Effect of hydrogen peroxide on the dezincification of brass in acidified sodium sulfate solution under free corrosion conditions

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Abstract

The dissolution of brass in acidified sodium sulfate solution containing different concentrations of H2O2 (0-1% m/v) was investigated under free corrosion conditions. The effect of temperature on the dissolution of brass was also addressed. Testing solution was analyzed for Zn²⁺ and Cu²⁺ using Inductively Coupled Plasma (ICP) technique. Surface characterization of brass surface was performed after each experiment. The increase of H2O2 concentration leads to the increase of the concentration of zinc and copper ions. These increases become more obvious at 0.5% m/v H2O2 while large increases are noticed at 1% m/v H2O2. Dissolution of brass was also enhanced by the increase of temperature. Strong dezincification of brass was obtained after prolonged testing (72 h). This strong dezincification was supported by SEM and XPS investigations. The extent of selective dissolution of zinc was expressed in the form of a dezincification factor \(Z\) i.e. Dezincification factor \(Z\) = \(\frac{[\text{C}_\text{Zn}]_{\text{solution}}}{[\text{C}_\text{Zn}]_{\text{alloy}}}\).

Key words: Brass, dissolution, sodium sulfate, H2O2, free corrosion.

1. Introduction

Brass alloys are characterized by their excellent thermal conductivity and mechanical workability [1]. They are widely used as tubing material in condensers and as heat exchangers for water cooling systems [2]. In spite of its important industrial applications, brass suffers from corrosion in aqueous environments containing corrosive ions such as chloride and sulfate. Corrosion manifests itself as dezincification when the active component zinc tends to dissolve selectively out of the alloy, leaving its surface enriched in copper [3-4]. 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 [5-6]. Dezincification has been widely investigated [7-14] especially in salt water [3, 8-9].

The majority of research papers on brass corrosion were done in environments of high pH values or in the presence of complexing ions specially chloride ions. In these environments, copper and zinc form protective films which affect the corrosion behavior of the alloy by differing tendencies of copper and zinc to form complexes with chloride ions. These papers are mostly carried out at ambient temperature though dissolution of brass in the salt solutions is an activated process [15]. On the other hand, most work on brass dissolution addressed its oxidation under the effect of potential. Very little literature [16-17] investigated the effect of oxidizing agents (e.g. oxygen, chlorine, hydrogen peroxide) on the corrosion of brass under free corrosion conditions.

In a previous work of the authors, the effect of oxygen, as oxidizing agent, on the dissolution of brass was addressed [18]. It is found that bubbling of oxygen in the testing solution enhances brass dissolution. The present work is a continuation of the afore mentioned work with the use of hydrogen peroxide as the oxidizing agent.
2. Experimental

Brass foil from Alfa Aesar having a thickness of 0.51 mm was used as the testing material. The typical composition of alloy is: Cu 70%, Pb 0.07% max, Fe 0.05% max, Zn remainder. Brass foil samples measuring 4 cm x 5 cm were tested in an electrolyte of 1 M Na₂SO₄ and 0.1 M H₂SO₄ under open circuit potential. Prior to testing, samples were polished on both sides using SiC papers successively up to 2400 grits to obtain a bright surface. Temperature was varied from 25°C to 80°C using Haake DC3 water bath. 1.66, 3.3, 5, 8.3 and 16.6 ml of hydrogen peroxide Analytical Reagent (30% m/v) were added to the testing solution to give concentrations of 0.1, 0.2, 0.3, 0.5 and 1% m/v in a final volume of 500 ml. 5 ml samples were taken from the testing solution every 1 h for a period of 6 h and analyzed to determine the concentration of zinc and copper ions using Inductively Coupled Plasma (ICP) technique. The surfaces of tested samples were examined using JEOL JSM-6300 scanning electron microscope (SEM) and XPS, VG SCIENTIFIC 200 Spectrometer (UK), using MgKα radiation (1253.6 eV) operating at 300W, 13 kV and 23 mA.

3. Results and Discussion

3.1. Zn⁺² and Cu⁺² resulted from brass dissolution

Concentrations of zinc and copper ions resulted from the dissolution of brass in the acidified sodium sulfate solution under different conditions of temperature and H₂O₂ concentration were determined using Inductively Coupled Plazma (ICP) Technique. Figs.1-2 illustrate the effect of H₂O₂ concentration (0.1-1% m/v) on the dissolution of brass treated for 6 h at 25°C. The increase of H₂O₂ concentration leads to the increase of the concentration of both zinc and copper ions. These increases become more obvious at 0.5% m/v H₂O₂ while large increases are noticed at 1% H₂O₂ m/v. The increase of H₂O₂ concentration from 0.1 to 0.5% m/v leads to the increase of the concentrations of zinc and copper ions from 132.3 ppm and 275.7 ppm to 365 ppm and 1396.7 ppm, respectively. On the other hand, when the concentration of H₂O₂ is increased from 0.5 to 1% m/v, the concentration of zinc and copper ions are increased from 365 ppm and 1396.7 ppm to 1806.89 ppm and 3772.57 ppm, respectively.

![Fig.1: Effect of H₂O₂ concentration on the concentration of Zn⁺² results from brass treated for 6 h in aqueous solution of 1M Na₂SO₄ and 0.1 M H₂SO₄ at 25°C. Experiment was carried out under Ar in the absence of H₂O₂ for comparison.](image-url)
The extent of selective dissolution of zinc can be expressed in the form of a dezincification factor (Z) [19] i.e.:

\[
\text{Dezincification factor (z)} = \frac{[\text{C}_{\text{Zn}}/\text{C}_{\text{Cu}}]_{\text{solution}}}{[\text{C}_{\text{Zn}}/\text{C}_{\text{Cu}}]_{\text{alloy}}}
\]  

(1)

where \(\text{C}_{\text{Zn}}\) and \(\text{C}_{\text{Cu}}\) represents the contents of zinc and copper, respectively, in a designated phase. A value of \(Z=1\) indicates that the concentrations of \(\text{Zn}^{2+}\) and \(\text{Cu}^{2+}\) 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.

Table 1 represents the effect of \(\text{H}_2\text{O}_2\) concentration on the dezincification factor (Z) of brass treated for 6 h in the acidified sodium sulfate solution. The increase of \(\text{H}_2\text{O}_2\) concentration has no pronounced effect on Z during the 6 h testing time. A dezincification factor ranging between 1.07 and 1.17 is obtained during the 6 h testing time. The \(\text{pH}\) of the solution measured at the start of the experiments was 1.87. This value was changed slightly after testing. For example, the solution contained 1% m/v \(\text{H}_2\text{O}_2\) showed a \(\text{pH}\) of 2.46 after 24 h.

Table 1: Effect of concentration of \(\text{H}_2\text{O}_2\) on the dezincification factor of brass treated for 6 h in 1 M \(\text{Na}_2\text{SO}_4\) and 0.1 M \(\text{H}_2\text{SO}_4\) at 25°C.

<table>
<thead>
<tr>
<th>(\text{H}_2\text{O}_2), % m/v</th>
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<th>0.5</th>
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<td></td>
<td></td>
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<td>1.17</td>
<td>1.07</td>
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<td>1.11</td>
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<td>1.11</td>
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<td>1.13</td>
<td>1.12</td>
<td>1.11</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Fig. 3 shows the variation of Z for brass tested for prolonged time in the acidified sodium sulfate solution in the presence of 1% m/v \(\text{H}_2\text{O}_2\). Note the big jump in Z obtained after 72 h testing time. The Z value is jumped from
1.06 obtained after 6 h to 2.9 obtained after 72 h i.e. Z is tripled. This observation is further assisted by SEM imaged, EDS and XPS results shown below.

Fig.3: Effect of time on the dezincification factor of brass treated in acidified sodium sulfate solution (1 M Na₂SO₄ and 0.1 M H₂SO₄) in the presence of 1% H₂O₂ at 25°C.

Figs.4-5 represent the effect of temperature on the concentration of both zinc and copper ions results from dissolution of brass in acidified sodium sulfate solution in the presence of 0.5% H₂O₂. The concentrations of both ions are increased with the increase of temperature from 25°C to 60°C. However, the concentrations of zinc and copper ions obtained at 40°C are very closed to those obtained at 60°C. Further increase of temperature to 80°C leads to the decrease of zinc and copper ions concentrations. It is noted that the concentrations of zinc and copper ions are increased linearly with time at various temperatures except for 80°C which shows steady concentrations.

Table 2 shows the effect of temperature on the dezincification factor of brass in acidified sodium sulfate solution in the presence of 0.5% m/v H₂O₂. It is noticed that Z values obtained at 60 and 80°C are nearly the same (~1). Slightly higher Z is obtained at 40°C (1.02). At 25°C, Z starts at relatively high value of 1.28 and then decreases with time till it reaches a steady value of 1.04.
Fig. 5: Effect of temperature on the concentration of Cu\textsuperscript{2+} results from dissolution of brass treated for 6 h in acidified sodium sulfate solution (1 M Na\textsubscript{2}SO\textsubscript{4} and 0.1 M H\textsubscript{2}SO\textsubscript{4}) in the presence of 0.5% H\textsubscript{2}O\textsubscript{2}.

Table 2: Effect of temperature on the dezincification factor of brass treated for 6 h in acidified sodium sulfate solution (1 M Na\textsubscript{2}SO\textsubscript{4} and 0.1 M H\textsubscript{2}SO\textsubscript{4}) in the presence of 0.5% H\textsubscript{2}O\textsubscript{2}.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>25</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>1</th>
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<tbody>
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<td>1.27</td>
<td>1.03</td>
<td>1.03</td>
<td>1.00</td>
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<td>1.08</td>
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<tr>
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<td>0.99</td>
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<td>1.07</td>
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<td>4</td>
<td>1.05</td>
<td>1.02</td>
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</tr>
<tr>
<td>5</td>
<td>1.03</td>
<td>1.01</td>
<td>0.99</td>
<td>0.98</td>
<td>1.07</td>
</tr>
<tr>
<td>6</td>
<td>1.06</td>
<td>1.00</td>
<td>0.99</td>
<td>1.02</td>
<td>1.07</td>
</tr>
</tbody>
</table>

3.2. Surface characterization

The effect of H\textsubscript{2}O\textsubscript{2} concentration on the surface morphology of brass is illustrated in Fig. 6. The surface roughness is increased in the presence of H\textsubscript{2}O\textsubscript{2} compared to the untreated brass. This increase in surface roughness is characteristic of dezincification of brass or dealloying in other alloys [3]. The increase in surface roughness becomes more pronounced with the increase of H\textsubscript{2}O\textsubscript{2} concentration. It is also noted that at 0.3% m/v H\textsubscript{2}O\textsubscript{2} voids start to appear on the brass surface. These voids are increased in numbers and size at 0.5% m/v H\textsubscript{2}O\textsubscript{2}. In the presence of 1% m/v H\textsubscript{2}O\textsubscript{2} the brass surface is covered with a layer of Cu\textsubscript{2}O which is evidenced by the EDS and XPS analysis.

Fig. 7 represents the surface morphology of brass treated in the presence of 1% m/v H\textsubscript{2}O\textsubscript{2} for 72 h. It is clear that brass suffers from severe corrosion attack as represented by the quite high surface roughness characteristic of brass dezincification. The EDS analysis (Fig. 9) revealed a surface enriched in copper (>86%) with very low content of Zn (2.3%) indicating the occurrence of strong dezincification. This dezincification seems to be of the uniform-layer type since corrosion attacks the entire surface while the thickness of the brass sample is decreased uniformly from 1 mm to about 0.5 mm. Areas of dezincification can be distinguished by being deeper than the alloy surface.
Fig. 6: SEM micrographs of brass oxidized for 6 h in 1 M Na₂SO₄ + 0.1 M H₂SO₄ in the presence of 0.1% H₂O₂ (b), 0.2% H₂O₂ (c), 0.3% H₂O₂ (d), 0.5% H₂O₂ (e) and 1% H₂O₂ (f) while (a) represents the untreated brass.
Fig. 7: SEM micrographs (different magnifications) of brass treated for 72 h in acidified sodium sulfate (1 M Na$_2$SO$_4$ and 0.1 M H$_2$SO$_4$) in the presence of 1% H$_2$O$_2$. 
The strong dezincification exhibited by brass after prolonged exposure to the acidified sodium sulfate in the presence of 1% m/v H₂O₂ is also substantiated by XPS analysis. Chemical composition of the surface (At%) resulted from XPS analysis is shown in Table 3. Brass surface shows a very low amount of Zn (~7 at%) which is 23% of its original percentage in the alloy (30%) while copper shows about 32% which is 46% of its original percent in the alloy (70%) where as oxygen represents the major constituent (59%). These results substantiate the strong dezincification as well as the formation of the copper oxide layer denoted by SEM and EDS analysis. The difference in the ratios of zinc obtained using XPS and EDS analysis lies on the fact that XPS scan the entire surface while EDS scan a very small area of the surface.

Table 3: XPS results of brass treated for 72 h in acidified sodium sulfate (1M Na₂SO₄ and 0.1 M H₂SO₄) in the presence of 1% H₂O₂ at 25°C.

<table>
<thead>
<tr>
<th>Binding energy, BE</th>
<th>Counts / C</th>
<th>Compound</th>
<th>Atomic percent, At%</th>
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<tbody>
<tr>
<td>Zn2p3</td>
<td>1021.72</td>
<td>28350.78</td>
<td>Zn</td>
</tr>
<tr>
<td>Cu2p1</td>
<td>952.69</td>
<td>40025.84</td>
<td>Cu₂O</td>
</tr>
<tr>
<td>O1s</td>
<td>531.5</td>
<td>44847.6</td>
<td>Cu₂O / CuO/ZnO</td>
</tr>
<tr>
<td>S2p1</td>
<td>169.27</td>
<td>254.69</td>
<td></td>
</tr>
</tbody>
</table>

Fig.8 shows the effect of temperature on the surface morphology of brass treated in the presence of 0.5% H₂O₂. The increase of temperature from 25 to 60°C enhances corrosion attack to a considerable extent. The surface becomes rougher with the appearance of intergranular corrosion. Further increase of temperature to 80°C does not brought considerable changes on the surface morphology instead, the surface roughness is decreased indicating less corrosion attack.

3.3. Mechanism of brass dissolution

The alloy dissolution process begins with the simultaneous dissolution of both components of the alloy (Cu and Zn). The dissolution reaction occurs according to [20]:

Brass (Cu + Zn) → xCu²⁺ + yZn²⁺ +2 (x +y) e         (2)

Where x and y are the fractions of dissolved copper and zinc, respectively. At the free corrosion potential, the electrons resulting from equation 2 are consumed in the cathodic reduction of hydrogen peroxide.

A mechanism involving decomposition (or disproportionation) of H₂O₂ leading to the formation of O₂ followed by the electrochemical reduction of O₂ may be suggested [21].

2H₂O₂ → 2H₂O + O₂                (3)
O₂ + 4H⁺ + 4e⁻ = 2H₂O            (4)

Another mechanism depends on the direct reduction of H₂O₂ in acidic medium may also possible, i.e.

H₂O₂ + 2H⁺ + 2e⁻ → 2H₂O         (5)

The electroreduction of H₂O₂ can be considered to occur through the formation of adsorbed OH⁻ ad species.

H₂O₂(bulk) → H₂O₂(surface)          (6)
H₂O₂(surface) + e⁻ → OH⁻ ad + OH⁻   (7)
OH⁻ + H⁺ → H₂O                   (8)
OH⁻ ad + e⁻ → OH⁻               (9)
OH⁻ ad + H⁺ + e⁻ → H₂O         (10)

OH⁻ ion thus formed combine with H⁺ ion (reaction 8) at the electrode to produce the reaction H₂O. Alternately, OH⁻ ad can simultaneously accept an electron and H⁺ ion producing H₂O in reaction 10. The adsorbed OH⁻ ad species are very reactive since they are free radicals.
Fig. 8: Effect of temperature on the SEM micrographs of brass treated in acidified sodium sulfate (1 M Na₂SO₄ and 0.1 M H₂SO₄) in the presence of 0.5% H₂O₂ for 6 h. (a) At 25°C, (b) At 60°C and (c) At 80°C.
The second mechanism is likely to occur based on the fact that brass dissolution occurs at much higher rates in the presence of H₂O₂ compared to the rates obtained under bubbling O₂ gas in the testing solution. In a previous study of the authors [18], maximum concentrations of 46 ppm Zn²⁺ and 90 ppm Cu²⁺ were obtained under oxygen bubbling. These values are quite low compared to those obtained in the presence of hydrogen peroxide. In presence of 1% H₂O₂ where a maximum of 1800 ppm Zn²⁺ and 3770 ppm Cu⁺² were obtained. These results reveal that free oxygen does not play a major rule in brass dissolution in the presence of H₂O₂.

The corrosion of brass is an activated process [15]. The corrosion rate is increased with temperature increase. However at much high temperature of 80°C, the rate of decomposition of H₂O₂ into water and O₂ is high and so its action is suppressed.

Fig. 9: EDS of brass treated in acidified sodium sulfate (1 M Na₂SO₄ and 0.1 M H₂SO₄) in the presence of 1% H₂O₂ for 72 h.
It is also worthy to note the strong dezincification after prolonged time of exposure. This can be explained as follows: For the processes of dezincification, the following two hypotheses have been proposed [22-28]:
(1) Selective dissolution of zinc from α-brass into the aqueous solution, leaving copper behind and followed by surface migration of atomic copper and formation of a copper crystal lattice at energetically stable sites.
(2) Complete dissolution of α-brass, followed by re-deposition of copper on the specimen surface.

The process (1) is improbable, because this process includes only dissolution of zinc which is not the case as high concentration Cu²⁺ were detected in solution. The present experimental results well coincide with hypothesis (2) i.e., complete dissolution of α-brass from the specimen surfaces into a corrosive solution takes place, followed by re-deposition of copper on the specimen surfaces. Copper was likely to redeposit with a surface structure similar to that of α-brass before dissolution. The process of copper redeposition would occur after prolonged time of exposure as predicted in Fig.4.

4. Conclusions

Brass dissolution process begins with the simultaneous dissolution of both components according to:

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

The electrons are consumed in the cathodic reduction of hydrogen peroxide, i.e.

\[
\text{H}_{2}\text{O}_{2} + 2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{2H}_{2}\text{O}
\]

The electroreduction of H₂O₂ can be considered to occur through the formation of adsorbed OHad species which gain an electron to give OH⁻ and finally combine with H⁺ to give H₂O.

Strong dezincification of brass in acidified sodium sulfate solution containing 1% H₂O₂ was observed after prolonged time of exposure (72 h). The process of the dezincification is the result of dissolution of α-brass into corrosive solutions followed by re-deposition of copper on the specimen surface.

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References