Raman Spectra of the Anodic Oxide Film on Titanium in Acidic Sulfate and Neutral Phosphate Solutions

Toshiaki Ohtsuka, Jiaju Guo, and Norio Sato

Corrosion Research Group, Faculty of Engineering, Hokkaido University, Sapporo, 060 Japan

ABSTRACT

Laser Raman spectroscopy has been applied under in situ and ex situ conditions to the anodic oxide films formed on titanium at various potentials in neutral phosphate and acidic sulfate solutions. The Raman spectra reveal that the anodic oxide film is primarily composed of an anatase type of TiO₂. From the relation between the Raman band intensity, film thickness, and surface morphology, it is likely that the film changes from the amorphous state to the crystalline state beyond a certain critical potential.

In our previous work (1) the anodic oxide film on titanium was examined with respect to the film thickness-potential relation, polarization curve, and surface morphology in solutions of sulfuric acid, hydrochloric acid, and sodium phosphate. In the work, it was found that a kind of breakdown of the film occurred at a critical potential of 7.5V. In the potential region more negative than the breakdown potential, the film grew linearly with potential at a thickness-potential ratio of about 2.5 nmV⁻¹, while, in the potential region more positive than E蜕变, the film thickness increased at a higher ratio, giving rise to surface roughening.

In this paper the anodic oxide film is further studied by in situ Raman scattering spectroscopy to check its composition. In situ Raman spectroscopy is one of the promising methods for checking the composition of electrode surface layers (2, 3). For some special electrode systems, such as silver with pyridine absorbers, surface-enhanced Raman scattering (SERS) can be used. With the present titanium electrodes, the SERS effect cannot be expected to occur and, therefore, normal Raman scattering spectroscopy, which is not sensitive enough to detect a surface oxide layer as thin as 10 nm, has to be used.

In this paper, application of normal Raman spectroscopy to anodic surface oxide films on titanium is discussed in terms of the composition and crystallinity of the films.

EXPERIMENTAL

The Raman spectrometer used was a triple type of monochromator, JASCO R-800/1, and excitation was made by a single line of 514.5 nm wavelength of an argon ion laser, NEC M-GLS 3200. The incidence power of the light was about 300 mW. The intensity of the scattering light was detected by a photomultiplier and a photon counter.

Figure 1 shows the experimental cylindrical cell for the Raman spectrometric measurements of electrodes. In the cell, the Luggin tube leading to a reference electrode Ag/AgCl, and the counterelectrode of a platinum plate were inserted. The working electrode of titanium was fixed at the center of the cell, facing an optical window at a distance about 5 mm. The laser light for excitation was polarized in the parallel direction to the incidence plane and its incidence angle was about 50°. The Raman scattering light was collected in the incidence plane at an angle about 70° to the incidence light.

The electrolytes used were 0.1 mol dm⁻³ aqueous phosphate buffer solution at pH 6.9 and 0.1 mol dm⁻³ aqueous sulfuric acid solution, which were prepared from doubly distilled water and analytical grade reagents. The electrolytes were bubbled by purified nitrogen gas for more than 24h before being introduced into the cell for experiments. The pretreatment of the titanium electrode (99.9% pure) was the same as that described in our previous paper (1).

RESULTS

Figure 2 shows in situ Raman spectra of the anodic oxide films formed on titanium by 1h oxidation at constant potential at 5.80V and 10.60V vs. RHE in neutral phosphate solution of pH 6.9. During these Raman scattering
measurements, the titanium electrodes that had been oxidized for 1 h at the above potentials were kept at a constant potential of 1.60 V to avoid evolution of oxygen bubbles, which prevents accurate optical measurements of the electrode surface at potentials higher than 4 V. The Raman spectra of the anodic oxide films formed in 0.1 mol cm$^{-3}$ sulfuric acid were also measured and the results are given in Table I. In Table I, comparison is made between the Raman spectra measured in this work and those found in literature (4-7) for various titanium oxides. From Table I, the anodic oxide film is identified with an anatase type of TiO$_2$.

The ex situ measurements of the Raman spectra in air were conducted after the anodic oxidation and the results were compared with the in situ spectra. Figures 4 and 5 show the spectra thus obtained for the anodic oxide film formed at potentials lower than 8 V and at potentials higher than 8 V, respectively. For the oxide formed at potentials higher than 8 V four relatively intense peaks are seen in Fig. 5, and the peak intensity becomes smaller, the lower the potential.

For the oxide formed at 2.6 V the four Raman bands corresponding to the anatase type of TiO$_2$ are not distinguishable on the spectrum where only the weak Raman bands corresponding to air and to optical elements such as condenser lenses are observed. The ex situ spectra of the anodic oxide film formed in sulfuric acid solution were also measured and results similar to Fig. 4 and 5 were obtained.

**Discussion**

The intensity of Raman bands of a thin transparent oxide film on a metal surface is supposed to be almost proportional to the thickness of the film. In Fig. 6, comparison is made between the intensity of the Raman peak at $\Delta \nu = 145$ cm$^{-1}$ and the film thickness found in the previous work (1), where the peak height as the intensity and
the thickness are plotted against potential. The data of Fig. 6 for the Raman peak height are based on the results shown in Fig. 4 and 5. The peak height, estimated in counts/s from subtracting the background level of the spectrum, is reproducible within an error limit of about 20% at each measurement. The Raman peak begins to appear at about 4V, and its intensity increases with potential. At a potential of 4V, although the film thickness is about 13 nm, no definite Raman bands are observed. This suggests that the Raman intensity of the oxide film is determined not only by its thickness but also by other factors. We believe that one of these factors is the crystallinity of the oxide film. The oxide film appears to change from an amorphous to a crystalline state as the potential exceeds a certain value. The amorphous nature of solid compounds brings about Raman bands, which are broader than those of the crystalline compounds, and thus results in the loss of peak sharpness.

Figure 7 shows the surface morphology observed by electron microscopy using a replica technique. In the low potential region, the surface exhibits a similar morphology to that of the polished surface. When the titanium electrode is oxidized at 5.6V, a crater-like pattern is observed with each crater having a diameter about 3 μm. When the titanium electrode is oxidized at potentials more positive than 10V, a ripple-like pattern appears on the electrode surface. The change of the surface mor-

---

Fig. 5. Ex situ Raman spectra of the anodic oxide films formed on titanium at constant potential for 1h in 0.1 mol dm⁻³ neutral phosphate solution. The bandpass of the spectrometer was about 10 cm⁻¹.

Fig. 6. Film thickness and Raman peak height at Δν = 150 cm⁻¹ as a function of potential. The film thickness data were referred to the previous work (1).

Fig. 7. Electron microscopic appearance of the surface of titanium covered with the anodic oxide film. The oxidation was made potentiostatically for 1h in 0.1 mol dm⁻³ neutral phosphate solution.
Corrosion-Related Aspects of the Chemistry and Frequency of Occurrence of Precipitation

T. E. Graedel

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

ABSTRACT

Surfaces exposed to the atmosphere receive water in several forms: adsorption of water vapor, condensation of dew and fog, and deposition of rain and snow. The natural deterioration of wetted materials is enhanced by the corrodents contained in the water as well as by gaseous molecules subsequently incorporated into the water. This paper reviews the chemistry of the different atmospheric precipitation forms, combines those data with typical annual durations of the precipitation forms in four cities (Albuquerque, Los Angeles, Minneapolis-St. Paul, and New York), and deduces the contribution of each precipitation form to annual exposures of materials surfaces to corrodents. A limited assessment for indoor corrosion gases is also included. Among the results of interest are that the nitrate exposure of surfaces appears to be predominantly due to gaseous deposition; that deposition of organic corrodents is as high or higher indoors than it is outside; and of the duration of the atmospheric processes. It is worth noting in Table I that dew and fog typically deposit more moisture per unit time than rain or snow (in climates where both occur).

Precipitation contains a number of trace constituents that have the potential to produce materials degradation. Partly because of their known interactions with materials and partly because of the availability of sufficient logical phenomena, as summarized in Table I. There are, of course, wide ranges of moisture deposition amount and of the duration of the atmospheric processes. It is worth noting in Table 1 that dew and fog typically deposit similar amounts of moisture to a surface, as do rain and snow (in climates where both occur).

Table I. Occurrence of atmospheric phenomena at mid-latitude North American sites

<table>
<thead>
<tr>
<th>Phenomenon</th>
<th>Annual moisture deposition (mm)</th>
<th>Annual duration (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dew</td>
<td>0-100</td>
<td>0-1500</td>
</tr>
<tr>
<td>Fog</td>
<td>0-40</td>
<td>0-150</td>
</tr>
<tr>
<td>Rain</td>
<td>30-8000</td>
<td>10-5000</td>
</tr>
</tbody>
</table>

Acknowledgment

The authors wish to thank Mr. Noboru Goto and Mr. Minoru Masuda of the Faculty of Engineering, Hokkaido University, for their assistance.

Manuscript submitted Jan. 27, 1986; revised manuscript received May 20, 1986.

Hokkaido University assisted in meeting the publication costs of this article.

REFERENCES