\[ \Gamma, \Gamma \] anode and cathode, respectively, part of the boundary
\[ \Gamma_i \] insulating part of the boundary
\[ \delta \] disc delta function
\[ \eta_1, \eta_2 \] overpotential on anode and cathode
\[ \eta', \eta'' \] derivative of \( \eta \) and \( \eta \) with respect to \( U' \)
\[ \theta \] current efficiency
\[ \rho \] electrolyte resistivity
\[ \rho_m \] metal density
\[ \sigma \] electrolyte conductivity
\[ \phi_0 \] shape function
\[ \psi \] function defined to be zero after convergence
\[ \Omega \] computational domain

**REFERENCES**


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**Technical Notes**

**Electrochemical Determination of Hydrogen Transport Through Copper**

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The diffusion of hydrogen into metals and other materials has been widely studied because of its importance in embrittlement, permeation through vessels and pipelines, and hydrogen storage in metal alloys (1). The diffusion of hydrogen in many metals is rapid, and there are many cases, e.g., in a hydrogen pipeline, where a practical impermeable material is desired. We became interested in this problem in connection with submarine fiber optic cable systems, where a transmission loss increase caused by hydrogen permeation occurs at wavelengths important in communications (2-5). The question of finding a suitable material to block this permeation led to consideration of copper. We report here studies of hydrogen permeation in copper by the electrochemical method of Devanathan and Stachurski (6, 7). This method has been applied to hydrogen and oxygen diffusion studies in a number of materials (8-15).

**Experimental**

The basic experiment followed previous studies (6-8). A thin (15 and 25 \( \mu m \)) copper foil was clamped as a separator (bielectrode) between two half-cells; the clamping arrangement consisted of O-ring seal joints and utilized Teflon spacers. The area of Cu exposed to each half-cell was 0.78 cm\(^2\). The counterelectrodes in each half-cell compartment were Pt foil. A saturated calomel electrode (SCE) served as a reference electrode in the detection half-cell. The Cu foil bielectrode acted as an anode. This compartment was filled with 0.2M KOH, and this side of the Cu foil was coated with Pt to improve the kinetics of hydrogen oxidation. The potential of the Cu bielectrode side was 0.78 cm\(^2\). The counterelectrodes in each half-cell were Pt foil. A Princeton Applied Research Model 173 potentiostat. A thin (15 and 25 \( \mu m \)) copper foil was clamped as a separator (bielectrode) between two half-cells; the clamping arrangement consisted of O-ring seal joints and utilized Teflon spacers. The area of Cu exposed to each half-cell was 0.78 cm\(^2\). The counterelectrodes in each half-cell compartment were Pt foil. A saturated calomel electrode (SCE) served as a reference electrode in the detection half-cell. The Cu foil bielectrode acted as an anode. This compartment was filled with 0.2M KOH, and this side of the Cu foil was coated with Pt to improve the kinetics of hydrogen oxidation. The potential of the Cu bielectrode side was 0.78 cm\(^2\).

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vacuum evaporation. All solutions were prepared with reagent-grade chemicals and milli-Q (Millipore Corporation) water.

### Results and Discussion

The nature of the anodic current (\(i\)) for the oxidation of hydrogen with time (\(t\)) for the platinum side of the Cu held at \(-0.30\) V vs. SCE and with a constant current of 19.5 mA applied to the cathode side was used to determine the diffusion coefficient, \(D\). The basic experiment and treatment followed previous practice (12). The anode side was pre-electrolyzed at \(-0.30\) V for 4-6h before the constant current was applied to oxidize any residual hydrogen or impurities. Background currents less than 1 nA were obtained. A typical \(i-t\) curve is shown in Fig. 1. This transient can be fit to the equation (12)

\[
\frac{i}{i_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left( -\frac{2(n+1)^2 \tau^2}{4} \right)
\]

where \(i\) is the permeation current at time \(t\), \(i_0\) is the steady-state permeation current, and \(\tau = D/L^2\) (where \(L\) is the foil thickness). The \(\tau\) values were obtained by a computer fit of Eq. [1] to the experimental results. An initial guess for \(\tau\) could be obtained by noting that at \(i/i_0 = 0.5\), \(\tau = 0.60\). Values of \(D\) determined in this way at 23°C for two different Cu samples and several thicknesses are given in Table I. The agreement of \(D\) values for the 99.999% sample for the three thicknesses demonstrates that hydrogen permeation occurs by diffusion. An alternative way of showing this is a plot of \(\tau vs. L^2\) for several values of \(\tau\) (Fig. 3). As predicted by the equation defining \(\tau\), straight lines that intersect the original with a slope of \(D\) result.

The diffusion coefficient was significantly higher for the 99.8% sample than for the 99.999% one, suggesting that impurities have an important effect on the rate of hydrogen permeation in Cu. A comparison of the \(D\) value reported here at 23°C to earlier studies is given in Table II; most involved determinations at much higher temperatures and thus long extrapolations based on the reported heats of activation. The value we report is considerably higher than that previously measured at ambient temperature (13, 14).

The diffusion coefficient measurement on Cu required that As\(_2\)O\(_3\) as a "poison" be added to the catholyte. If As (III) was not added to the catholyte, no detectable hydrogen permeation current through the Cu foil was found, even after 6h of electrolysis. This effect is similar to that observed for hydrogen diffusion through Pt (8, 20), where hydrogen permeation is found only when the cathodic side of the metal membrane is poisoned. For other materials, e.g., Pd (20) and pyrite (12), such poisoning is unnecessary. This effect of As (III) has been ascribed to blockage of sites on the electrode surface for recombination of atomic hydrogen to molecular hydrogen, thus increasing the concentration of atomic hydrogen at the surface. Presumably, it is atomic hydrogen that diffuses through the Cu lattice (1, 14, 18, 21). Evidence for the lack of penetration of H\(_2\) through the copper film was obtained by the following experiment. When the catholyte was replaced by moist hydrogen gas, with exactly the same anode and anolyte configuration as before, no detectable permeation current was observed after 30h. Even when a 0.05 μm Pd covering was deposited on the cathodic side and gaseous hydrogen introduced, no permeation current was observed. Since Pd is known to dissociate H\(_2\) and allow permeation measurements in the absence of a poison (20),

### Table I. Results from electrochemical measurements of hydrogen permeation through copper foil at 23°C

<table>
<thead>
<tr>
<th>Foil type</th>
<th>(L(μm))</th>
<th>Number of trials</th>
<th>(D_{src}) (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Puratronics (99.999%)</td>
<td>25.0</td>
<td>3</td>
<td>(2.6 \times 10^{-9})</td>
</tr>
<tr>
<td></td>
<td>27.5</td>
<td>3</td>
<td>(2.3 \times 10^{-9})</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>3</td>
<td>(2.1 \times 10^{-9})</td>
</tr>
<tr>
<td>Total</td>
<td>15.5</td>
<td>5</td>
<td>(2.3 (±0.3) \times 10^{-9})</td>
</tr>
</tbody>
</table>

\[\frac{D}{i} = \frac{D}{i} \exp \left[\frac{-\Delta H}{kT}\right] \]

\* The value reported by the authors at 227 K is based on application of a constant current to generate hydrogen, but the application of a constant potential boundary condition for the theoretical treatment. This value is a recalculation based on a constant current treatment.

### Table II. Comparison of diffusion coefficients found in this study at 23°C with previous values

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Cu Purity</th>
<th>Temperature range (K)</th>
<th>(D_s) (cm²/s)</th>
<th>(ΔH_s) (kJ/mol)</th>
<th>(D_{src}) (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(17)</td>
<td>99.999%</td>
<td>500-900</td>
<td>(1.1 \times 10^{-9})</td>
<td>39.64</td>
<td>(1.11 \times 10^{-9})</td>
</tr>
<tr>
<td>(18)</td>
<td>99.999%</td>
<td>700-1200</td>
<td>(1.13 \times 10^{-9})</td>
<td>38.65</td>
<td>(1.57 \times 10^{-9})</td>
</tr>
<tr>
<td>(19)</td>
<td>99.999%</td>
<td>800-1000</td>
<td>(2.29 \times 10^{-8})</td>
<td>47.28</td>
<td>(1.04 \times 10^{-9})</td>
</tr>
<tr>
<td>(13)</td>
<td>99.99%</td>
<td>280-336</td>
<td>(4.96 \times 10^{-9})</td>
<td>40.54</td>
<td>(3.46 \times 10^{-9})</td>
</tr>
<tr>
<td>This work</td>
<td>99.999%</td>
<td>296</td>
<td>(2.33 \times 10^{-10})</td>
<td>5.2 x 10^{-10}</td>
<td></td>
</tr>
</tbody>
</table>
the lack of permeation for the Pd-coated Cu configuration suggests rapid H atom recombination at the Pd/Cu interface. A number of studies have been concerned with the mechanism of "poisoning" by arsenic species (22-26). It is interesting that As acts in a similar way for such different metals as Pt and Cu. From the point of view of blockage of H₂ permeation, the slow step in penetration of different metals such as molybdenum is increased to provide improved resistance to localized corrosion.

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REFERENCES


Electrochemical Observations as Related to Marine Atmospheric Corrosion of Chrome-Flashed Stainless Steels

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Generally, stainless steels are susceptible to localized corrosion (such as pitting) in chloride containing environments. This occurs in environments where the alloys are totally immersed as well as in those where intermittent wetting occurs, such as marine atmospheres and splash and spray zones. Often the concentration of alloying elements such as molybdenum is increased to provide improved resistance to localized corrosion.

Stainless steels have been plated with a thin layer of chromium (chrome flashed) for decorative purposes for automotive applications (1-3). The chromium electrodeposition is usually about 0.01 mil thick and does not completely cover the stainless steel. It provides a better color match with other trim components, improves appearance, and adds abrasion resistance. It has been established that chrome-flashed stainless steels have better resistance to localized corrosion than their base counterparts in marine atmospheres and chloride environments such as the salt-belt region for automobiles (1-3). Little is known, however, about the performance of chrome-flashed stainless steels under total immersion conditions. The purpose of this work was to elucidate the mechanisms of corrosion resistance of chrome-flashed stainless steels in chloride containing atmospheres and compare its performance in these atmospheres to its performance when totally immersed.

Experimental

The comparative performance of bare and chrome-flashed stainless steels was evaluated in laboratory accelerated tests and environmental exposure tests. A cyclic immersion testing procedure was used in the laboratory to simulate marine atmospheric exposure. This test for pitting resistance of stainless steels for automotive service consisted of a 10s immersion period in a 5% sodium chloride solution followed by a 90s drying period at 105°F. A multiple crevice washer (ASTM G78-83) was tightened to a torque of 75 in.-lb in the center of 4 × 6 in. sections of 434 stainless steel-clad aluminum and chrome-flashed 434 stainless steel-clad aluminum. These specimens were then run for 100 cycles in the cyclic immersion test.

Bare and chrome-flashed 301 stainless steel-clad aluminum bumpers were exposed in the splash and spray zone at the LCCT test facility in Wrightsville Beach, North Carolina, to determine their performance in an alternate immersion environment. These same materials were totally immersed in seawater at the Texas Instruments test facility in Buzzards Bay, Massachusetts. The aluminum was masked in the total immersion tests so that it could not provide galvanic protection to the stainless steel.

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