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 H_2O_2 (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 Zn^{+2} and Cu^{+2} using Inductively Coupled Plazma (ICP) technique. Surface characterization of brass surface was performed after each experiment. The increase of H_2O_2 concentration leads to the increase of the concentration of zinc and copper ions. These increases become more obvious at 0.5% m/v H_2O_2 while large increases are noticed at 1% m/v H_2O_2. 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) = $[C_{Zn}/C_{Cu}]_{solution} / [C_{Zn}/C_{Cu}]_{alloy}$.

Key words: Brass, dissolution, sodium sulfate, H_2O_2, 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 the 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 Na_2SO_4 and 0.1 M H_2SO_4 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 MgK_α 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 H_2O_2 concentration were determined using Inductively Coupled Plazma (ICP) Technique. Figs.1-2 illustrate the effect of H_2O_2 concentration (0.1-1% m/v) on the dissolution of brass treated for 6 h at 25°C. The increase of H_2O_2 concentration leads to the increase of the concentration of both zinc and copper ions. These increases become more obvious at 0.5% m/v H_2O_2 while large increases are noticed at 1% H_2O_2 m/v. The increase of H_2O_2 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 H_2O_2 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.

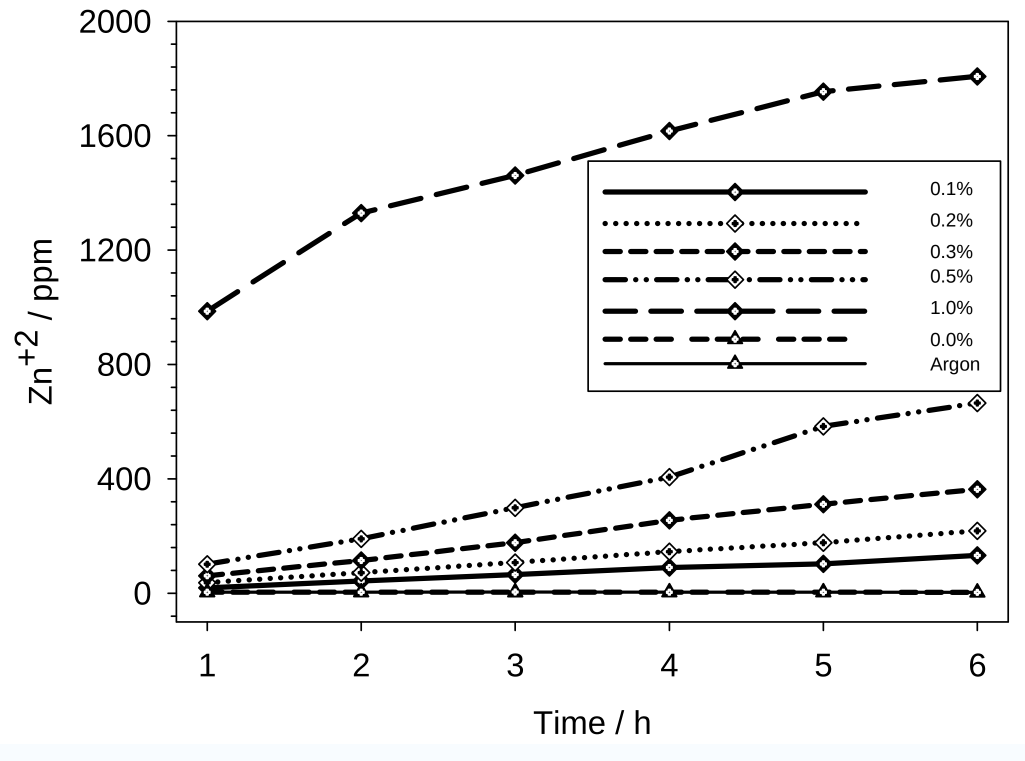


Fig.1: Effect of H_2O_2 concentration on the concentration of Zn^{+2} results from brass treated for 6 h in aqueous solution of 1M Na_2SO_4 and 0.1 M H_2SO_4 at 25°C. Experiment was carried out under Ar in the absence of H_2O_2 for comparison.

The extent of selective dissolution of zinc can be expressed in the form of a dezincification factor (Z) [19] i.e.:

$$\text{Dezincification factor (z)} = [C_{Zn}/C_{Cu}]_{solution} / [C_{Zn}/C_{Cu}]_{alloy} \quad (1)$$

where C_{Zn} and CCu represents the contents of zinc and copper, respectively, in a designated phase. 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.

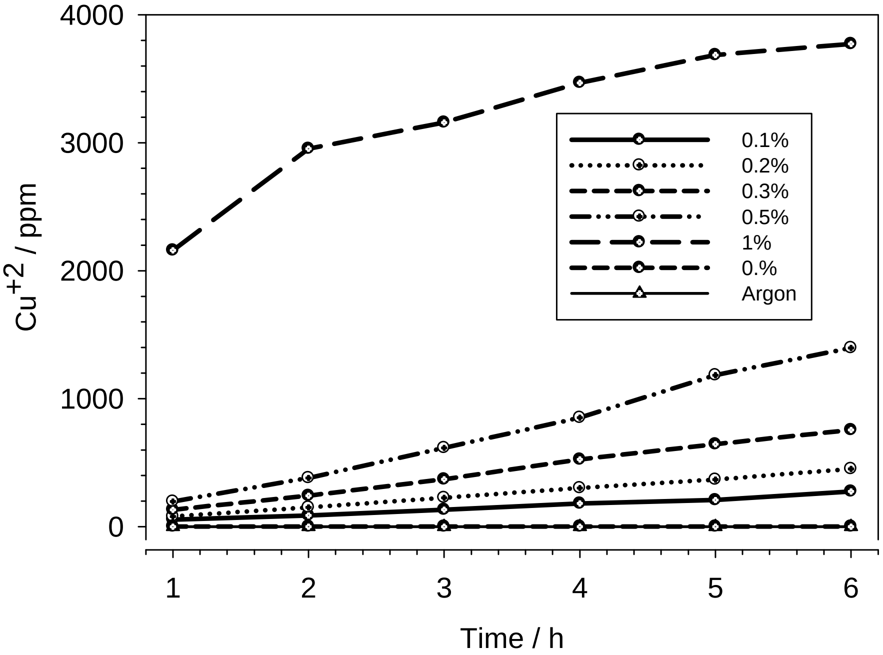


Fig.2: Effect of H_2O_2 concentration on the concentration of Cu^{+2} results from brass treated for 6 h in an electrolyte containing 1M Na_2SO_4 and 0.1M H_2SO_4 at 25°C .

Table 1 represents the effect of H_2O_2 concentration on the dezincification factor (Z) of brass treated for 6 h in the acidified sodium sulfate solution. The increase of H_2O_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 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 H_2O_2 showed a pH of 2.46 after 24 h.

Table 1: Effect of concentration of H_2O_2 on the dezincification factor of brass treated for 6 h in 1 M Na_2SO_4 and 0.1 M H_2SO_4 at 25°C.

H_2O_2, % m/v Time, h	0.1	0.2	0.3	0.5	1
1	1.07	1.07	1.08	1.17	1.07
2	1.12	1.11	1.11	1.16	1.08
3	1.14	1.11	1.11	1.13	1.07
4	1.15	1.12	1.13	1.11	1.06
5	1.15	1.12	1.13	1.15	1.07
6	1.12	1.13	1.12	1.11	1.07

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 H_2O_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.

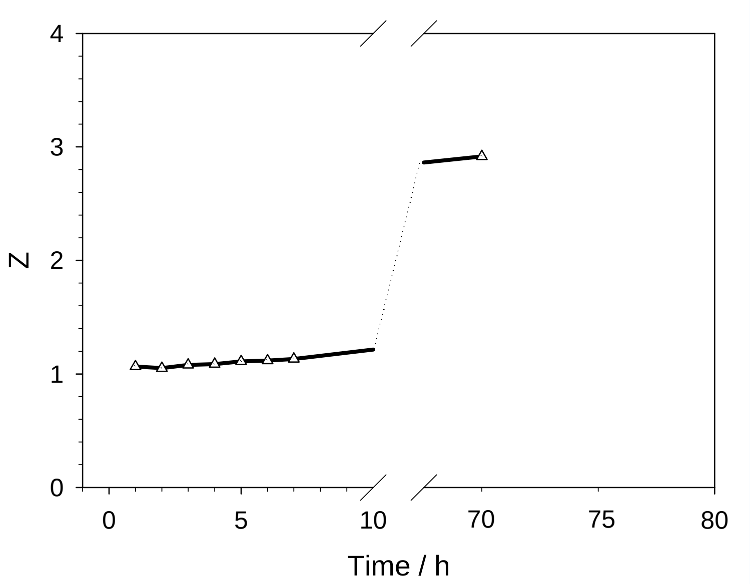


Fig.3: Effect of time on the dezincification factor of brass treated in acidified sodium sulfate solution (1 M Na_2SO_4 and 0.1 M H_2SO_4) in the presence of 1% H_2O_2 at 25°C.

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% H_2O_2. 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.

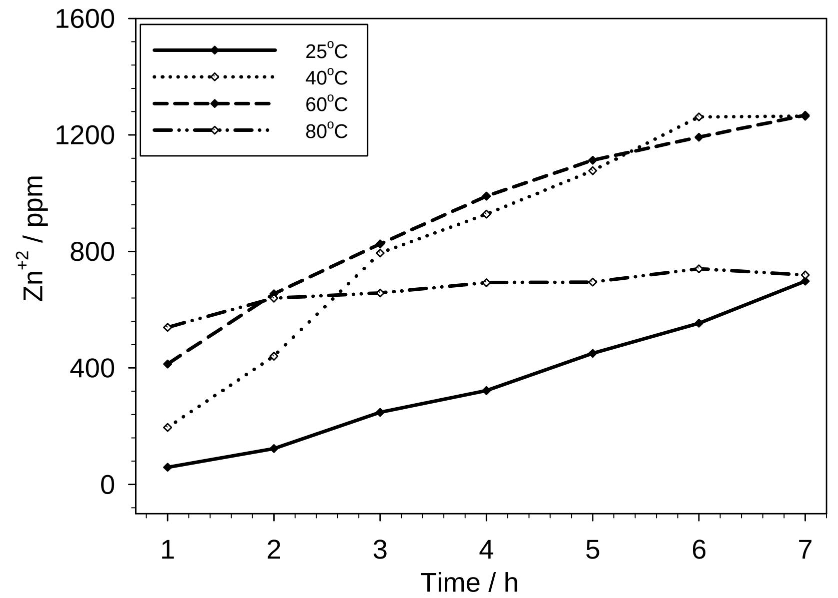


Fig.4: Effect of temperature on the concentration of Zn^{+2} results from dissolution of brass treated for 6 h in acidified sodium sulfate solution (1 M Na_2SO_4 and 0.1 M H_2SO_4) in the presence of 0.5% H_2O_2.

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 H_2O_2. 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.

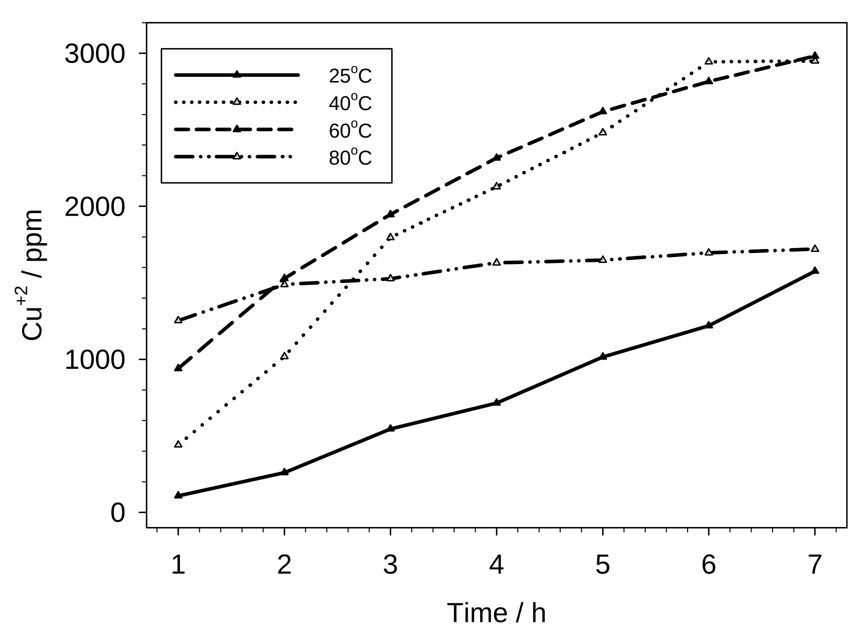


Fig.5: Effect of temperature on the concentration of Cu^{+2} results from dissolution of brass treated for 6 h in acidified sodium sulfate solution (1 M Na_2SO_4 and 0.1 M H_2SO_4) in the presence of 0.5% H_2O_2.

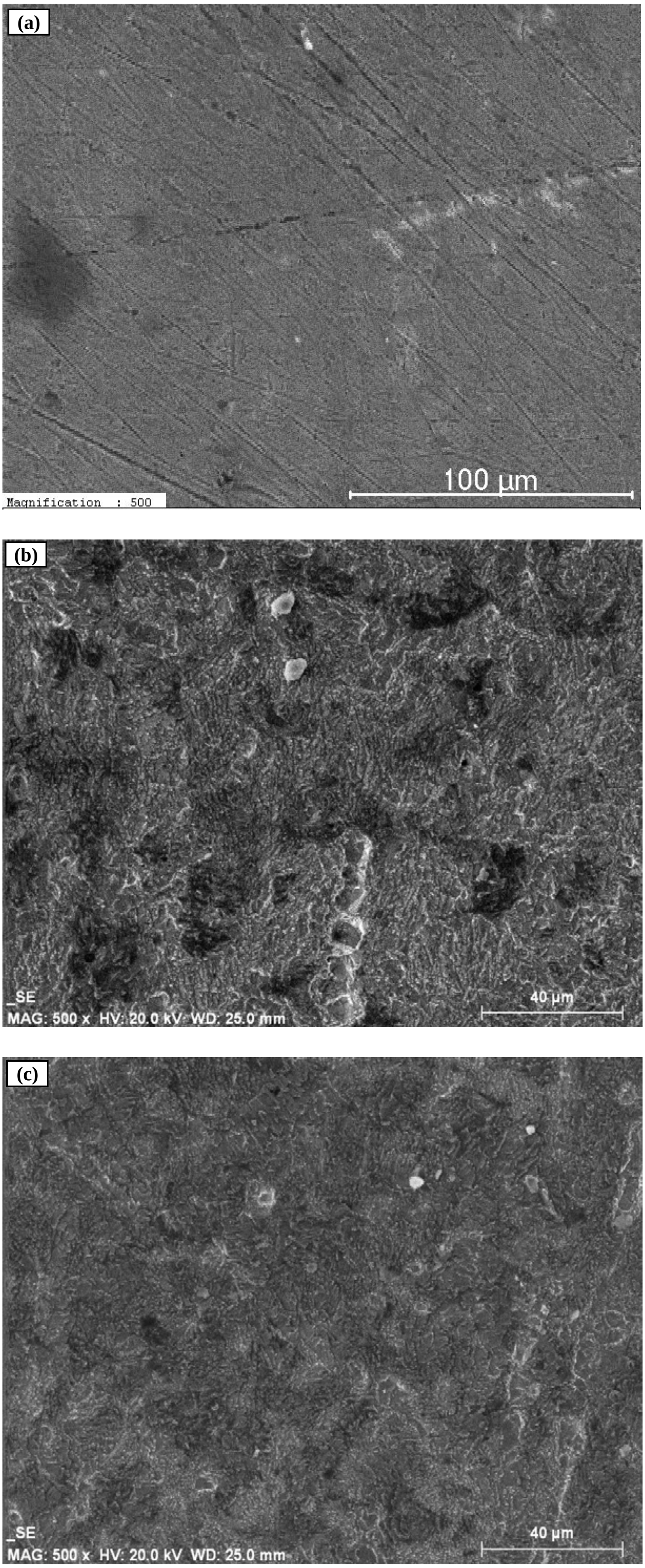
Table 2: Effect of temperature on the dezincification factor of brass treated for 6 h in acidified sodium sulfate solution (1 M Na_2SO_4 and 0.1 M H_2SO_4) in the presence of 0.5% H_2O_2.

Temperature, °C Time, h	25	40	60	80	1
1	1.27	1.03	1.03	1.00	1.07
2	1.11	1.01	1.00	1.00	1.08
3	1.06	1.03	0.99	1.01	1.07
4	1.05	1.02	1.00	0.99	1.06
5	1.03	1.01	0.99	0.98	1.07
6	1.06	1.00	0.99	1.02	1.07

3.2. Surface characterization

The effect of H_2O_2 concentration on the surface morphology of brass is illustrated in Fig.6. The surface roughness is increased in the presence of H_2O_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_2O_2 concentration. It is also noted that at 0.3% m/v H_2O_2 voids starts to appear on the brass surface. These voids are increased in numbers and size at 0.5% m/v H_2O_2. In the presence of 1% m/v H_2O_2 the brass surface is covered with a layer of Cu_2O 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_2O_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 uniformally from 1 mm to about 0.5 mm. Areas of dezincification can be distinguished by being deeper than the alloy surface.


(a)
Magnification : 500
100 µm
(b)
_SE
MAG: 500 x HV: 20.0 kV WD: 25.0 mm
40 µm
(c)
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40 µm

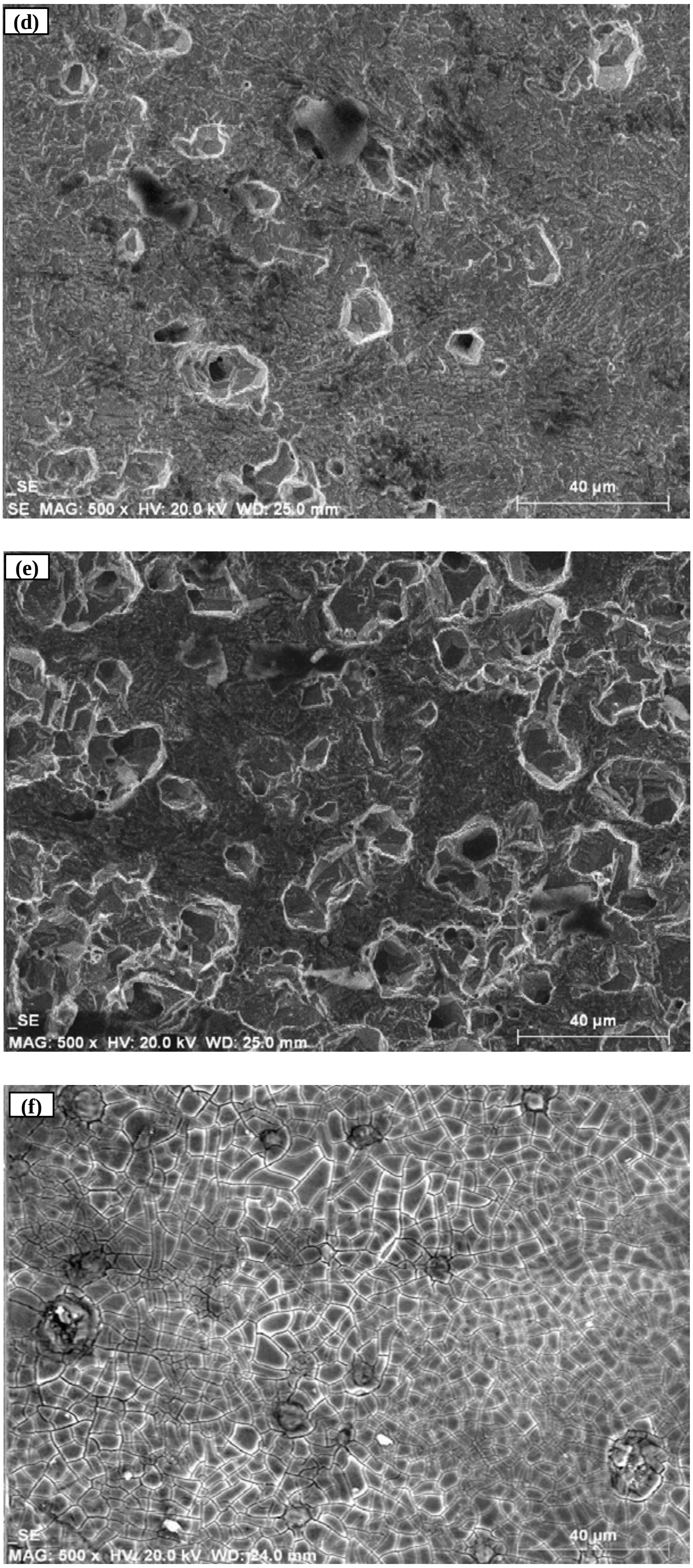


Fig.6: SEM micrographs of brass oxidized for 6 h in 1 M Na_2SO_4 + 0.1 M H_2SO_4 in the presence of 0.1% H_2O_2 (b), 0.2% H_2O_2 (c), 0.3% H_2O_2 (d), 0.5% H_2O_2 (e) and 1% H_2O_2 (f) while (a) represents the untreated brass.

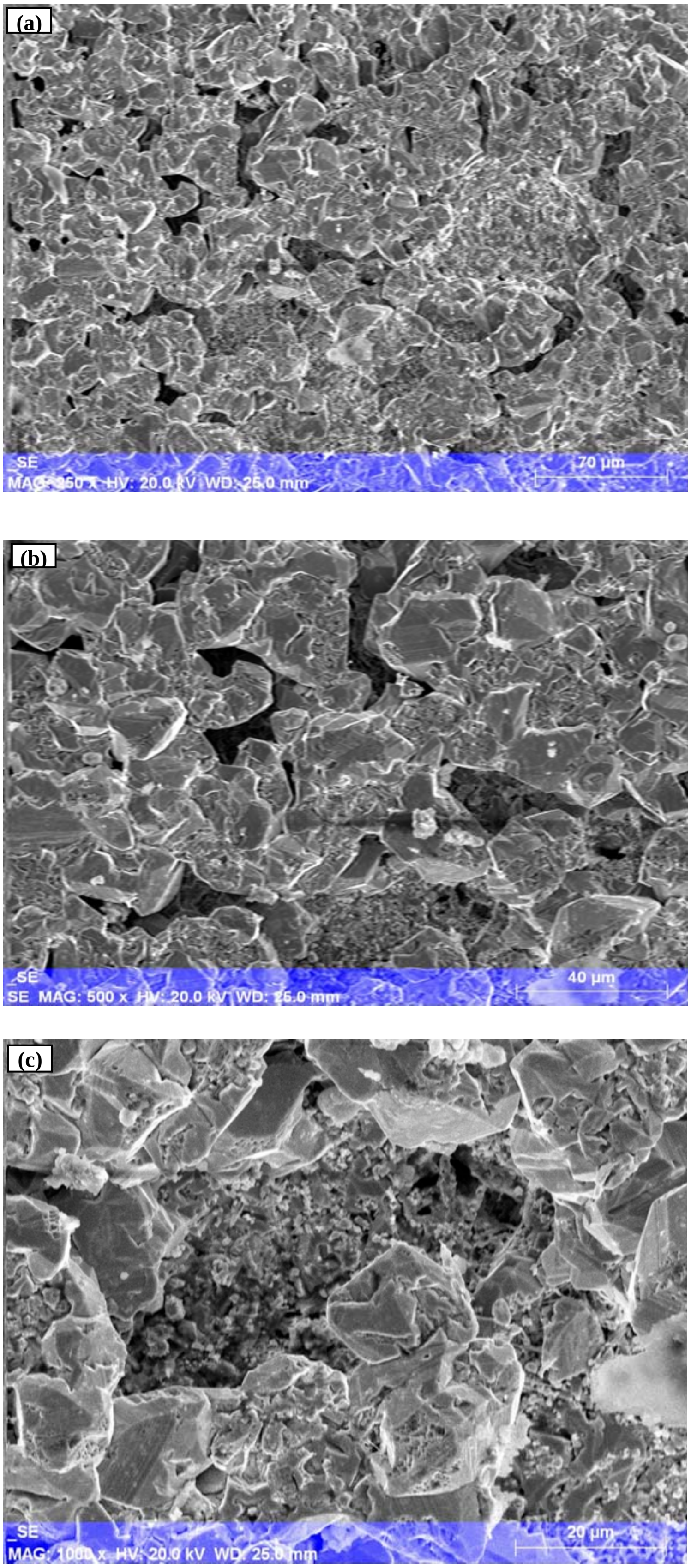


Fig.7: SEM micrographs (different magnifications) of brass treated for 72 h in acidified sodium sulfate (1 M Na_2SO_4 and 0.1 M H_2SO_4) in the presence of 1% H_2O_2.

The strong dezincification exhibited by brass after prolonged exposure to the acidified sodium sulfate in the presence of 1% m/v H_2O_2 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 Na_2SO_4 and 0.1 M H_2SO_4) in the presence of 1% H_2O_2 at 25°C.

	Binding energy, BE	Counts / C	Compound	Atomic percent, At%
Zn2p3	1021.72	28350.78	Zn	7.01
Cu2p1	952.69	40025.84	Cu_2O	32.83
O1s	531.5	44847.6	Cu_2O / CuO/ZnO	59..14
S2p1	169.27	254.69		1.02

Fig.8 shows the effect of temperature on the surface morphology of brass treated in the presence of 0.5% H_2O_2. The increase of temperature from 25 to 60°C enhances corrosion attack to a considerable extent. The surface becomes rougher with the appearance of intergrannular 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]:

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

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 H_2O_2 leading to the formation of O_2 followed by the electrochemical reduction of O_2 may be suggested [21].

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (3)$$
$$O_2 + 4H^+ + 4e^- = 2H_2O \qquad (4)$$

Another mechanism depends on the direct reduction of H_2O_2 in acidic medium may also possible, i.e.

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad (5)$$

The electroreduction of H_2O_2 can be considered to occur through the formation of adsorbed OH_{ad} species.

$$H_2O_{2(bulk)} \rightarrow H_2O_{2(surface)} \qquad (6)$$
$$H_2O_{2(surface)} + e^- \rightarrow OH_{ad} + OH^- \qquad (7)$$
$$OH^- + H^+ \rightarrow H_2O \qquad (8)$$
$$OH_{ad} + e^- \rightarrow OH^- \qquad (9)$$
$$OH_{ad} + H^+ + e^- \rightarrow H_2O \qquad (10)$$

OH^- ion thus formed combine with H^+ ion (reaction 8) at the electrode to produce the reaction H2O. Alternately, OHad can simultaneously accept an electron and H^+ ion producing H_2O in reaction 10. The adsorbed OH_{ad} species are very reactive since they are free radicals.

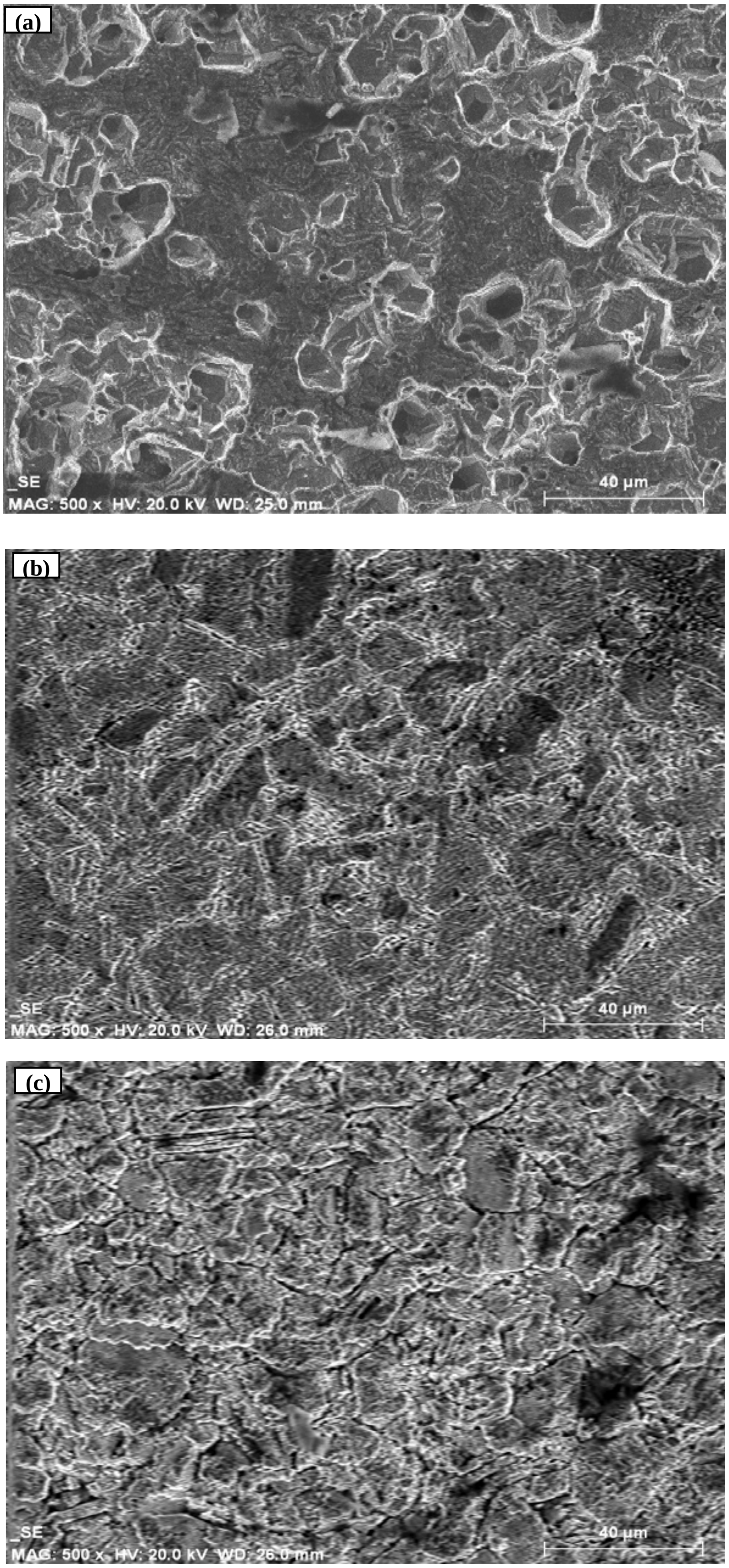
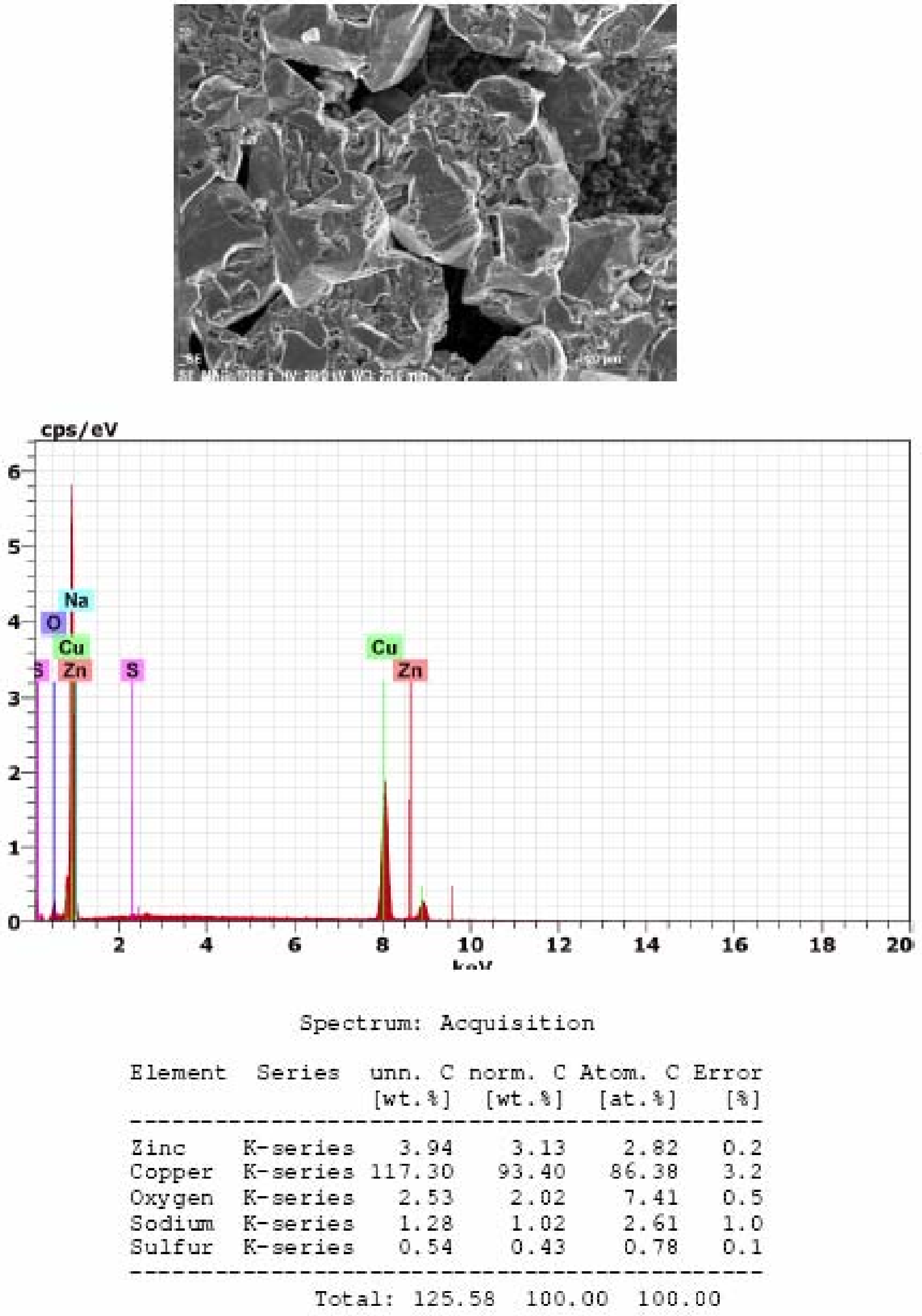


Fig.8: Effect of temperature on the SEM micrographs of brass treated in acidified sodium sulfate (1 M Na_2SO_4 and 0.1 M H_2SO_4) in the presence of 0.5% H_2O_2 for 6 h. (a) At 25^{o}C, (b) At 60^{o}C and (c) At 80^{o}C.

The second mechanism is likely to occur based on the fact that brass dissolution occurs at much higher rates in the presence of H_2O_2 compared to the rates obtained under bubbling O_2 gas in the testing solution. In a previous study of the authors [18], maximum concentrations of 46 ppm Zn^{+2} and 90 ppm Cu^{+2} were obtained under oxygen bubbling. These values are quite low compared to those obtained in the presence of hydrogen peroxide. In presence of 1% H_2O_2 where a maximum of 1800 ppm Zn^{+2} 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 H_2O_2.

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 H_2O_2 into water and O_2 is high and so its action is suppressed.



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Spectrum: Acquisition

Element  Series   unn. C norm. C Atom. C Error
                  [wt.%]  [wt.%]  [at.%]   [%]
-----------------------------------------------
Zinc     K-series   3.94    3.13    2.82   0.2
Copper   K-series 117.30   93.40   86.38   3.2
Oxygen   K-series   2.53    2.02    7.41   0.5
Sodium   K-series   1.28    1.02    2.61   1.0
Sulfur   K-series   0.54    0.43    0.78   0.1
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           Total: 125.58  100.00  100.00
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Fig.9: EDS of brass treated in acidified sodium sulfate (1 M Na_2SO_4 and 0.1M H_2SO_4) in the presence of 1% H_2O_2 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 Cu^{+2} 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:

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

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

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

The electroreduction of H_2O_2 can be considered to occur through the formation of adsorbed OH_{ad} species which gain an electron to give OH^- and finally combine with H^+ to give H_2O.

Strong dezincification of brass in acidified sodium sulfate solution containing 1% H_2O_2 was observed after prolonged time of exposure (72 h). The process of the dezinfication is the result of dissolution of α-brass into corrosive solutions followed by re-deposition of copper on the specimen surface.

Acknowledgements

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