Corrosion Morphologies and Products of Copper Immersed in Dimethyl Sulfite Hydrolysis Solution

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Abstract. The corrosion products and morphologies of copper when immersed in the dimethyl sulfite hydrolysis solution for half a month in a sealed container were investigated by optical microscopy (OM), X-ray diffraction (XRD), scanning electron microscopy (SEM). The Cu\textsubscript{2}O phase could be identified in the corrosion products. Two typical corrosion morphologies could be found in the SEM image, namely corrosion pits and cracks. This observation provided better understanding of the corrosion behaviors of copper in dimethyl sulfite hydrolysis solution.

Introduction

Lubricating oil is always used in the production process of some copper parts. However, the residual lubricating oil combines with water and oxygen will result in oxidation discoloration and corrosion on the surface of copper [1]. The contents of the lubricating oil is so complicated that it’s not easy to find out which part will contribute to the corrosion reaction [2]. It was found that the sulfur-containing lubricating oil had the same substructures with dimethyl sulfite [3]. So in this study we choose dimethyl sulfite as the corrosion medium to study the effects of the sulfur-containing parts on the corrosion reaction of copper. Dimethyl sulfite will directly affect the corrosion process. Firstly, dimethyl sulfite was hydrolyzed to generate sulfurous acid, sulfuric acid and methanol in the sodium hydroxide solution. Then, the obtained hydrolysis solution was used as the corrosion medium in the subsequent immersion corrosion.

Experimental Details

Materials and Reagents

The copper sheet used in this study was 99.9\% in purity and 8×8×2 mm in size. Before immersion corrosion, the sample was polished with metallographic sandpaper followed by diamond abrasion paste [4]. Then the surface of the sample was cleaned by deionized water and absolute alcohol, and then dried in cold wind by drier [5]. Then, 10 ml dimethyl sulfite and 10 ml (1M) NaOH aqueous solution were mixed in a round-bottomed flask. The flask was heated on a thermal control electric heater for 1.5 h and the temperature was controlled ranging between 70\(^\circ\)C and 100\(^\circ\)C for the hydrolysis reaction to occur. The polished Cu sheet was immersed in the hydrolysis solution for 15 days (heat corrosion experiment, held at 40 \(^\circ\)C for 8 h and then at 25 \(^\circ\)C for 16 h, circularly).

Materials Characterization

Optical microscopy analysis.—macroscopic morphologies were observed by MV-5000 Optical Microscopy (OM).
XRD analysis.—the corrosion products formed on the surface of the copper sheets were identified by XRD analysis using Cu Kα radiation (operating at 35 kV and 40 mA) from 10° to 100° with a scanning rate of 10°/min.

SEM/EDS analysis.—The morphologies and the thickness of the corrosion layer were observed using a JSM-5610 LV scanning electron microscope (Electron Co., Japan) [6].

Results and Discussions

Fig.1 showed the morphology of the Cu sheet after corrosion treatment. Two typical corrosion morphologies could be observed, namely cracks and corrosion pits. We could clearly see lots of cracks on the surface of the Cu sheet, and around the cracks there were a large number of small and dense corrosion pits. This was mainly due to the generation of imperfections caused by the cracks.

![Figure 1. Optical micrograph of Cu after corrosion treatment for 15 days.](image)

Fig. 2 showed the XRD patterns of the Cu sheet after corrosion test. The diffraction peaks of Cu and Cu₂O could be identified, indicating that Cu₂O was one of the main corrosion products.

![Figure 2. The XRD spectra for the copper after immersing in the hydrolysis solution for 15 days.](image)
Figure 3. SEM/EDS spectrum analysis of Cu after immersing in the hydrolysis solution for 15 days.

Fig. 3 showed the SEM images of the corrosion pits on the surface of the Cu sheet with different magnifications. The ravine-like corrosion morphology was unevenly distributed on the surface of the Cu sheet. Some of the mountain-shape corrosion products were scattered around the pits and some were isolatedly distributed on the surface.

<table>
<thead>
<tr>
<th>Area</th>
<th>O</th>
<th>S</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.09</td>
<td>0</td>
<td>95.91</td>
</tr>
<tr>
<td>2</td>
<td>7.67</td>
<td>2.2</td>
<td>90.13</td>
</tr>
</tbody>
</table>

Table. 1 showed the element components of region 1 and region 2 marked in Fig. 3(b). Mainly Cu, O and S could be identified in the corrosion products. Combined with the XRD spectra in Fig. 2, we could conclude that copper ions start to react with sulfur and oxygen in the solution to form Cu$_2$O. The phase analysis of the corrosion medium showed that the S was mainly existed in the form of CuSO$_3$ or CuSO$_4$, indicating that the two compounds were also the main corrosion products. The two compounds could not be detected in Fig. 2, which was mainly owing to the small contents.

Conclusions

The hydrolysis products of dimethyl sulfite was used as corrosion medium in this study. With the coexistence of water and oxygen, the polished Cu sheet would react with the solution to generate Cu$_2$O, CuSO$_3$ and CuSO$_4$ under given circumstances. In this immersion corrosion experiment, two kinds of corrosion morphologies could be observed, namely cracks and corrosion pits.

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References


