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EVALUATION OF POLARIZATION CURVES FOR COPPER ALLOYS
EXPOSED TO NATURAL AND ARTIFICIAL SEAWATER

F. Mansfeld, G. Liu, C. H. Tsai and H. Shih
Corrosion and Environmental Effects Laboratory (CEEL)
Department of Materials Science and Engineering
University of Southern California
Los Angeles, CA 90089-0241

B. Little
Naval Oceanographic and Atmospheric Research Laboratory
Stennis Space Center, MS 39529-5004

ABSTRACT

Polarization curves have been recorded in the vicinity of the corrosion potential $E_{corr}$ as a function of rotation rate $r$ for rotating cylinder electrodes of 99Cu, 90Cu:10Ni, 70Cu:30Ni, admiraltry brass and aluminum bronze which had been exposed to natural and artificial seawater for time periods up to 10 weeks. The polarization curves were analyzed with the POLFIT software to determine the Tafel slopes $b_a$ and $b_c$ and the corrosion current density $i_{corr}$. While $i_{corr}$ showed a linear dependence on $r^{0.7}$ in most cases, $E_{corr}$ was independent of mass transport. This result was explained by mass transport control of both the anodic and the cathodic reaction determining the corrosion rate. Corrosion rates have also been obtained for a 30 day period using a commercial corrosion rate monitor and by weight loss for periods up to three months. While corrosion rates obtained with these two methods agreed for exposure in artificial seawater, corrosion rates determined with the linear polarization technique underestimated corrosion rates based on weight loss data in natural seawater by a factor of two or more.

Keywords: microbiologically influenced corrosion, mass transport, charge transport, polarization curves, corrosion rates, Tafel slopes, linear polarization, weight loss, copper alloys, seawater.
INTRODUCTION

Microbiologically induced corrosion (MIC) is due to the activities of microorganisms on metal surfaces which may lead to changes of the rates and/or types of electrochemical reactions involved in the corrosion process. In MIC corrosion rates can be increased because of an increase of the rate of the anodic and/or cathodic partial reaction involved in the corrosion process without a change of the corrosion mechanism. It is also possible that the nature of these processes is changed and that a different reaction mechanism occurs in the presence of microorganisms. Recent reviews of the MIC literature (1) and the use of electrochemical techniques in studies of MIC (2-4) have shown that most experimental studies have demonstrated that MIC can occur in a wide variety of media without reporting mechanistic data. In the present study of MIC of copper alloys an attempt was made to determine kinetic parameters characteristic of corrosion processes such as the Tafel slopes $b_a$ and $b_c$ which are determined by the mechanism of the anodic and cathodic reactions, respectively. In addition, corrosion current densities $i_{corr}$ and corrosion potentials $E_{corr}$ were determined in abiotic and biotic media. Since it can be expected that the formation of corrosion product layers and biofilms during exposure to natural seawater can affect these parameters, polarization curves were recorded as a function of exposure time in both media. Finally, it is well known that for Cu in chloride media, both the anodic and the cathodic partial reaction are affected by mass transport (5-7). Therefore a rotating cylinder electrode (RCE) was used to determine polarization curves as a function of rotation rate. Since a number of polarization curves had to be run with the same aged sample, it was necessary to record these curves in a narrow region around the corrosion potential $E_{corr}$ in order to avoid irreversible changes of the electrode surface. Use of the software POLFIT (8) makes it possible to determine $b_a$, $b_c$ and $i_{corr}$ from the non-Tafel region (9). It was also of interest to compare corrosion rates obtained from polarization curves for RCEs with weight loss data obtained in natural and artificial seawater. Finally, it was desired to obtain a continuous record of corrosion rates over a certain time period. This goal was achieved using a commercial corrosion rate monitor. The results obtained so far in this on-going study will be presented in this paper.

EXPERIMENTAL APPROACH

The copper-based materials 99Cu (CDA 110), 90Cu:10Ni (CDA 706), 70Cu:30Ni (CDA 715), admiralty brass (CDA 443) and aluminum bronze (CDA 614) were exposed to natural seawater in Port Hueneme, CA and to artificial seawater (Instant Ocean). Samples were in the form of cylinders with $h = 0.8$ cm and $d = 1.2$ cm. These samples were placed in a plastic holder which exposed only the walls of the cylinder. After a given exposure period impedance measurements were performed at a constant rotation rate $r$ as discussed elsewhere (9,10). A polarization curve was then recorded at a scan rate of 0.1 mV/sec in the potential region $E_{corr} \pm 30$ mV at rotation rates $r$ between 225 and 1600 rpm. For a RCE turbulent flow occurs at all rotation rates. The highest value $r = 1600$ rpm corresponds to a linear velocity of 1m/sec. A separate sample was used for each exposure period. Weight loss data were obtained for samples (10.0 x 0.6 x 0.1 cm) which were placed in a plastic holder such that there was minimal contact between the metal and the holder. This approach was used to minimize the possibility of crevice corrosion. Instantaneous corrosion rate measurements were performed using the 9030 Corrater instrument (Rohrback Cosasco). The two electrodes were in the form of cylinders with the dimensions $d = 0.5$ cm and $h = 3.2$ cm. A linear polarization measurement was carried out every 30 min. over
a 30 d period.

EXPERIMENTAL RESULTS

Fig. 1 shows a comparison of the experimental and fitted polarization curves recorded at $r = 1200$ rpm for 99 Cu after exposure to natural seawater for 5 weeks. Excellent agreement between the two sets of data is observed as also demonstrated in Fig. 2 in which the deviation (in %) between the current for the experimental and the fitted curves is plotted vs. the applied potential (expressed as the number of the data points in Fig. 2). The deviation is less than 5 % in the entire potential range except for the data point closest to $E_{corr}$. This point is often not located exactly at $E_{corr}$ where $i = 0$, and therefore the relative deviation can be quite large. POLFIT allows elimination of data points with excessive scatter, however in the case shown in Fig. 2 all measured data points were used. Table 1 summarizes the results of the analysis of the data in Fig. 1. The fit of the data results in the values of $b_a$, $b_c$ and the corrosion current $I_{corr}$. $E_{corr}$ is also determined as the potential where $I = 0$. $R_p$ (in ohm) is calculated as $R_p = B/I_{corr}$. Based on the value of the exposed electrode area the corrosion current density $i_{corr}$ and $R_p$ (in ohm.cm$^2$) are calculated. The quality of the fit can be judged based on the value of $R^2$ and the standard deviation. Fig. 3 and 4 are plots of the anodic ($b_a$) and cathodic ($b_c$) Tafel slopes, $i_{corr}$ and $E_{corr}$ as a function of $r$. For 99Cu (Fig. 3) and 70Cu:30Ni (Fig. 4) after exposure to natural and artificial seawater for two different time periods. The exponent 0.7 is appropriate for the RCE (11). For 99Cu (Fig. 3) $b_a$, $b_c$ and $E_{corr}$ are independent of $r$, while $i_{corr}$ increases linearly with $r^{0.7}$ except for exposure to natural seawater for 38 d (30,NS in Fig. 3), where $i_{corr}$ was independent of $r$. For 70Cu:30Ni the Tafel slopes and $E_{corr}$ were also independent of $r$, $i_{corr}$ showed only a slight dependence on $r$ (Fig. 4). In some cases, fairly large scatter occurred as can be seen in the data for 99Cu after 33 d in artificial seawater (Fig. 3) and for 70Cu:30Ni after 21 d in artificial seawater (Fig. 4). Occasionally, $i_{corr}$ seemed to increase sharply at the highest rotation speeds, however in the limited time available for these experiments it could not be decided whether this increase was due to flow effects on the biofilm and/or the corrosion product layer or due to experimental difficulties. The experimental data were fit to equations of the form:

$$y_i = y^0_i + b_i r^{0.7}$$

(1)

where $y_i$ is one of the parameters in Fig. 3 and 4 and $b_i$ is the slope of the regression line for this parameter. By extrapolation of the regression lines according to Eq.1 the parameters $b_a^0$, $b_c^0$, $i_{corr}^0$ and $E_{corr}^0$ can be determined which correspond to the value of each parameter for stagnant conditions ($r = 0$) (12). These data are summarized in Fig. 5 - 8 for the five materials as a function of exposure time to natural seawater for times between one and 9 weeks and to artificial seawater for times between 2 h and 5 weeks. The average values of $b_a^0$ were close to 60 mV in both media independent of exposure time (Fig. 5). There was considerably more scatter in the values of $b_c^0$ with an average value of about 100 mV in both media (Fig. 6). Fig. 7 shows that $i_{corr}^0$ decreased in both media with exposure time from about 1 - 3 $\mu$A/cm$^2$ after one week to less than 1 $\mu$A/cm$^2$ at the end of the test. The lowest $i_{corr}^0$-values were found for 70Cu:30Ni (Fig. 7). For the materials studied here $i_{corr}^0 = 1$ $\mu$A/cm$^2$ corresponds to about 11.5 $\mu$m/y. No significant differences of $i_{corr}^0$ in the two solutions were detected at a given exposure time. $E_{corr}^0$ did not change much with exposure time (Fig. 8). The most positive values of $E_{corr}$ were observed for 70Cu:30Ni. In order to determine the
time dependence of corrosion rates in natural and artificial seawater corrosion rates were determined over a 30 d period with the 9030 Corrater for 99Cu, 90Cu:10Ni, 70Cu:30Ni and admiralty brass (Fig. 9). For 99Cu an initial decrease of corrosion rates was followed by a pronounced increased and an even steeper decrease in natural seawater, while in artificial seawater corrosion rate stabilized at about 35 μm/y after one week. At the end of the test the corrosion rate in natural seawater was about 6 μm/y. For 90Cu:10Ni corrosion rates decreased continuously in both media reaching 2.5 μm/y in natural seawater and 6 μm/y in artificial seawater. The time dependence of the corrosion rate was similar for 70Cu:30Ni and admiralty brass in natural and artificial seawater, respectively (Fig. 9). For 70Cu:30Ni the corrosion rate was about 1.5 μm/y in both media at the end of the test, while for admiralty brass much higher values of 10 μm/y in natural and 25 μm/y in artificial seawater were observed.

As a further test of the effects of exposure time and medium on corrosion rates weight loss data were obtained for the five materials after one week, and after one, two and three months exposure to natural and artificial seawater. These data are shown as corrosion rates in Fig. 10. In most cases corrosion rates obtained from weight loss are higher in natural seawater than in artificial seawater. 99Cu is an interesting case since corrosion rates decreased faster in natural seawater than in artificial seawater. Therefore after two and three months the average corrosion rate over these time periods was lower in artificial seawater. The time dependence of corrosion rates $r_{corr}$ has been found to agree with a time law in the form:

$$r_{corr} = k t^n$$

(2)

where $k$ is the corrosion rate after 1 d. The fitted values of $k$ and $n$ are listed in Table 2, which shows that the average value of $n$ is about -0.5. This result is usually explained by diffusion control through a surface layer. The parameter $k$ is higher in natural seawater for all materials except for 90Cu:10Ni, for which $k$ has the same value in both media.

**DISCUSSION**

Emphasis has been placed on the determination of the parameters which determine the corrosion behavior of Cu-based materials as a function of exposure time, mass transport and type of corrosive medium. As discussed elsewhere (9,10,13,14) the situation is much more complicated for these materials than for stainless steels and Ti exposed to seawater which are in the passive state and for which mass transport does not affect the corrosion behavior. With increasing exposure time the Cu alloys are covered with corrosion products and - in natural seawater - biofilms. Wood et al (7) have reported changes in $b$ and $b$, with exposure time for Cu and 70Cu:30Ni. While it is understood that detailed mechanistic understanding of the corrosion process involving microorganisms can only be obtained by the use of a combination of electrochemical, surface analytical and microbiological techniques (1 - 4), the present study has focused on the use of electrochemical techniques for the determination of Tafel slopes and corrosion rates. Little and Mansfeld (9,10,13,14) have presented results of surface analysis for the materials studied here after exposure to natural and artificial seawater. These results demonstrate that microorganisms affect the corrosion behavior to an extent which depends on the nature of the material. For 70Cu:30Ni intergranular corrosion was observed after exposure to natural seawater, but not to artificial
seawater (13, 14). The corrosion product layer on 99Cu exposed to natural seawater was covered with a gelatinous biofilm containing numerous bacteria and crystalline deposits after three weeks (9, 10).

An attempt was made to determine whether the anodic and cathodic Tafel slopes and the corrosion rates for the five copper-based materials are affected by the formation of corrosion products and biofilms. By conducting the experiments in biotic and abiotic media, it was considered possible to separate the effects of corrosion products on the corrosion kinetics from those produced by biofilms. The time dependence of corrosion rates determined by weight loss (Eq. 2) which decrease with \( t^1 \) suggests that diffusion processes of reactants such as \( O_2 \) or \( Cl^- \) or corrosion products such as \( CuCl_2^- \) are involved.

The experiments with RCEs proved to be quite complicated, since \( b_a \), \( b_c \), \( i_{corr} \) and \( E_{corr} \) data had to be determined first for a given exposure time as a function of rotation rate (Fig. 3 and 4). By fitting these data to equations of the type shown in Eq. 1, values of these parameters for stagnant conditions (\( r = 0 \)) were obtained (\( b_0^a, b_0^c, i_{corr}^0, E_{corr}^0 \) (Fig. 5 - 8)). Considering the scatter in the data such as those shown in Fig. 3 and 4, which affects the extrapolation of the data to \( r = 0 \), it is not surprising that the plots in Fig. 5 - 8 show some scatter also. However, an analysis of these results demonstrates agreement with literature data as far as such data are available for the materials and media used in the present study. Kato et al (5) citing earlier literature suggested that \( b_a = 60 \) mV can be attributed to a one-electron transfer reaction with diffusion of a reactant or a product in the aqueous phase being the rate determining step. For the materials studied here this reaction is considered to be:

\[
Cu + 2 Cl^- \rightarrow CuCl_2^- + e^- \tag{3}
\]

Wood et al (7) determined that \( b_a \) was close to 60 mV in the vicinity of \( E_{corr} \), but changed to 120 mV at more anodic potentials. After prolonged exposure times to natural seawater, \( b_a \) was found to be 120 mV at potentials close to \( E_{corr} \), but 60 mV at more anodic potentials. For 70Cu:30Ni \( b_a \) was about 120 mV in the vicinity of \( E_{corr} \), but changed to 60 mV for an aged surface after longer exposure times. In the present study no significant effects of rotation rate on \( b_a \) and \( b_c \) was found and very similar values of Tafel slopes for \( r = 0 \) were obtained in both media and for all exposure times (Fig. 5 and 6). A significant finding of the present study is the linear increase of \( i_{corr} \) with \( r^{0.7} \) and the independence of \( E_{corr} \) on \( r \) observed in this study (Fig. 3 and 4). These results can be explained using mixed potential theory assuming that both the anodic and the cathodic partial reactions are under mass transport control (9, 10). Increased mass transport increases the rate of the anodic reaction according to Eq. 2 and the rate of the cathodic reaction, which is under mixed charge transfer and mass transport control. Mansfeld and Kenkel (15) have shown that anodic polarization curves for 99Cu in artificial seawater shifted parallel to higher current densities as \( r \) increased. As both the anodic and cathodic polarization curve shift to higher current densities with increasing rotation rate of the RCE, it is possible that \( E_{corr} \) remains constant, while \( i_{corr} \) increases. Previous studies for stainless steels and Ti in artificial seawater showed that both \( E_{corr} \) and \( i_{corr} \) were independent of mass transport (9, 14). The \( i_{corr} ^0 \) - data obtained from the POLFIT analysis of polarization curves obtained as a function of rotation rate and extrapolation to \( r = 0 \) show similar values in both media after about one month exposure with average values corresponding to about 10 to 20 \( \mu m/y \) except for 70Cu:30Ni for which much lower values were obtained. Corrosion rates determined from weight loss data and as average values over the 30-
day period from the data measured with the 9030 Corrater (Fig. 9) are compared in
Table 3. Several observations can be made by inspection of the data in Table 3.
For the four materials listed, corrosion rates obtained by weight loss are higher
in natural seawater than in artificial seawater, while the opposite result is
obtained for the data obtained with the Corrater. Fairly good agreement is observed
for the two types of corrosion rate data in artificial seawater, but in natural
seawater corrosion rates measured with the Corrater are less than one half of those
obtained by weight loss. This large discrepancy between corrosion rates determined
in natural seawater by the two different methods leads to the result mentioned above
that corrosion rates obtained with the Corrater appear to be lower in the biotic
medium. At present no satisfactory explanation for this discrepancy can be offered.
Since the average value of corrosion rates obtained with the Corrater have been used
for the comparison with weight loss data, time effects can be ruled out. The
argument that the B-factor, which has to be used to convert the experimental R
data measured by the Corrater into icorr-values, might be higher by a factor of two
or more in natural seawater, does not seem to be valid in light of result that the
b° and b° values determined in this study were practically the same in both media
(Fig. 5 and 6). Since the main difference between the two media is the presence
of microorganisms in natural seawater, one can conclude that the disagreement
between corrosion rates obtained from weight loss data and the linear polarization
technique is due to the action of microorganisms. Further work is needed to clarify
the details of these processes. Since MIC is often of a very localized nature -
for the materials studied here dealloying and intergranular corrosion have been
observed in natural seawater only (4, 9, 10, 13, 14) - efforts are directed towards
development of electrochemical techniques which can be used for monitoring of
localized corrosion phenomena such as electrochemical noise analysis.

ACKNOWLEDGEMENT

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press)
127, 1890 (1980)
15. F. Mansfeld and J. V. Kenkel, Corrosion 33, 376 (1977)

Table 1. Results of POLFIT Analysis for 99Cu after 5 Weeks in Natural Seawater

File name : C:\S\S\Cu12S
Initial Potential= -256mV; Final Potential= -216mV
Estimated Solution Resistance Rs = 800 ohms
Number of Iterations : 5

<table>
<thead>
<tr>
<th>Results</th>
<th>Error</th>
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<tr>
<td>Rp = 5443.2</td>
<td>6.5882 ohms</td>
</tr>
<tr>
<td>ba = 62.348</td>
<td>0.43227 mV</td>
</tr>
<tr>
<td>bc = 52.220</td>
<td>0.55478 mV</td>
</tr>
<tr>
<td>I_corr = 2.2662</td>
<td>0.21574E-01 microamps</td>
</tr>
<tr>
<td>B = 12.341</td>
<td>1.1331</td>
</tr>
<tr>
<td>Icorr = 1.1331</td>
<td>1.18707E-01 microamps/sq cm</td>
</tr>
<tr>
<td>Rp * area = 18806</td>
<td>13.168 ohm*sq cm</td>
</tr>
<tr>
<td>Ec Orr = -246.87</td>
<td>.12727E-01 mV (E_ref)</td>
</tr>
</tbody>
</table>

Sum of Squared Observations = 1759.2
Sum of Squared Deviations = .17652
R-squared = .99996
Correlation = .99994
Standard Deviation = .28924E-01 with 211 d.f.
Table 2. Time Dependence of Corrosion Rate

<table>
<thead>
<tr>
<th>alloy - medium</th>
<th>k (µm/year)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>99Cu - SW</td>
<td>158</td>
<td>-0.4</td>
</tr>
<tr>
<td>99Cu - IO</td>
<td>63</td>
<td>-0.1</td>
</tr>
<tr>
<td>90Cu:10Ni - SW</td>
<td>126</td>
<td>-0.6</td>
</tr>
<tr>
<td>90Cu:10Ni - IO</td>
<td>126</td>
<td>-0.8</td>
</tr>
<tr>
<td>70Cu:30Ni - SW</td>
<td>50</td>
<td>-0.5</td>
</tr>
<tr>
<td>70Cu:30Ni - IO</td>
<td>20</td>
<td>-0.3</td>
</tr>
<tr>
<td>Adm. Brass - SW</td>
<td>200</td>
<td>-0.5</td>
</tr>
<tr>
<td>Adm. Brass - IO</td>
<td>79</td>
<td>-0.4</td>
</tr>
<tr>
<td>Al Bronze - SW</td>
<td>158</td>
<td>-0.6</td>
</tr>
<tr>
<td>Al Bronze - IO</td>
<td>79</td>
<td>-0.6</td>
</tr>
</tbody>
</table>

(SW - natural seawater; IO - artificial seawater)

Table 3. Comparison of Corrosion Rates Obtained by Weight Loss and by Linear Polarization

<table>
<thead>
<tr>
<th>Materials</th>
<th>Corrosion Rate (µm/year)</th>
<th>Artificial seawater</th>
<th>Natural seawater</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>weight loss</td>
<td>9030 Corrater</td>
</tr>
<tr>
<td></td>
<td></td>
<td>weight loss</td>
<td>9030 Corrater</td>
</tr>
<tr>
<td>copper</td>
<td>41.4</td>
<td>34.0</td>
<td>46.2</td>
</tr>
<tr>
<td>Cu90Ni10</td>
<td>9.4</td>
<td>14.2</td>
<td>15.2</td>
</tr>
<tr>
<td>Cu70Ni30</td>
<td>8.6</td>
<td>6.6</td>
<td>20.7</td>
</tr>
<tr>
<td>Adm. Brass</td>
<td>22.2</td>
<td>26.8</td>
<td>41.0</td>
</tr>
</tbody>
</table>

Figure 1 - Comparison of experimental and fitted polarization curves for 99Cu after 5 weeks exposure to natural seawater.
Figure 2 - Deviation plot for data in Fig. 1.

Figure 3 - Dependence of $b_a$, $b_c$, $i_{corr}$ and $E_{corr}$ on rotation rate $r^{0.7}$ for 99 Cu exposed to natural seawater for 7 d (7, NS) and 38 d (38, NS) and to artificial seawater for 7 d (7, AS) and 33 d (33, AS).
Figure 4 - Dependence of $b_a$, $b_c$, $i_{oer}$ and $E_{oer}$ on rotation rate $\tau^{0.7}$ for 70Cu:30Ni exposed to natural seawater for 21 d (21, NS) and 38 d (38, NS) and to artificial seawater for 21 d (21, AS) and 30 d (30, AS).
Figure 5 - Time dependence of $b^*$ for five Cu-based materials exposed to natural (Fig. 5 a) and artificial (Fig. 5 b) seawater.
Figure 6 - Time dependence of $b_\circ$ for five Cu-based materials exposed to natural (Fig. 6 a) and artificial (Fig. 6 b) seawater.
Figure 7 - Time dependence of $i_{\text{corr}}$ for five Cu-based materials exposed to natural (Fig. 7 a) and artificial (Fig. 7 b) seawater.
Figure 8 - Time dependence of $E_{corr}$ for five Cu-based materials exposed to natural (Fig. 8 a) and artificial (Fig. 8 b) seawater.
Figure 9 - Time dependence of corrosion rates obtained with a commercial corrosion rate monitor in natural and artificial seawater.
Figure 10 - Corrosion rates calculated from weight loss data for natural (SW) and artificial (IO) seawater for different time periods.