsequently applied. When sufficient anodic oxidation was carried out so that the potential could exceed 1.9 volts and anodic polarization was conducted again after cutting-off of the current, the potential was found to reach a high value without passing through the arrest.

Further, polarization curves were obtained in the 0.02N sulphuric acid solution to which a small amount

of ammonium fluoride, highly corrosive to titanium, was added. In this case, the potential arrest did not appear, as shown in Fig. 3.

It is clear from the above experimental results that the potential arrest is related to the existence of oxide film formed in air.

The fact that the range of current density at the potential arrest becomes wider with the lowering of the sulphuric acid concentration seems to have bearing on the fact that the titanium oxide films formed in air are less soluble in dilute sulphuric acid solutions than

in the concentrated solutions.

2. Polarization in 2N sulphuric acid solutions containing potassium dichromate.

Polarization curves of titanium were obtained in 2N

cut off after the potential of titanium reached 1.9 volts or above and then made anodic again, the potential of titanium rose drastically to the positive direction at a very low current density. This fact indicates the compactness and high electric resistance of the

Fig. 2 Cyclic polarization of titanium in the 0.2N-H₂SO₄ solution at 20°C.

Fig. 3 Polarization of titanium in naturally aerated 0.02N-H₂SO₄ solutions containing varying amounts of NH₄F at 20°C.

sulphuric acid solutions containing various amounts of potassium dichromate ranging from 0.00001 to 0.01 mol/l. Fig. 4 shows the results. The potential-time curves are shown in Fig. 4 a.

The stage where the potential remains arrested at 1.7 to 1.9 volts appears on anodic polarization curves obtained in the solutions in which the spontaneous potential changes to the positive direction with time. The range of current density at the potential arrest widens as the concentration of potassium dichromate increases. As in the case of Fig. 2, if the titanium was once subjected to cathodic polarization in these solutions, no potential arrest was observed in a subsequent anodic polarization. It was confirmed that the dichromate ion had no relation to the anodic reaction, because no potential arrest was observed in a study of polarization properties of platinum in the same solutions. When the anodic oxidation current was once

film formed by the anodic oxidation.

In the cathodic polarization curves, the evolution of hydrogen is not observed until the current density is raised to a certain level during the cathodic reduction of the oxidizing agent (dichromate ion). When the cathodic reduction of dichromate ion has ceased, the potential moves suddenly to a more negative value and the hydrogen evolution appears. Consequently, the greater the amount of dichromate ion is, the higher is the current density at which the evolution of hydrogen occurs.

3. Polarization in 2N sulphuric acid solutions containing potassium permanganate.

Similar anodic polarization behaviours to those in Fig. 4 can be seen in 2N sulphuric acid solutions containing 0.00002 to 0.02 mol of potassium permanganate, as shown in Fig. 5. That is, a higher concen-

tration of the oxidizing agent would give rise to a better preservation of the oxide film, a wider range of current density at the potential arrest on the anodic polarization curves, and a higher current density of the cathodic hydrogen evolution.

even if they have a high concentration. This may be ascribed to the fact that a cation such as cupric or ferric ion does not act as the oxidizing agent for anode metal. In the polarization experiments, the test pieces were left immersed in the solutions for 30 min prior

Fig. 4 and Fig. 5 Polarization of titanium in 2N sulphuric acid solutions containing varying amounts of the oxidizing agent (K₂Cr₂O₇ or KMnO₄) at 20°C.

4. Polarization in 2N sulphuric acid solutions containing cupric sulphate

Polarization curves obtained in 2 N sulphuric acid solutions containing 0.0001 to 0.01 mol of cupric sulphate are shown in Fig. 6. Here again, the potential arrest appears on the anodic polarization curves. No effect of the cupric ion concentration, however, is seen on the curve.

5. Polarization in 2N sulphuric acid solutions containing ferric sulphate

The measurements in 2 N sulphuric acid solutions containing 0.0001 to 0.01 mol of ferric sulphate gave the results similar to those with cupric sulphate, as shown in Fig. 7. Unlike the aforesaid case of dichromate or permanganate, the cupric or ferric ion causes practically no change on the anodic polarization curves

to the experiment. These two agents seem to have served to form an oxide film during the period of 30 min. This can be corroborated in the cathodic polarization curves where, as in the case of dichromate or permanganate, the evolution of hydrogen starts at higher current density when the amount of cupric or ferric ion is higher.

6. Crystal structure of oxides

The experimental results by the electron diffraction method are also mentioned.

IV. Discussion

It is now clear that the stage where potential is kept at 1.7 to 1.9 volts has relation to the oxide films formed in air and reinforced by an oxidizing agent. In other words, the stage of potential arrest appears only

in a sulphuric acid solution of low concentration in which the oxide film remains undissolved or in a sulphuric acid solution in which the oxide film is reinforced by an oxidizing agent. The arrest disappears when the oxide film is cathodically reduced or chemi-

to form through pits and cracks in the film until all the oxide becomes non-conductive when oxygen evolution ceases, and finally the potential starts to rise. For instance, the anodic polarization curves of titanium in sulphuric acid solutions shown in Fig. 1 can be clas-

Fig. 6 and Fig. 7 Polarization of titanium in 2N sulphuric acid solution containing varying amount of the oxidizing agent (Cu²⁺ or Fe³⁺) at 20°C.

cally dissolved, so that properties of the oxide film formed chemically in air on the surface of titanium must differ from those of the oxide film formed electrochemically in the electrolyte. Judging from the value of the arrest potential, the stage having a nearly unchanged potential is equivalent to the stage where the evolution of oxygen occurs. The linear portion of the E - $\log D$ curves is the Tafel line indicating the oxygen overvoltage of titanium. It will therefore be quite reasonable to consider that the electrochemically formed oxide film has high electric resistance and thereby the potential of titanium rises with the amount of electricity passed. The chemically formed oxide film may be electrically conductive, and therefore, when the oxygen evolution potential has been reached by polarization, the potential is kept almost constant by the evolution of oxygen. During the evolution of oxygen the non-conductive oxide continues

sified into the following three groups :

(1) In sulphuric acid solutions whose concentration is above 4N :

The oxide film dissolves. Even if the current density is raised, titanium has little polarization in the early stage, but when a certain critical current density has been reached, the potential suddenly rises with the formation of a non-conductive oxide.

(2) In sulphuric acid solutions whose concentration is below 0.2 N :

The oxide film formed in air is scarcely dissolved. The anodic polarization increases with increase of the current density ; since the film is conductive, the polarization finally gives rise to the evolution of oxygen.

(3) In 2 N sulphuric acid solution :

The degree of oxide film dissolution is between the above two categories. (In Fig. 1a, the spontaneous potential first changes to the positive direction, and

then turns to the negative direction.) In this solution the non-conductive oxide grows with the increase of current density, so that the oxide film formed in air is perfectly replaced by this oxide at least at the oxygen evolution potential. The oxidizing agents in the solutions, shown in Fig. 4 and Fig. 5, must have effects on the increase of polarization along with the anodic oxidation.

The oxide formed in air by the room temperature oxidation appeared to be TiO_2 of the rutile type, but this could not be confirmed. On the other hand, the oxide formed by the anodic oxidation in the aqueous solution was definitely of the rutile type. Ogawa and

others⁽¹⁾ reported the easy formation of oxides of the anatase type, but not of the rutile type in aqueous solutions. It has been found in the present experiment, however, that the rutile type oxide also appears readily when an electrolytic current is applied.

V. Conclusion

The polarization curves of titanium were measured in various sulphuric acid solutions, and it is concluded that the oxide film of titanium produced by electrochemical oxidation in the electrolyte is different from the natural oxide film formed in air.

(1) S. Ogawa, D. Watanabe: *Jour. Japan Inst. Metals.*, **18**(1954), 523.