



Growth and Degradation of an Anodic Oxide Film on Titanium in Sulphuric Acid Observed by Ellipso-microscopy



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ABSTRACT

The surface of polycrystalline titanium polarised anodically in 0.05 mol dm⁻³ sulphuric acid was monitored using an ellipso-microscope. During dynamic polarisation, a patch-like bright image was seen on an ellipso-microscopic view, and the brightness and image changed with increase in potential. The change in the brightness and image mainly corresponded to growth of an anodic oxide film on the surface. An *in situ* monitoring using the ellipso-microscope revealed that the film formation rate was dependent on the crystallographic orientation of the substrate. Breakdown of the film induced in a solution containing bromide ions was also monitored using the microscope. Prior to the pitting propagation, the surface was partially changed with flow of a large anodic current. AES measurement revealed that the formation of bromo-oxide resulted in localised film degradation followed by pitting corrosion.

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1. Introduction

A passive film, which is a chemically stable oxide film that forms on a material surface in a corrosive environment, plays an important role in protecting the surface from further oxidation. In an environment containing aggressive anions, however, local breakdown of the film occurs, resulting in the flow of a huge oxidation current and initiation of pitting propagation or pitting corrosion. In order to prevent pitting corrosion, which can cause serious accidents in industry and society, the mechanism and kinetics of film breakdown must be elucidated. Frankel reviewed roles of aggressive ions in passive film breakdown and critical factors influencing pitting corrosion [1]. Penetration of ions into the film [2], adsorption of ions on the film [3], and stress induced in the film [4] have been proposed as factors causing film breakdown, but the details are still not clear.

In order to investigate the mechanism and kinetics of pitting initiation, many researchers have tried to monitor changes in a passive film by using sophisticated methods. The scanning electrochemical probe technique is one of the useful methods for *in situ* analysis of passive films. Casillas et al. used a scanning electrochemical microscope (SECM) to monitor the precursor site of pitting on passive titanium in bromide-containing sulphuric acid [5]. An SECM was also used to observe the precursor of pitting

on type-304L stainless steel in chloride-containing sodium perchlorate solution [6]. The scanning vibrating electrode technique [7], scanning reference electrode technique [8], and an electrochemical atomic force microscope [9] have also been used to analyse changes in the passive states of metal surfaces. These scanning probe techniques enable imaging of passive surfaces with a lateral resolution of micrometers to sub-micrometers. However, high-resolution imaging of a large surface is a time-consuming process and is disadvantageous for analysing an event that occurs rapidly such as pitting initiation. On the other hand, ellipsometry is also a useful method for *in situ* analysis of a passive film. It has been used to determine the thickness and/or optical properties of a film. McBee and Kruger showed by using an electrochemical method that significant changes occur in the optical properties of an iron passive film upon introduction of chloride ions [10]. Sugimoto and Matsuda developed a method of microscopic ellipsometry to monitor the changes in a passive film on stainless steel [11,12]. Recently, Punckt et al. have developed an ellipso-microscope to monitor nucleation and evolution of individual pits on type-316 stainless steel [13,14]. Ellipso-microscopic imaging with a high speed camera has advantages of assessment of large sample sizes with high temporal resolution and correlation with macroscopic electrochemical behavior of passive surface while scanning probe techniques provide local electrochemical information. However, imaging of a surface smaller than the whole surface of a sample electrode makes it difficult to correlate the image with current flowing through the sample electrode. A small sample electrode must be used for microscopic imaging and electrochemical measurement in order to find the site where film breakdown

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occurs and to determine how the pitting initiation leads to pitting propagation with current transient.

Titanium is one of the so-called valve metals for which a relatively thick oxide film can be formed by oxidation including anodic polarisation. The oxide film formed on titanium is chemically stable and has an n-type semiconductive property [15,16]. Therefore, titanium and titanium alloys are frequently used as corrosion-resistant materials in chloride-containing environments such as desalination facilities or seashores. However, titanium can suffer localised corrosion from a bromide-containing environment [5,17]. It has been reported [18] that breakdown of a titanium oxide film occurs at sites where oxidation of bromide is active and is determined either by the magnitude of the electric field in the film or by the interfacial potential at the oxide/bromide-containing solution interface. However, details of the site where oxide film breakdown occurs preferentially and details of conditions under which breakdown is induced are still not known.

In this study, the growth and degradation of oxide film formed on titanium in 0.05 mol dm^{-3} sulphuric acid were investigated by *in situ* ellipso-microscopy. By using a microelectrode, monitoring of film growth or degradation simultaneously with recording of current transient was realised. Crystallographic orientation dependence of film growth and mechanism of film degradation due to the existence of bromide ions in the solution are discussed.

2. Experimental

2.1. Material and electrochemistry

A titanium plate or a titanium wire (Nilaco) with a purity of 99.5% was used as the specimen. After connecting an electric terminal and embedding in epoxy resin (Tecknovit 5071, Kulzer), the specimen surface ($2 \text{ mm} \times 0.5 \text{ mm}$ or 0.5 mm in dia.) was polished with grinding discs (MD-Piano220 and MD-Largo, Struers) and burnished with colloidal silica of $0.04 \mu\text{m}$ in particle size. The surface orientation was identified by an Auger electron spectroscopy apparatus (AES; JAMP-9500F, JEOL) equipped with an electron backscatter diffraction (EBSD; SC-200, TSL) detector.

The electrolyte used was 0.05 mol dm^{-3} sulphuric acid aqueous solution or a solution containing KBr at maximum concentration of 2 mol dm^{-3} , deaerated by bubbling with pure Ar gas before measurement. The specimen was set as a working electrode at the bottom of a three-electrode-type electrochemical cell with a volume of 100 cm^3 . The cell had two parallel quartz plates for optical windows. A Pt wire was used as a counter electrode. An Ag/AgCl/saturated KCl electrode was connected with a Luggin-Haber capillary and used as a reference electrode. Whole electrode potential in this study was converted to the standard hydrogen electrode potential (SHE). Most of the potentiodynamic polarisation of the specimen was carried out in stagnant solution using a Solartron potentiostat (SI1287) with a potential sweep rate of 5 mV s^{-1} from an open circuit potential to 10.2 V (SHE) in an air-conditioned room at 295 K . After the polarisation, the specimen surface was rinsed with Milli-Q water and immediately subjected to AES for surface analysis.

2.2. Ellipso-microscopy

A schematic diagram of the ellipso-microscope used in this study is shown in Figure 1. Monochromatic light with a wavelength of 532.0 nm and an output power of 0.1 W from an Nd:YVO₄ laser (JUNO 532-100S, Showa Optorionics Co.) was divided into a sample beam and a reference beam at a cube-type half mirror. Intensity of the reference beam attenuated with neutral density filters was normalised by an optical power sensor (TQ82010+TQ8215, Advantest Co.). The sample beam passing

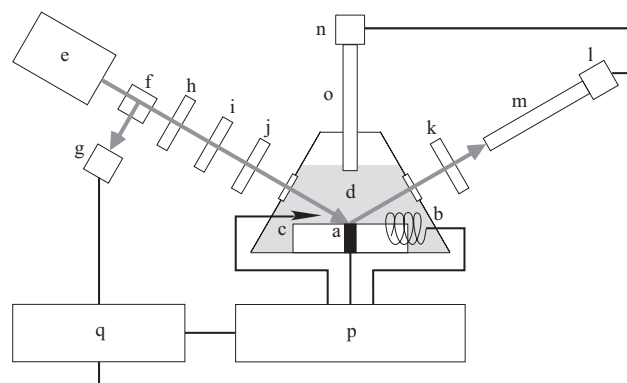


Fig. 1. Schematic diagram of the experimental set-up used. (a) specimen S, (b) counter electrode, (c) reference electrode, (d) electrolyte solution, (e) laser, (f) beam splitter, (g) optical sensor, (h) depolarizer, (i) polarizer P, (j) compensator C, (k) analyser A, (l) CMOS camera and (m) macro-lens for ellipso-microscopy, (n) CMOS camera and (o) macro-lens for optical microscopy, (q) potentiostat and function generator, and (q) PC.

through a polariser (P) and compensator (C; $1/4$ wavelength compensation plate) was specularly reflected at the specimen (S) surface immersed in solution in the electrochemical cell at an incident angle of 60.0° and guided to an analyser (A). The null ellipsometric condition of PCSA optical configuration was established by controlling azimuths of P and A with an azimuth of C at 45.0° before polarisation of the specimen. The surface change was monitored by light intensity deviated from the initial null condition under the initial azimuths of P, C, and A. The spot light intensity change through the PCSA configuration was measured by a 3 M pixels CMOS camera (ARTCAM-300MI, Artray Inc.) or 3.2 M pixels CMOS camera (Flea3 USB3.0, Viewplus Inc.) with a macro lens (LFSHA4, Misumi), which provided magnification of four times with a working distance of 75 mm in air. The surface was also monitored from a perpendicular direction by a 3.2 M pixels CMOS camera (Flea3 USB3.0, Viewplus Inc.) with a macro lens (LFSHB6, Misumi). LabVIEW (ver. 2011, National Instruments) software with a synchronizing strobe was employed to monitor the camera images and to record current transient with a time resolution of 6 or 60 Hz .

3. Results and discussion

3.1. Growth of an anodic oxide film on titanium

Figure 2a shows an anodic polarisation curve of titanium in 0.05 mol dm^{-3} sulphuric acid solution. The anodic current reveals a maximum at 0.3 V and then gradually decreases to 2 V . The current increase at potentials higher than 2 V corresponds to an oxygen evolution, although oxygen dissolves into solution and no gas bubbles are observed until 5.5 V . During dynamic polarisation, the passive oxide grows with increase in potential. Ohtsuka et al. found by using ellipsometry that the mean thickness of a film formed on titanium increases linearly with increase in potential in a range up to 7.5 V (RHE) at a formation rate of 2.4 nm V^{-1} in 0.1 mol dm^{-3} sulphuric acid [19]. The total intensity of light detected by the CMOS camera in the ellipso-microscope also increases gradually with increase in potential (Fig. 2a), indicating that the initial null condition of the PCSA configuration is no longer valid and the deviation from the initial null condition becomes larger with growth of the oxide film on the specimen surface. Therefore, the light intensity in the ellipso-microscopic image increases with increase in thickness of the passive film. It is reasonable that the deviation from the initial null condition is dependent on thickness as well as optical parameters of the film. The light intensity change

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