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The effect of arsenic on the hydrogen evolution reaction on titanium

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The effect of the addition of arsenic on hydrogen evolution on titanium in acid solution was investigated. The hydrogen uptake of the metal increased with increasing arsenic concentration, and the Tafel slope of cathodic polarization changed from 110 to 170 mV decade^{-1}. A mechanism which explains these phenomena is proposed.

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1. Introduction

It is well known that the electrochemical absorption of hydrogen by metals is enhanced by the presence of catalytic poisons in the electrolyte. These 'poisons' or 'promoters' consist of certain elements of groups V and VI.

The hydrogen evolution reaction (HER) at the cathode occurs in two steps: ionic discharge followed by either (a) chemical desorption (combination of two adsorbed hydrogen atoms to give H_2) or (b) an electrodic discharge (combination of an adsorbed hydrogen atom with a proton to give H_2). The relationships between the rate equations of the hydrogen evolution reaction were analysed by Pöpperling and Schwenk [1]. They showed that the Tafel slope depends on the exact mechanism, i.e., which step is rate determining, and whether equilibrium has been attained.

The hydrogen absorption reaction occurs as a side reaction to the HER, since the hydrogen is adsorbed as the atomic species, and enters the metal by diffusion from the surface into the bulk. Arsenic and other promoters effectively increase the energy barrier for the desorption step and thus favour the competing absorption step.

The influence of promoters on hydrogen entry into steel and iron has been studied extensively [2–10]. Their influence on Pd and Ni-alloys has also been reported [11]. This work deals with the effect of arsenic on the entry of hydrogen into titanium.

2. Experimental procedure

The material used in the experiments was commercially pure titanium sheet, 0.08 cm thick, from which 1 × 1 cm specimens were cut. A length of titanium wire was spot welded to each specimen. After polishing with several grades of emery paper and cleaning with acetone, the specimens were vacuum annealed at 1000° C to remove all hydrogen.

Hydrogen charging was carried out in a simple electrochemical cell. A platinum electrode was used as the anode and the titanium specimen as the cathode in the circuit. The charging solution was 0.5 mol dm^{-3} H_2SO_4. The sulphuric acid solutions were prepared from reagent grade sulphuric acid and triple distilled water. Various concentrations of $NaAsO_2$ were added to the charging solution. The potential source was a Kepco d.c. power supply. A constant current density of 10 mA cm^{-2} was maintained during the charging, which lasted for up to 75 h. The hydrogen content of the specimens was determined by vacuum extraction at 1000° C.

The specimens used in the polarization experiments were prepared in the same way as those used in the charging experiments. They were inserted into perspex holders and embedded in RTV silicone rubber in such a manner that only one of their surfaces came into contact with the solution. Nitrogen was bubbled through the solutions during these experiments, which followed

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the potentiokinetic method. The apparatus consisted of a PAR 171 potentiostat-recorder system and a high impedance voltmeter. The potentials were measured against a saturated calomel electrode (SCE), and the counter electrode was platinum.

The titanium electrodes were activated in 1 mol dm^{-3} HF for 1 min, washed in distilled water and then introduced into the solution. The open circuit potential was monitored, and the polarization experiment was begun after the potential had been steady for 2 h.

The temperature of the cell was maintained constant at 25 ± 1° C. Most experiments were carried out at a rate of 0.5 mV s^{-1}.

3. Results and discussion

The cathodic polarization behaviour of titanium in 0.5 mol dm^{-3} H_2SO_4 is shown in Fig. 1. The HER Tafel slope is 110 mV decade^{-1}, down to − 1000 mV SCE, where a deviation from normal Tafel behaviour occurs. Slower polarization curves (at 0.1 mV s^{-1}) show a distinct hysteresis in forward/reverse runs.

When the promoter was added the behaviour changed (Fig. 2). The initial slope was again 110 mV decade^{-1} down to − 1000 mV, but at more negative potentials the slope increases, and becomes 170 mV decade^{-1}.

The results of cathodic charging of titanium in sulphuric acid containing various concentrations of arsenic are shown in Fig. 3. The amount of hydrogen is expressed as the pressure in the extraction apparatus. The curves are characterized by an increase of solubility of hydrogen with time until saturation, while the saturation concentration increases with increasing concentration of the promoter.

The hydrogen content is directly proportional to the square root of time. This points to a simple diffusion process.

The slope of the HER in pure sulphuric acid indicates, according to Pöpperling and Schwenk [1], a fully equilibrated Volmer–Heyrovsky mechanism:

$$H^+_{aq} + e^- \rightleftarrows H \text{ (Volmer reaction)}$$

$$H^+_{aq} + H + e^- \rightleftarrows H_2 \text{ (Heyrovsky reaction).}$$

For cathodic polarization the Volmer and Heyrovsky current densities are given as i_V and i_H, respectively, by:

$$i_V = -\frac{i_{0V}}{1-\theta_0}(1-\theta)\exp\left(-\frac{(1-\alpha_V)F}{RT}\eta\right)$$

$$i_H = \frac{i_{0H}}{\theta_0}\,\theta\exp\left(-\frac{(1-\alpha_H)F}{RT}\eta\right)$$

where α = charge transfer coefficient, i_0 = exchange current density, θ = degree of coverage and θ_0 = equilibrium degree of coverage.

It has been suggested by Thomas and Nobe [12] that the Heyrovsky reaction is the rate determining step in the HER on titanium. Therefore its current must be negligible with respect to that of the Volmer reaction, thus:

$$\log i \propto -(1-\alpha_H)\frac{F\eta}{RT}\,.$$

Since the charge transfer coefficient $\alpha_H \sim 0.5$, we

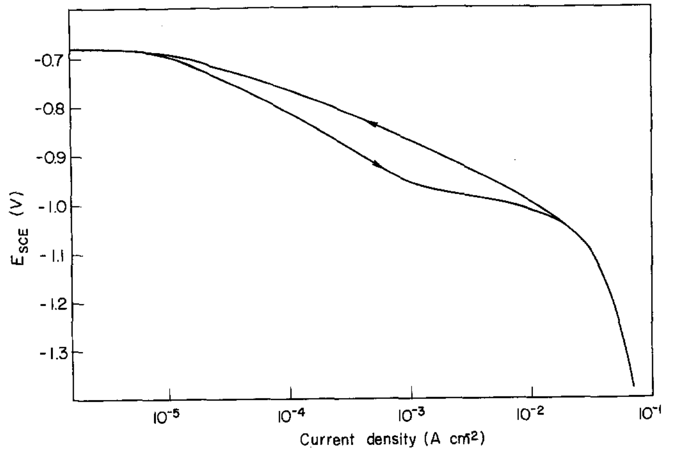

Fig. 1. Cathodic polarization of Ti in 0.5 mol dm^{-3} H_2SO_4.

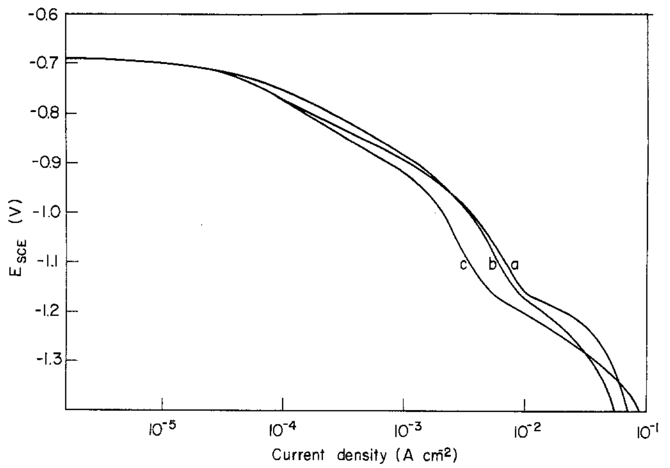

Fig. 2. Cathodic polarization of Ti in 0.5 mol dm^{-3} H_2SO_4 with various concentrations of As: a, 20.3; b, 35; c, 55 mg dm^{-3} As.

obtain a Tafel equation

$$\log i = a - b\eta$$

with a slope of 120 mV decade^{-1}. The observed slope of 110 mV decade^{-1} agrees well with this value.

The observed deviation from the normal Tafel behaviour at − 1000 mV SCE indicates that at this potential a new mechanism becomes rate determining.

Calculations based on thermodynamic data obtained from Pourbaix [13] point to the possibility of the formation of titanium hydride according to one of the two reactions

$$Ti_2O_3 + 10H^+ + 10e^- \rightarrow 2TiH_2 + 3H_2O;$$

$$E^\circ = -1.027 \text{ V versus SCE}$$

or

$$TiO_2 + 6H^+ + 6e^- \rightarrow TiH_2 + 2H_2O;$$

$$E^\circ = -0.910 \text{ V versus SCE}$$

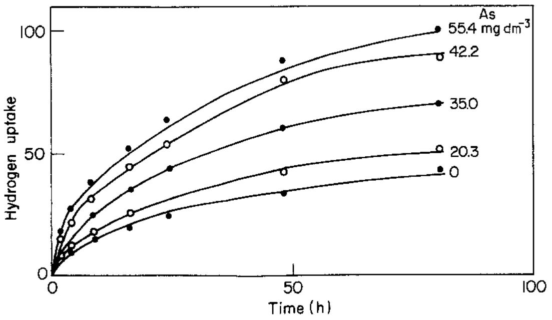

Fig. 3. The hydrogen uptake (in arbitrary units) of Ti from 0.5 mol dm^{-3} H_2SO_4 at various concentrations of As as a function of time.

between the protons and the oxide which is always present on titanium as a thin film.

The new slope of 170 mV decade^{-1} at about − 1000 mV in solutions containing arsenic can be explained by the analysis of Pöpperling and Schwenk [1]. It can be shown [14] that such a slope corresponds to a mechanism in which the recombination step is the Tafel reaction. This relatively rare case occurs when the concentration of the protons near the cathode becomes too low to maintain the Heyrovsky recombination reaction. This decrease of the proton concentration is the result of the competition for the protons between the adsorbed hydrogen atoms and the promoter. According to Pourbaix [15] arsenic exists as a hydride at a potential of − 1000 mV SCE and the pH of the working solution. Since the Tafel reaction is purely chemical, it is slower than the electrochemical Heyrovsky recombination. Consequently a surplus of adsorbed hydrogen is created; these atoms penetrate into the bulk of the metal by diffusion, resulting in an increased hydrogen uptake.

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