Effect of oxygen and oxidizers on the electrochemical behaviour of $\alpha$-brass in aqueous solutions of different pH

F M Al-Kharafi & W A Badawy
Department of Chemistry, Faculty of Science, University of Kuwait, P.O.Box 5969, Safat -13060 Kuwait

Received 1 August 1997; accepted 20 November 1997

The electrochemical behaviour of $\alpha$-brass ($\text{Cu:Zn} \approx 70:30$) in naturally aerated, oxygen saturated and oxygen free acidic, neutral and basic solutions of constant pH has been investigated. The effect of oxygen and oxidizers on the corrosion behaviour of the alloy in the different solutions has been discussed. The effect of oxygen or oxidizers on the corrosion parameters of the alloy is dependent on the solution pH. The removal of oxygen or oxidizers from acidic solutions increases the corrosion resistance of the alloy. In these solutions, the presence of oxygen or oxidizers enhances disproportionation reactions which lead to the breakdown of the passive film formed on the alloy surface. The preferential dissolution of zinc has been found to destroy the passive film, especially in acidic solutions. X-ray photoelectron spectroscopic investigations (XPS) of the alloy surface after long immersion time in solutions containing $\text{Cr}_2\text{O}_7^{2-}$ ions have shown that chromium is not incorporated in the barrier film. Scanning electron microscopy (SEM) does not show remarkable difference between the polished surface and the surface after immersion in the test solutions. In acidic solutions containing dichromate ions increased corrosion rates have been measured and clear corrosion patterns in the scanning electron micrographs have been recorded.

The wide range of industrial applications of brass alloys is behind the extensive efforts which have been directed towards the understanding of the corrosion and passivation behaviour of these alloys in different media. Studies of the electrochemical behaviour of brasses are in essence of the study of the dezincification process. Many attempts have been made to understand the mechanism of this process. It was found that the alloy dissolution mode is dependent on the zinc content in the alloy and its polarization condition. Different techniques, electrochemical, radiometric and optical, have been used to investigate the electrochemical behaviour of the alloy and to understand the selective leaching of zinc. The corrosion and passivation processes were found to depend on the alloy composition, the corrosion medium and the presence of oxygen or oxidizers in the electrolyte. In the present work, the electrochemical behaviour of a widely used brass alloy ($\text{Cu:Zn} \approx 70:30$) was investigated in solutions of different pH, in order to understand the effect of oxygen and oxidizers on the corrosion and passivation processes taking place at the electrode/electrolyte interface. It was important to specify the stability of the passive film formed on the alloy surface in different solutions.

Experimental Procedure

The working electrodes were made in the form of cylindrical rods from commercial grade brass alloy of the composition 70.04% Cu, 29.94% Zn and traces of iron and lead (0.004% Fe and 0.011% Pb) as confirmed by the mass spectroscopic analysis of the alloy. The alloy samples were annealed at 600°C, then air cooled and have the $\alpha$-phase. For comparison spectroscopic pure copper and zinc rods (Alderich Chemie) were also used as working electrodes.

The open-circuit potential was recorded each minute from the moment of electrode immersion in the test solution until it reached the steady state. Polarization measurements and electrochemical impedance spectroscopy (EIS) experiments were carried out. At lower or higher frequencies, no reproducible impedance data could be obtained. XPS
investigations were performed using an ESCA-Lab 200 (VG instruments). Scanning electron micrographs were obtained by means of SEM model JSM-6300 JEOL. Except otherwise stated, the experiments were carried out at constant room temperature of ~25°C. Solution deaeration and oxygen saturation were performed by bubbling purified N₂ and O₂ gas, respectively, in the test electrolyte at least 20 min before electrode immersion and throughout the whole experiments. All potentials were measured and referred to the Ag/AgCl/Cl⁻ (3 M KCl) reference electrode \(E^0 = 0.197 \text{ V (nhe)}\). Details of experimental procedures were as described elsewhere^{5,6,13,14}.

Results

Corrosion behaviour in naturally aerated solutions—In this series of experiments, the open-circuit potential, potentiodynamic and EIS experiments were conducted in naturally aerated unstirred solutions of \(pH\) 2, 7 and 12. The steady state potential is reached within 15 min from the electrode immersion in the test solution, and the behaviour of the alloy is very near to that of pure copper. The values of the steady state potentials of the alloy, copper and zinc in different solutions are summarized in Table 1. The open-circuit potential behaviour of the alloy in solutions of \(pH\) 2, \(pH\) 7 and \(pH\) 12 is presented collectively in Fig.1. It is clear that the steady state potential of the alloy in acidic solutions is more negative than that recorded in basic or neutral solutions. This is an indication that the acidic solutions are more corrosive for brass alloys.

Polarization experiments after 15 or 180 min of electrode immersion in the test solution gave approximately the same results which indicate that the alloy surface reaches a steady corrosion state after few minutes of electrode immersion in the test solution. Fig.2 shows the potentiodynamic polarization curves of the brass alloys in solutions of \(pH\) 2. The impedance behaviour of the alloy after 180 min of electrode immersion in the different solutions is presented in Fig.3. The Bode-phase plot in basic solutions is very similar to that of metal electrodes covered with passive films^{13,15}. The values of the corrosion resistance, \(R_{corr}\), corrosion current density, \(i_{corr}\), and corrosion potential, \(E_{corr}\), of the brass alloy in the different solutions were calculated and presented in Table 2. As can be seen from this table, the corrosion resistance of the alloy increases with the electrode immersion time in basic solutions. In acidic or neutral solutions no appreciable change in the values of the corrosion parameters was recorded.

Effect of oxygen—The effect of oxygen on the corrosion and passivation behaviours of the brass alloy in the different solutions was investigated. Fig. 4 shows the impedance behaviour of the brass electrodes in oxygen free (Fig. 4a) and oxygen saturated (Fig. 4b) solutions. In acidic and neutral

<table>
<thead>
<tr>
<th>Solution</th>
<th>(E_{corr}), mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(pH)</td>
<td>brass</td>
</tr>
<tr>
<td>2</td>
<td>-115</td>
</tr>
<tr>
<td>7</td>
<td>-70</td>
</tr>
<tr>
<td>12</td>
<td>-163</td>
</tr>
</tbody>
</table>

Fig. 1—Collective potential-time curves of the brass alloy in acidic, neutral and basic solutions.

Fig. 2—Potentiodynamic polarization curves of the brass alloy in acidic solution of \(pH2\) after (1) 15 min and (2) 180 min of electrode immersion in the test solution.
solutions, the removal of oxygen increases the corrosion resistance of the alloy. The corrosion resistance in oxygen free acidic solutions is more than 20 times to that recorded in oxygen saturated solutions. In basic solutions, on the other hand, bubbling of O₂ or N₂ gas decreases the corrosion resistance of the electrode. The change in the corrosion resistance in this case cannot be compared to the change occurring in acidic or neutral solutions. The effect of the gas in basic solutions is mainly mechanical. It removes the corrosion products from the electrode surface leading to higher corrosion rates. The values of the corrosion resistance of the alloy in the different solutions were calculated and summarized in Table 3. Both polarization and impedance experiments gave consistent data.

Effect of oxidizers—The effect of Cr₂O₇²⁻ ions as oxidizer on the electrochemical behaviour of the brass alloy in solutions of pH 2, 7 and 12 was also investigated. Typical Bode plots of the alloy electrodes in solutions containing the same concentration (0.01 M) of dichromate ions are presented in Fig. 5. In solutions of pH 2, the presence of dichromate ions decreases the corrosion resistance of the alloy and high corrosion rates were recorded. In neutral or basic solutions, a slight increase in the corrosion resistance in the presence of oxidizer was recorded. The calculated values of the corrosion resistance in different solutions are summarized in Table 4. The values presented in this table also show the effect of concentration of oxidizer on the corrosion resistance of the alloy in each solution. The high corrosion rates recorded in the presence of dichromate ions in acidic solutions indicate that the oxidizer enhances the anodic dissolution reaction of the alloy in this medium, which is not the case in neutral or basic media. This behaviour can be attributed to the oxidizing power of the oxidizing ions in each medium.

Surface analysis of the brass electrodes—The electrode surface was analyzed by XPS before and after immersion in the test solutions. The XP survey spectra of the electrode surface show characteristic peaks of carbon (C 1s at 285.5 eV, as residual from oil vapours of the diffusion pump), oxygen (O 1s at 523.5 eV), copper (Cu 2p₃ at 932.5 eV and Cu 2p₁ at 952.5 eV) and zinc (Zn 2p₃ at 1021.5 eV and Zn2p₁ at 1044.5 eV).
Table 2—Corrosion resistance, $R_{\text{corr}}$, corrosion current density, $i_{\text{corr}}$, and corrosion potential, $E_{\text{corr}}$, for the brass alloy after 15 and 180 min of electrode immersion in solutions of different pH

<table>
<thead>
<tr>
<th>$pH$</th>
<th>$15 \text{ min}$</th>
<th>$180 \text{ min}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_{\text{corr}} \text{ k}\Omega \text{ cm}^2$</td>
<td>$i_{\text{corr}} \text{ mA/cm}^2$</td>
</tr>
<tr>
<td>2</td>
<td>0.293</td>
<td>25.85</td>
</tr>
<tr>
<td>7</td>
<td>4.780</td>
<td>1.289</td>
</tr>
<tr>
<td>12</td>
<td>9.721</td>
<td>5.66</td>
</tr>
</tbody>
</table>

Table 3—Corrosion resistance, $R_{\text{corr}}$, of the brass alloy after 180 min of electrode immersion in naturally aerated, oxygen saturated and oxygen free solutions of different pH.

<table>
<thead>
<tr>
<th>Solution</th>
<th>$pH$</th>
<th>$R_{\text{corr}} \text{ k}\Omega \text{ cm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naturally aerated</td>
<td>2</td>
<td>0.324</td>
</tr>
<tr>
<td>Oxygen saturated</td>
<td>7</td>
<td>4.16</td>
</tr>
<tr>
<td>Oxygen saturated</td>
<td>12</td>
<td>16.83</td>
</tr>
</tbody>
</table>

Table 4—Corrosion resistance, $R_{\text{corr}}$, of the brass alloy recorded after 180 min of electrode immersion in naturally aerated acidic, neutral and basic solutions containing different concentrations of $\text{Cr}_2\text{O}_7^{2-}$.

<table>
<thead>
<tr>
<th>Concentration of $\text{Cr}_2\text{O}_7^{2-}$ mol/L</th>
<th>$pH$2</th>
<th>$pH$7</th>
<th>$pH$12</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000 M</td>
<td>0.324</td>
<td>4.16</td>
<td>16.83</td>
</tr>
<tr>
<td>0.001 M</td>
<td>0.087</td>
<td>7.84</td>
<td>84.0</td>
</tr>
<tr>
<td>0.010 M</td>
<td>0.040</td>
<td>6.85</td>
<td>21.78</td>
</tr>
</tbody>
</table>

Fig. 5—Bode plots of the brass alloy in acidic, neutral and basic solutions containing 0.01 $M \text{ Cr}_2\text{O}_7^{2-}$ after 180 min of electrode immersion. (-----) $pH$ 2, (----) $pH$ 7, (---) $pH$ 12.

Further for the mechanically polished surface or the surface after 180 min immersion in the test solution ($pH$ 2, $pH$ 7 or $pH$ 12), the same spectra were obtained. The only difference is that, the oxygen peak for the surface treated in the test solution is intensive. In all cases the oxygen and carbon peaks diminish after surface sputtering by argon ion bombardment which means that both are only adsorbed on the electrode surface. In dichromate containing solutions, chromium was found to occur on the electrode surface in neutral or basic solutions only. The XP survey spectra of the brass alloy after 3 h of electrode immersion in solutions of $pH$ 7 containing 0.01 $M \text{ Cr}_2\text{O}_7^{2-}$ is presented in Fig. 6. The spectrum shows chromium peaks (Cr 2p3 at 578.4 eV and Cr 2p1 at 587.8 eV). Unlike the leaded brass, the chromium was not found to be incorporated in the $\alpha$-brass used in these investigations. The chromium peaks disappear completely after surface sputtering by argon ion bombardment even for few seconds. This means that

Fig. 6. The spectrum shows chromium peaks (Cr 2p3 at 578.4 eV and Cr 2p1 at 587.8 eV). Unlike the leaded brass, the chromium was not found to be incorporated in the $\alpha$-brass used in these investigations. The chromium peaks disappear completely after surface sputtering by argon ion bombardment even for few seconds. This means that
the dichromate ions are adsorbed on the electrode surface and do not form a thick continuous layer as was observed with leaded brass in both neutral and basic solutions\textsuperscript{17}. In acidic solutions containing dichromates, no chromium peaks could be recorded.

Scanning electron microscopy was used to investigate the electrode surface before and after immersion in the different solutions in presence and absence of oxidizers. After 3h immersion of the alloy in different solutions free from oxidizers, similar micrographs to the polished surface were obtained, which means that the corrosion process occurs more or less uniformly in absence of oxidizers. The presence of dichromate ions in acidic solutions leads to the appearance of clear corrosion patterns. Fig. 7 presents the effect of dichromate ions on the corrosion behaviour of the brass alloy in acidic solutions (Fig. 7a), and in neutral solutions (Fig. 7b). It is clear that the presence of dichromate ions in the acidic solutions enhances the corrosion process and hence clear corrosion patterns were recorded. The alloy surface in this case undergo disproportionation and oxidation reactions and the rate of selective leaching of zinc increases. The selective leaching of zinc and disproportionation of Cu(I) leads to the deposition of Cu on the alloy surface which increases the cathodic to anodic area distribution and galvanic corrosion takes place. In neutral and basic solutions, the oxidation of Cu(I) is not favourable and hence the electrode surface retains its passivity even in the presence of oxygen or dichromate ions and no clear corrosion patterns can be recorded (cf. Fig. 7b).

Discussion

The electrochemical behaviour of brass alloy is dependent on the solution pH as well as the presence of oxygen or oxidizer in the solution. The alloy dissolution process begins with the preferential dissolution of zinc followed by the simultaneous dissolution of both components according to\textsuperscript{4,10}:

\[
\text{Brass (Cu + Zn)} \rightarrow x \text{Cu}^{2+} + y \text{Zn}^{2+} + 2(x+y) \text{e}^{-} \quad \ldots \quad (1)
\]

where \(x\) and \(y\) are the fractions of dissolved copper and zinc, respectively.

The cathodic part of this anodic dissolution process is the oxygen reduction. During simultaneous dissolution of the alloy in aqueous solutions Cu(I) ions are formed which undergo further oxidation to Cu(II)\textsuperscript{18,19}.

\[
\text{Cu} \rightarrow \text{Cu}^+ + \text{e}^{-} \quad \ldots \quad (2)
\]

\[
\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{e}^{-} \quad \ldots \quad (3)
\]

The investigated brass alloy is of the \(\alpha\)-phase and contains copper as the major alloying element (70%)\textsuperscript{20}. The open-circuit potential behaviour of the alloy is very close to that of copper. The formation of Cu(I) occurs rapidly and the dissolution reaction is controlled by the rate of reaction (3). The presence of one phase maximum in the impedance plots of the alloy electrodes in the differ-
ent solutions indicates that the corrosion process is controlled by one time constant representing the rate controlling step. In leaded brass and especially in acidic solutions two step dissolution process of comparable rate constants was recorded. The accumulation of Cu(I) compound on the electrode surface leads to a decrease in the corrosion rate of the alloy. The formation of Cu(I) passive film in the form of Cu₂O was confirmed by XPS measurements. Such passive films are not stable, they undergo disproportionation reactions leading to the formation of Cu(II) which is responsible for the red copper patches observed on the alloy surface after longer time of immersion in the corrosion medium.

In oxygen rich acidic solutions, the passive Cu(I) film oxidizes to the soluble Cu(II) and the rate of disproportionation increases, and hence higher rates of corrosion are recorded.

\[ 8Cu (I) + O_2 \rightarrow 2Cu_2O + 4Cu (II) \]  \hspace{1cm} (4)

The formation of Cu(II) enhances the preferential dissolution of zinc leading to an increase in the rate of disproportionation.

In oxygen free solutions, stabilization of Cu(I) occurs, and the rate of disproportionation decreases, leading to a decrease in the corrosion rate. This explains why the corrosion resistance of the alloy increases in oxygen free solutions, especially in the acidic media (cf. Table 3).

The presence of dichromate ions in the acidic solutions oxidizes the Cu(I) passive film to the soluble Cu(II) and hence the corrosion rate increases (cf. Table 4). The oxidation of Cu(I) takes place according to Eq. (5).

\[ 6Cu^+ + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Cu^{2+} + 2Cr^{3+} + 7H_2O \] \hspace{1cm} (5)

In neutral or basic solutions the presence of dichromate cannot oxidize the Cu(I) compound and hence no increase in the corrosion rate could be recorded.

Conclusions

The electrochemical behaviour of α-brass (Cu:Zn 70:30) is dependent on the pH of the ambient electrolyte. The alloy passivity is due to the formation of Cu(I) compound (mainly Cu₂O) which is relatively stable in neutral and basic solutions. The corrosion rate of the alloy increases in oxygen rich acidic solutions due to the oxidation of the Cu(I) passive film to the soluble Cu(II). The presence of oxidizers like dichromate ions enhances such oxidation reactions in acidic solutions leading to high corrosion rates.

Acknowledgment

The authors are grateful to the research administration, Kuwait University, for the financial support of this work under the research grant SC083.

References

17 Al-Kharafi F K & Badawy W A, Corrosion, (Accepted).