Effect of Oxygen Bubbling on the Dissolution of Brass in Acidified Sodium Sulfate Solution under Free Corrosion Conditions

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The effect of oxygen bubbling on the dissolution of brass was studied. Brass samples were immersed in acidified sodium sulfate solution at different temperatures (25-80°C) and subjected to bubbled oxygen during the testing period of 7 h. Samples of solution experiment were taken every hour and analyzed for zinc and copper using Inductively Coupled Plasma (ICP) technique. After experiment, sample surfaces were examined using scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS). Results show no appreciable dissolution either in inert atmosphere or in open atmosphere without bubbling. On the other hand, oxygen bubbling results in the enhancement of brass dissolution. This enhancement increases largely upon increasing the temperature from 25 to 50°C. Further increase in temperature has slightly negative effect on dissolution. The results of SEM and EDS support those of ICP.

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Ⅰ. INTRODUCTION

Copper zinc alloys (brasses) provide a favorable combination of cost, thermal, mechanical and electrical properties. They are widely used in Kuwait and the Gulf region in many industries such as desalination, power generation, refineries, etc. [1] The corrosion behavior of brass attracted the attention of researchers for decades and still active research subject in recent days [2–11]. Brass suffers from dezincification when the active component zinc tends to dissolve selectively out of the alloy, leaving its surface enriched in copper [12, 13]. Dezincification causes undesirable changes in the surface and mechanical properties of the alloy. It caused the premature failure in heat exchanger tubes in power stations in Spain and in Turkey [14, 15]. Dezincification has been addressed in many studies over many years [16–23] particularly in salt water [12, 17, 18].

Most works on brass were performed in media of high pH values or in the presence of complexing ions specially chloride ions. Under these conditions, copper and zinc form protective films and hence the corrosion behavior of the alloy is affected by the protective films and by the differing tendencies of copper and zinc to form complexes with chloride ions. It is also noticed that most work on brass was performed at ambient temperature, however, the dissolution of brass in the salt solutions is an activated process [24]. On the other hand, the majority of studies on brass addressed the oxidation of brass under the effect of potential. Very little literature [25, 26] investigated the effect of oxidizing agents (e.g. oxygen, chlorine, hydrogen peroxide) on the corrosion of brass under free corrosion conditions.

The objective of this paper is to study the effect of oxygen bubbling and temperature on the dissolution of brass under free corrosion conditions.

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values of 38 and 78 ppm for Zn$^{2+}$ and Cu$^{2+}$ ions, respectively. Increasing the temperature to 80°C does not show any appreciable effect on the concentrations of Zn$^{2+}$ and Cu$^{2+}$ ions. Concentrations obtained are almost the same as those obtained at 50°C indicating that the increase of temperature above 50°C has no detrimental effect on the dissolution of brass.

For the sake of comparison, the experiment was performed in acidified Na$_2$SO$_4$ solution open to air without oxygen bubbling at 50°C. Under such condition, very low concentrations of 3.8 ppm of Zn$^{2+}$ and 2 Cu$^{2+}$ ions are obtained after 7h testing (see Figs. 1 and 2). These results are in agree with the fact that the very low concentration of oxygen is dissolved with the increase of temperature [24]. At 50°C, this solubility amounts to 6 ppm in fresh water while being 4.6 ppm in sea water.

The extent of selective dissolution of zinc can be expressed in the form of a dezincification factor ($Z$) [27]

\[ Z = \frac{[Zn^{2+}]/\chi_{Zn}}{[Cu^{2+}]/\chi_{Cu}}, \]

where [Zn$^{2+}$] and [Cu$^{2+}$] are the molar concentrations in the electrolyte while $\chi_{Zn}$ and $\chi_{Cu}$ are the mole fractions of Zn and Cu in the alloy. A value of $Z = 1$ indicates that the concentrations of Zn$^{2+}$ and Cu$^{2+}$ ions in the electrolyte are directly proportional to their respective mole fractions in the alloy. This corresponds to simultaneous dissolution of both components of the alloy without enrichment of copper on the alloy surface. On the other hand, a value of $Z > 1$ indicates that zinc dissolves selectively, or preferentially while copper might also be dissolving to an extent lower than that required by its mole fraction in the alloy.

Figure 3 illustrates the effect of temperature on the dezincification factor, $Z$. At 25°C, a large value of $Z$, indicating a marked degree of dezincification, is obtained in the beginning of the experiment and then decreases with time till it reaches almost 1 after 5 h. The increase of temperature towards 50°C reduces the $Z$ towards lower values ranging from 2 in the beginning to about 1 after 5 h. Further increase in temperature up to 80°C show almost the same results as 50°C except for lower $Z$ in the beginning. It is also noticed that the $Z$ gets lower than unity after 5 h testing which indicating that the rate of dissolution of Cu exceeds that of Zn as time proceeds.

### B. Surface characterization

The surface morphology of brass treated under different temperatures is shown in Figs. 4(a)-(d). It is noticed that slight corrosion occurs at 25°C (Fig. 4(b)) in comparison to the untreated brass (Fig. 4(a)). At 50°C (Fig. 4(c)), the surface suffers severe corrosion in the form of voids spread along the surface. At 80°C (Fig. 4(d)), the corrosion attack shows the same features obtained at 50°C, however, it was less severe.

The surfaces of samples investigated under SEM were characterized using energy dispersive X-ray spectroscopy
FIG. 4: Effect of oxygen bubbling on the SEM of brass foil treated in aqueous solution of 1 M Na$_2$SO$_4$ and 0.1 M H$_2$SO$_4$ for 7 h at $E_{corr}$ at temperatures (b) 25°C, (c) 50°C and (d) 80°C, while (a) represents the untreated brass.

TABLE I: EDS results of brass treated for 7 h at different temperatures in aqueous solution of 1M Na$_2$SO$_4$ and 0.1M H$_2$SO$_4$ under oxygen bubbling.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Atomic percent</th>
<th>Blank</th>
<th>25°C</th>
<th>50°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>70.24</td>
<td>70.70</td>
<td>72.24</td>
<td>71.97</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>29.76</td>
<td>29.30</td>
<td>27.76</td>
<td>28.03</td>
</tr>
</tbody>
</table>

(EDS). EDS can be performed on selected regions of the corroded surface (on the scale of microns). It can detect the presence of a certain element, with no indication of its oxidation state. EDS results are summarized in Table I. EDS of the untreated brass shows a copper to zinc ratio of 70.24Cu/29.76Zn. The brass tested at 25°C shows the same ratio. At 50°C the copper to zinc ratio is 72.24Cu/27.76Zn indicating slight dezincification. At 80°C, the ratio is 71.97Cu/28.03Zn which is much closed to that obtained at 50°C.

C. Mechanism of brass dissolution

The alloy dissolution process begins with the preferential dissolution of zinc followed by the simultaneous dissolution of both components. This is shown in the present study by the high dezincification factor ($Z$) obtained during the first two hours of the experiment prior to its decrease as time proceeds. The dissolution reaction occurs according to [28]:

$$\text{Brass}(\text{Cu} + \text{Zn}) \rightarrow x\text{Cu}^{2+} + y\text{Zn}^{2+} + 2(x+y)e, \quad (2)$$

where $x$ and $y$ are the fractions of dissolved copper and zinc, respectively. At the free corrosion potential, the electrons resulting from reactions 1 are consumed in the cathodic reduction of oxygen, i.e.

$$\text{O}_2 + 4\text{H}^+ + 4e \rightarrow 2\text{H}_2\text{O}. \quad (3)$$

During simultaneous dissolution of the alloy in aqueous solutions Cu(I) ions are formed which undergo further oxidation to Cu(II) [28, 29].

$$\text{Cu} \rightarrow \text{Cu}^{1+} + e, \quad (4)$$

$$\text{Cu}^{1+} \rightarrow \text{Cu}^{2+} + e. \quad (5)$$

The investigated brass alloy is of the $\alpha$-phase and contains copper as the major alloying element (70%). The formation of Cu(I) occurs rapidly, and the dissolution reaction is controlled by the rate of reaction (5). The accumulation of Cu(I) compound in the form of Cu$_2$O on the electrode surface leads to a decrease in the corrosion rate of the alloy. Such passive films are not stable, they undergo disproportionation reactions leading to the formation of Cu(0).

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 concentrations of zinc and copper ions obtained in the oxygen free solutions is quite low in comparison to those...
obtained under oxygen bubbling. 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.

\[ 8\text{Cu(I)} + \text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 4\text{Cu(II)}. \]  

(6)

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

IV. SUMMARY AND CONCLUSIONS

The present work documents the effect of bubbling oxygen on the dissolution of brass. In the absence of oxygen bubbling no appreciable dissolution of brass was obtained. This can be attributed to the low solubility of oxygen in aqueous solutions especially with temperature increase. The bubbling of oxygen in the testing solution enhances brass dissolution. The enhancement increases to a large extent upon increasing the temperature from ambient to 50°C. Further increase of temperature towards 80°C has no detrimental effect on the brass dissolution. The surface morphology showed severe corrosion attack on brass at 50°C followed by 80°C and mild attack at 25°C.

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