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

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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 7.5 V. In the potential region more negative than the breakdown potential, Eₚ, the film grew linearly with potential at a thickness-potential ratio of about 2.5 nm/V, while, in the potential region more positive than Eₚ, 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-800T, 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 laser light was about 300 mW. The intensity of the scattering light was collected in the incidence plane and its incidence angle was about 50°.

Figure 1 shows the experimental cylindrical cell for the Raman spectroscopic measurements of electrodes. In the cell, the Luggin tube leading to a reference electrode Ag/AgCl, and the counter electrode 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 in a direction at 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 24 h 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 1 h oxidation at constant potential at 5.60 V and 10.60 V vs. RHE in neutral phosphate solution of pH 6.9. During these Raman scattering
In situ Raman spectroscopic measurements were also made for the anodic oxide films formed at potentials more negative than 7V in the phosphate and sulfuric acid solutions, but no definite peaks were detected on the spectra, where only the weak Raman bands corresponding to the aqueous solutions were observed as a background.

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 8V and at potentials higher than 8V, respectively. For the oxide formed at potentials higher than 8V four relatively intense peaks are seen in Fig. 5, and the peak intensity becomes smaller, the lower the potential.

For the oxide formed at 2.6V the four Raman bands corresponding to the anatase type of TiO$_2$ are not distinguishable on the spectrum where only the 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
Ti/Oxide Film, Air
Anodic Oxidation
Phosphate, pH 6.9
Potentiostatic Oxidation

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.

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. 7](image-url)
Corrosion-Related Aspects of the Chemistry and Frequency of Occurrence of Precipitation

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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 corrosive substances 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 corrosives. A limited assessment for indoor corrosion rates 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 corrosives is as high or higher indoors than it is outside, that materials exposure to the sulfate ion may occur more from dew than from other forms of precipitation, and that under some circumstances fog, rain, and perhaps snow can contribute substantial fractions of corrosive exposure burdens.

It is well established that materials of many different kinds are degraded upon exposure to the atmosphere. It is less obvious how that degradation takes place and what forms of atmospheric impacts play the principal roles. This uncertainty results from the wide ranges in frequency of occurrence of atmospheric phenomena, as well as substantial chemical diversity among those phenomena when they do occur.

A common thread in the several atmospheric processes that degrade materials is that the processes are markedly accelerated by water (1). This water may be provided by any of the several forms of precipitation or by the adsorption of water vapor during periods of moderate to high humidity (2). In the former case, the water brings with it any corrosives that may be present in precipitation. In both the former and latter cases gas phase corrosives may become incorporated into water that is present at the surfaces of the materials.

The purpose of the present study is to compare the exposures of materials to corrosives from six sources: dew, fog, rain, snow, gaseous molecules in outdoor air, and gaseous molecules in indoor air. The first step in doing so is to review the frequency of occurrence of the meteorological 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 I that dew and fog typically deposit similar amounts of moisture to a surface, as do rain and snow (in climates where both occur).

Precipitation contains a number of trace constituents which have the potential to produce materials degradation. Partly because of their known interactions with materials and partly because of the availability of sufficient

<table>
<thead>
<tr>
<th>Phenomenon</th>
<th>Annual moisture deposition (mm)</th>
<th>Typical value</th>
<th>Annual duration (h)</th>
<th>Typical value</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dew</td>
<td>0-100</td>
<td>30</td>
<td>0-1500</td>
<td>750</td>
<td>(3-7)</td>
</tr>
<tr>
<td>Fog</td>
<td>0-40</td>
<td>25</td>
<td>0-300</td>
<td>60</td>
<td>(7); (6)</td>
</tr>
<tr>
<td>Rain</td>
<td>30-8000</td>
<td>750</td>
<td>10-3000</td>
<td>300</td>
<td>(9)</td>
</tr>
<tr>
<td>Snow</td>
<td>0-9000</td>
<td>750</td>
<td>0-3000</td>
<td>300</td>
<td>(9)</td>
</tr>
</tbody>
</table>

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