In Situ Laser Raman Spectroelectrochemical Study of the Corrosion of Lead in Dilute Na$_2$SO$_4$ Solution at High Temperature

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ABSTRACT

The high temperature corrosion and passivation behavior of a lead electrode in a 100 ppm Na$_2$SO$_4$ solution was examined by in situ laser Raman spectroscopy and cyclic voltammetry. The experimental observations were compared with the thermodynamic predictions of the temperature-dependent Pourbaix diagram for lead in aqueous sulfate solution. At open-circuit condition and room temperature, the composition of the corrosion film was found to be $3\text{PbO}_2\text{PbSO}_4\text{H}_2\text{O}$. The latter composition is stabilized relative to PbSO$_4$ by an elevated local pH at the electrode surface which accompanies the reduction of dissolved oxygen at open circuit. At higher temperatures only PbO$_2$PbSO$_4$ and PbSO$_4$ were observed at open circuit. By correlating the temperature dependence of the cyclic voltammetry with the Pourbaix diagram, the PbSO$_4$ corrosion film was found to be a more effective passivator than the PbO$_2$PbSO$_4$ film.

Experimental

The high temperature/high pressure (HTHP) spectroelectrochemical cell used in these experiments was described in an earlier publication (1). The lead working electrode was fabricated by melting lead shot onto a nickel support under a helium atmosphere followed by filing to the desired size and shape. An external Ag/Ag$_2$SO$_4$ reference electrode was connected to the cell via a long Teflon tube which was filled with zirconium oxide sand (2) and saturated Na$_2$SO$_4$/Ag$_2$SO$_4$ solution. The Teflon tube was supported in 1/4 in. stainless steel tubing. The reference electrode assembly was maintained at room temperature by bending the tube in a downward direction to avoid convection of heat. The Ag/Ag$_2$SO$_4$ electrode measured +0.693V vs. NHE. The counter electrode was a platinum wire that was coiled around the working electrode. The supporting electrolyte was a 100 ppm Na$_2$SO$_4$ solution that contained 4-10 ppb dissolved oxygen. The electrolyte was circulated through the HTHP cell from a stainless steel reservoir using a high pressure pump; cell pressure was established by a back pressure regulator fixed a 1300 psi. (At the anticipated uppermost operating temperature of 300°C, the vapor pressure of water is 1246 psi.) Potential control was afforded by a PAR Model 173 potentiostat. The scattered radiation was collected at 90° and analyzed using a Spex Model 1403 double monochromator with photon counting detection. A Coherent Radiation Model CR6 argon ion laser, incident at 60° to the surface normal, was used to excite the Raman spectra. The excitation wavelength was 5145Å. Film composition at room temperature was also determined by x-ray powder diffraction analysis of samples scraped off the electrode surface. The laser power was maintained at 100 mW.

Results

In order to facilitate comparison of experimental observations with thermodynamic expectations, we have constructed the potential-pH (Pourbaix) diagram for lead in 100 ppm Na$_2$SO$_4$ at 298 K (Fig. 1). The standard free energies for the compounds in the diagram are given in Appendix A. Only the solid phases were considered in the construction of the diagram; solubility data are not included.

At 298 K, the open-circuit potential was found to be
-0.268 V vs. NHE and the solution pH was measured to be 6.2. Both are indicated in Fig. 1. From the open-circuit potential, the activity of Pb²⁺ was calculated to be $1.7 \times 10^{-5}$, which compares with the Pb⁴⁺ activity calculated from the $K_{sp}$ for PbSO₄, i.e., $1.67 \times 10^{-5}$. At the solution pH of 6.2, the Pourbaix diagram predicts establishment of equilibrium between the lead electrode and a PbO-PbSO₄ phase. The solution pH is, however, very close to the pH at which PbSO₄ and PbO-PbSO₄ are in equilibrium, i.e., pH = 6.01. Clarifying discussion as to which phase, PbSO₄ or PbO-PbSO₄, should be thermodynamically expected in this experiment depends upon accurate measurement of pH and accurate standard free energy values. Available literature values for the standard free energies of formation for PbSO₄, PbO-PbSO₄, and SO₄²⁻ allow for pH values for the PbSO₄/PbO-PbSO₄ vertical to range from 5.9 to 6.2. The solution pH has also been observed to range from 5.8 to 6.3 owing to a dependence on dissolved CO₂ content. We will defer further discussion of this point until later.

At open circuit, no in situ Raman spectrum was observable in our deoxygenated supporting electrolyte. In solutions where the dissolved oxygen content was permitted to rise, a Raman spectrum was observed at the open-circuit potential. This result suggests that the presence of dissolved oxygen is required for film formation at open circuit. The Raman spectrum is characterized by a strong line at 146 cm⁻¹ and a line of medium intensity at 961 cm⁻¹ as shown in Fig. 2. These lines can be assigned (3, 4) to vibrations of PbO and SO₄²⁻, respectively. The film composition was identified by x-ray diffraction as 3PbO-PbSO₄H₂O.

Consideration of the potential-pH diagram reveals that the 3PbO-PbSO₄H₂O phase is thermodynamically stable only above $\approx$ 9.73 at room temperature. So that we may better understand the apparent nonequilibrium observations and better appreciate the role of dissolved oxygen in the corrosion process, we have written electrochemical reactions to balance the oxidation of lead with the reduction of dissolved oxygen at open circuit. Thus, the redox pair at the solution pH of 6.2 would be

$$O_2 + 4H^+ + 4e^- = 2H_2O \quad [1]$$
$$2Pb + SO_4^{2-} + H_2O = PbO-PbSO_4 + 2H^+ + 4e^- \quad [2]$$

(net) $$2Pb + SO_4^{2-} + O_2 + 2H^+ = PbO-PbSO_4 + H_2O \quad [3]$$

The net reaction [3] identifies a consumption of protons in the oxidation of lead to PbO-PbSO₄. Reaction [3] would then increase the local pH at the electrode surface such that 3PbO-PbSO₄H₂O becomes the stable phase and the following redox pair proceeds

$$2O_2 + 8H^+ + 8e^- = 4H_2O \quad [4]$$
$$4Pb + SO_4^{2-} + 4H_2O = 3PbO-PbSO_4H_2O + 8e^- + 6H^+ \quad [5]$$

(net) $$4Pb + SO_4^{2-} + 2O_2 + 2H^+ = 3PbO-PbSO_4H_2O \quad [6]$$

The net consumption of protons in reaction [6] would maintain the increased local pH at the electrode surface that is required for the stability of the 3PbO-PbSO₄H₂O phase.

If the solution pH were slightly lower than that measured for the electrolyte holding tank, possibly resulting from an increase in the concentration of dissolved CO₂...

![Fig. 2. In situ Raman spectrum of a lead electrode in dilute Na₂SO₄ at open circuit. Excitation wavelength: 5145 Å.](image)

![Fig. 3. Temperature-dependent Pourbaix diagram for lead in dilute Na₂SO₄. The diagram was constructed from data provided in Appendix B. The arrows identify the solution pH at each of the selected temperatures. The open-circuit potentials at each of the selected temperatures are indicated. Potentials are referenced to the normal hydrogen electrode.](image)

![Fig. 4. Temperature dependence of the cyclic voltammogram for lead in dilute Na₂SO₄. Potentials are referenced to Ag/Ag₂SO₄, which was maintained at 298 K. Ramp rate was 1 mV/s. The electrode surface area was approximately 0.1 cm².](image)
upon circulation of the electrolyte through the cell, the following redox pair would be operative at open circuit

\[
\begin{align*}
\text{O}_3 + 4\text{H}^+ + 4e^- & = 2\text{H}_2\text{O} \quad [7] \\
2\text{Pb} + 2\text{SO}_4^{2-} & = 2\text{PbSO}_4 + 4e^- \quad [8] \\
(\text{net}) 2\text{Pb} + 2\text{SO}_4^{2-} + \text{O}_2 + 4\text{H}^+ & = 2\text{PbSO}_4 + 2\text{H}_2 \quad [9]
\end{align*}
\]

Again the net consumption of protons in reaction [9] could drive the local surface pH above 9.73 as is required for the stability of the observed 3\(\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}\) phase.

When the temperature is increased, the thermodynamic properties of the system change accordingly. Appendix B contains values of the Gibbs free energies at selected temperatures relative to 298 K for \(\text{H}_2\text{O} \cdot \text{SO}_4^{2-} \cdot \text{PbSO}_4 \cdot \text{PbOPbSO}_4 \cdot \text{PbOPbSO}_4 \), and 3\(\text{PbOPbSO}_4 \) along with the corresponding equilibrium equations. Using these data, the temperature-dependent Pourbaix diagram (Fig. 3) was constructed for the potential-pH region near the open-circuit potential.

It can be observed in Fig. 3 that the pH for the \(\text{PbSO}_4 / \text{PbOPbSO}_4 \) equilibrium drops well below the solution pH at 383 and 423 K, assuring the thermodynamic stability of the \(\text{PbOPbSO}_4 \) phase at open circuit for those temperatures. At the still higher temperatures of 493 and 553 K the \(\text{PbSO}_4 / \text{PbOPbSO}_4 \) vertical shifts to pH values above the solution pH and \(\text{PbSO}_4 \) is predicted to be the thermodynamically stable phase at open circuit.

The temperature dependence of the cyclic voltammogram for lead in dilute \(\text{Na}_2\text{SO}_4\) (Fig. 4) can be understood in terms of the Pourbaix diagram. At 298 K the anodization of lead in dilute sulfate demonstrates two waves followed by passivation. According to the Pourbaix diagram, only one phase, \(\text{PbOPbSO}_4 \), is expected to be stable at the solution pH and within the anodic range of Fig. 1. We examined the film composition associated with each of the two anodic waves by judicious selection of applied potential. While holding the potential at \(-0.85\) V, relative to the \(\text{Ag/Ag}_2\text{SO}_4\) reference electrode, i.e., on the leading edge of the first wave, the spectra shown in Fig. 5 were recorded. The film composition was subsequently identified as \(\text{PbOPbSO}_4\) by x-ray diffraction. The spectrum at 323 K is dominated by two lines at 976 and 149 cm\(^{-1}\). These lines can again be assigned to the symmetric stretching vibrations of the \(\text{SO}_4^{2-}\) and \(\text{PbO}\) groups, respectively (though the sulfate vibration is distinguished by a shift of 15 cm\(^{-1}\) from the same vibration in \(3\text{PbOPbSO}_4\)). The relative intensities of the two Raman lines assigned to motions of the \(\text{PbO}\) and \(\text{SO}_4^{2-}\) groups in the two phases, \(\text{PbOPbSO}_4\) and \(3\text{PbOPbSO}_4\), reflect the ratio of \(\text{PbO}\) to \(\text{PbSO}_4\) in each

\[
\text{V}_{\text{app}} = -0.85 \text{ volts}
\]

Fig. 5. Temperature dependence of the Raman spectrum observed for lead in dilute \(\text{Na}_2\text{SO}_4\) with an applied anodic potential of \(-0.85\) V vs. \(\text{Ag/Ag}_2\text{SO}_4\).

\[
\text{V}_{\text{app}} = -0.1 \text{ volts}
\]

Fig. 6. Temperature dependence of the Raman spectrum observed for lead in dilute \(\text{Na}_2\text{SO}_4\) with an applied anodic potential of \(-0.1\) V.
phase. The film composition persists to high temperature with slight drops in the vibrational frequencies for both lines. The persistence of the spectrum to high temperature is not unexpected, since a thick corrosion film was created at 323 K and then the temperature was increased without reducing the film and reoxidizing the metal at each temperature.

We are confident that the first anodic wave in the cyclic voltammogram is associated with oxidation of lead to PbOPbSO₄. The expectations of the Pourbaix diagram would appear to have been born out. However, oxidation of the clean lead surface at more anodic voltages yields a film of composition other than PbOPbSO₄, in spite of the thermodynamic predictions outlined in the Pourbaix diagram.

In Fig. 6, we show the Raman spectrum that was observed with an applied voltage of −0.1V vs. Ag/Ag₂SO₄. The spectrum corresponds exactly to that of polycrystalline PbSO₄; this composition was confirmed by x-ray diffraction analysis of material scraped from the electrode surface. Thus, the second anodic wave in the cyclic voltammogram represents oxidation of lead to PbSO₄ with a vertical equilibrium line between the PbSO₄ and PbOPbSO₄ phases on the potential-pH diagram it is incongruous to observe more than one phase within the potential range studied and at a fixed pH. Arguments similar to those used in the understanding of the open-circuit film composition are also applicable here.

In the potential range of the first anodic wave in the cyclic voltammogram dissolved oxygen is also being reduced cathodically. This process is accompanied by consumption of protons and would be expected, as above, to increase the local pH at the electrode surface. The increased local pH could stabilize the PbOPbSO₄ phase if in fact the PbSO₄ phase were the thermodynamically stable phase at the true solution pH. When driving the oxidation with an applied potential the rate of reduction of dissolved oxygen cannot keep up with the metal oxidation and the associated increase in the surface pH is not sufficient to stabilize the PbOPbSO₄H₂O phase. Finally, that the PbSO₄ phase is the true stable phase at the solution pH is supported by the Raman spectra recorded at −0.1V. Dissolved oxygen will not be reduced at such an anodic potential and the lead oxidation proceeds at the solution pH and produces a PbSO₄ corrosion film. Differences between the observed PbSO₄ phase and the prediction of the Pourbaix diagram can be attributed to the closeness of our solution pH to the PbSO₄/PbOPbSO₄ equilibrium and small errors in the thermodynamic properties and/or the solution pH.

Returning now to the temperature dependence of the cyclic voltammogram (Fig. 4) we find different passivation behavior at temperatures above 298 K. While passivation appears to occur at 298 K the film composition at 363 K appears ineffective in passivating the electrode, and a potential instability is observed. At 298 K, the passivating film composition is mostly PbSO₄ whereas, at 363 K, the corrosion film composition is mostly PbOPbSO₄, following the expectations of the temperature-dependent Pourbaix diagram. When the temperature is increased further the passivating effectiveness of the corrosion film improves. Figure 3 demonstrates that above 363 K the PbSO₄/PbOPbSO₄ equilibrium shifts to higher pH and above 438 K PbSO₄ is again the predicted stable phase. It seems clear that when the corrosion film is PbSO₄ the passivation behavior is good. The PbSO₄ lattice is orthorhombic with a density of 1.581 g/cm³, while the PbOPbSO₄ lattice is tetragonal with a density of 0.899 g/cm³. The large difference in density for the two films may explain the relatively good passivating behavior of the PbSO₄ film over that of PbOPbSO₄.

We examined the temperature dependence of the sulfate symmetric stretching vibration in the Raman spectrum of the lead electrode at open circuit (Fig. 7). The low temperature 3PbOPbSO₄H₂O phase was observed to persist to at least 323 K as indicated by the observation of a line at 961 cm⁻¹. At 383 K, a new line appears at 976 cm⁻¹. The 976 cm⁻¹ line completely replaces the 961 cm⁻¹ line at 383 K after long times. From analysis of Raman scattering by anodic films on lead (Fig. 5 and 6) and consideration of the temperature-dependent Pourbaix diagram, the 976 cm⁻¹ line can be assigned to sulfate motion in PbOPbSO₄. The higher frequency sulfate motion continues to be observed up to 553 K, where the film composition was found to be a mixture of PbOPbSO₄ and PbSO₄ X-ray diffraction and the absence of the 3PbOPbSO₄H₂O phase at high temperature indicates that the local pH effect caused by the reduction of oxygen is less pronounced at higher temperature due to much lower O₂ solubility.

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APPENDIX A

The following thermodynamic values were used in the preparation of the Pourbaix diagram at 298 K (Fig. 1).

<table>
<thead>
<tr>
<th>Substance</th>
<th>ΔG°(cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>59639</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>-177974</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>-179940</td>
</tr>
<tr>
<td>PbO</td>
<td>-44910</td>
</tr>
<tr>
<td>PbO₂</td>
<td>-50560</td>
</tr>
<tr>
<td>PbO₃</td>
<td>-147600</td>
</tr>
<tr>
<td>PbSO₄</td>
<td>-194369</td>
</tr>
<tr>
<td>PbO₂SO₄</td>
<td>-246700</td>
</tr>
<tr>
<td>3PbO₂SO₄</td>
<td>-341200</td>
</tr>
</tbody>
</table>

Ref. (4)
The equations of equilibrium between two solids are as follows: \( a_{SO_{4}^{2-}} = 6.38 \times 10^{-4} \).\(^1\)

1. \( \text{PbO} + 2e^- + 2H^+ = \text{Pb} + H_2O \)
   \( E = 0.255 - 0.059T \) pH

2. \( 3\text{PbO} \cdot \text{PbSO}_4 \cdot H_2O + 6H^+ + 6e^- = 4\text{Pb} + \text{SO}_{4}^{2-} + 4H_2O \)
   \( E = 0.061 - 0.0443T \)

3. \( \text{PbO} \cdot \text{PbSO}_4 + 2H^+ + 4e^- = 2\text{Pb} + \text{SO}_{4}^{2-} + H_2O \)
   \( E = -0.083 - 0.0295T \)

4. \( \text{PbSO}_4 + 2e^- = \text{Pb} + \text{SO}_{4}^{2-} \)
   \( E = -0.261 \)

5. \( \text{PbSO}_4 + H^+ + 2e^- = \text{Pb} + HSO_4^- \)
   \( E = -0.218 - 0.0295T \)

6. \( 4\text{PbO} + \text{SO}_{4}^{2-} \cdot 2H^+ = 3\text{PbO} \cdot \text{PbSO}_4 \cdot H_2O \)
   \( pH = 13.17 \)

7. \( 3\text{PbO} \cdot \text{PbSO}_4 \cdot H_2O + 2H^+ = 2(\text{PbO} \cdot \text{PbSO}_4) + 2H_2O \)
   \( pH = 9.73 \)

8. \( \text{PbO} \cdot \text{PbSO}_4 + \text{SO}_{4}^{2-} + 2H^+ = 2\text{PbSO}_4 + H_2O \)
   \( pH = 6.01 \)

9. \( \text{Pb}_2\text{O}_7 + 2e^- + 2H^+ = 3\text{PbO} \cdot \text{PbSO}_4 \cdot H_2O + 4H^+ \)
   \( E = 1.035 - 0.056T \)

10. \( 3\text{PbO}_3 \cdot \text{SO}_4^{2-} + 8e^- + 14H^+ = 3(\text{PbO} \cdot \text{PbSO}_4 \cdot H_2O) + 4H^+ \)
    \( E = 1.624 - 0.104T \)

\(^1\)\( a_{SO_{4}^{2-}} \) was estimated from application of the Debye-Huckel limiting law for the 7.04 x 10^-6 M NaSO_4 solution.

**APPENDIX B**

The data on Table IB were used in the construction of the temperature-dependent Fourbais diagram in the region around the open-circuit potential and solution pH.

The solution pH was measured experimentally at the electrolyte holding tank only at room temperature. The pH at other temperatures could be calculated from the temperature dependence of the equilibrium constants for water auto dissociation (5) and CO_2 hydrolysis at the elevated pressures of these experiments, i.e., 90 bar (8, 5).

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**Table IB.** \( \Delta G^\circ = \Delta G^\circ_{298} + \sum \Delta G^\circ + \Delta G^\circ_{298} - \sum \Delta G^\circ + \Delta G^\circ_{298} \)

<table>
<thead>
<tr>
<th>(mol)</th>
<th>H_2O</th>
<th>SO_{4}^{2-}</th>
<th>PbSO_4</th>
<th>PbO + PbSO_4</th>
<th>3PbO + PbSO_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>6.38 x 10^-4</td>
<td>-0.394</td>
<td>1.61 x 10^15</td>
<td>6.01</td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>6.25 x 10^-4</td>
<td>-0.394</td>
<td>1.61 x 10^15</td>
<td>6.01</td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>6.16 x 10^-4</td>
<td>-0.394</td>
<td>1.61 x 10^15</td>
<td>6.01</td>
<td></td>
</tr>
<tr>
<td>343</td>
<td>6.03 x 10^-4</td>
<td>-0.394</td>
<td>1.61 x 10^15</td>
<td>6.01</td>
<td></td>
</tr>
<tr>
<td>363</td>
<td>5.92 x 10^-4</td>
<td>-0.394</td>
<td>1.61 x 10^15</td>
<td>6.01</td>
<td></td>
</tr>
<tr>
<td>383</td>
<td>5.80 x 10^-4</td>
<td>-0.394</td>
<td>1.61 x 10^15</td>
<td>6.01</td>
<td></td>
</tr>
<tr>
<td>403</td>
<td>5.59 x 10^-4</td>
<td>-0.394</td>
<td>1.61 x 10^15</td>
<td>6.01</td>
<td></td>
</tr>
<tr>
<td>423</td>
<td>5.48 x 10^-4</td>
<td>-0.394</td>
<td>1.61 x 10^15</td>
<td>6.01</td>
<td></td>
</tr>
<tr>
<td>443</td>
<td>5.36 x 10^-4</td>
<td>-0.394</td>
<td>1.61 x 10^15</td>
<td>6.01</td>
<td></td>
</tr>
<tr>
<td>463</td>
<td>5.24 x 10^-4</td>
<td>-0.394</td>
<td>1.61 x 10^15</td>
<td>6.01</td>
<td></td>
</tr>
</tbody>
</table>

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**Solution pH**

| 298   | 4.68 x 10^7 | 1.02 x 10^-14 | 6.20 (measured) |
| 303   | 4.78 x 10^7 | 8.14 x 10^-12 | 6.00           |
| 323   | 4.88 x 10^7 | 2.28 x 10^-10 | 5.85           |
| 343   | 4.98 x 10^7 | 5.80 x 10^-12 | 5.62           |
Pulse-Stimulated Potentiostatic Deposition of Silver on Single Crystal RuO₂ (110) Surface

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ABSTRACT

It has been demonstrated that the RuO₂ single crystal electrode can serve as the model substrate for the nucleation and growth studies of crystallization processes on compound materials. The RuO₂ single crystals have the advantage of high electrical conductivity and extreme chemical resistance. The electrodeposition of Ag on the RuO₂ (110) surface has been investigated. It has been found that the deposit-substrate interactions are relatively weak in comparison to strong lateral attractions between the Ag adatoms. This allowed us to control the nucleation density in a wide range from 10⁰ to 10¹⁰ nuclei/cm² with the use of pulse-stimulated potentiostatic technique. At longer potential pulses with higher amplitudes, we have observed secondary nucleation processes leading to the formation of conglomerates of Ag nuclei. On the other hand, we have been able to grow large single crystals of silver at short potential pulses with small amplitude and very low overvoltage in the growth step. In the latter case, no secondary nucleation was observed and analysis of the SEM micrographs has revealed that the main supply of Ag adatoms to the growing centers is from the substrate rather than from direct Ag(II) ion discharge at Ag crystalites under the experimental conditions reported.

The electrodeposition of metals on foreign substrates is the subject of continuous interest for the plating industry, for corrosion protection, and for integrated semiconductor microcircuit fabrication. Although some progress in the basic understanding has been achieved, mostly due to the works of Bulgarian (1-9) and English (10-18) schools, various nucleation and growth phenomena leading to the deposition of metals require further extensive studies. In particular, the metallization of semiconductor structures requires a detailed knowledge of the substrate-deposit interactions, adhesive forces, strains and stresses, ohmic or rectifying properties of the junction, optical transmissivity, electrical and magnetic properties, etc.

The deposition process itself is controlled by two factors: the nucleation and the growth rates. The nucleation process may continue to occur during the growth, and this case is usually called progressive nucleation and growth. If under certain conditions all the active centers on the substrate are converted into nuclei at the very beginning of the deposition process and after that only growth of these preformed nuclei is observed, the process is called instantaneous nucleation and growth. Though usually difficult to be realized experimentally, the latter process proposed by Scheludko and Todorova (19, 20) offers in principle an excellent means to control the nucleation density and the grain size of the deposit.

The electrodeposition of metals on compound substrates (semiconductors and semimetallic metal oxides, chalcogenides, carbides, etc.) differs considerably from that on the foreign metal substrates since usually at least two chemically different kinds of atomic sites are available on the surface of compound substrates. Recently, we have observed considerable differences between the lateral in-

References