

Investigation of the effect of the addition H₂O₂ on the general corrosion of brass in hydrochloric acid

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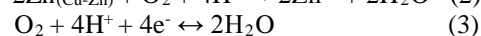
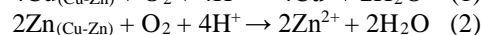
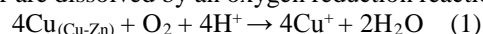
Abstract: In this paper, the influence of hydrochloric acid and the addition of oxidizing agents on the rate of general corrosion of brass was investigated. For comparison, the corrosion rate of copper and zinc in hydrochloric acid and in hydrochloric acid with oxidizing agent was also tested. The Taffel extrapolation method was used to examine the general corrosion of brass, copper and zinc. The Taffel extrapolation method involves scanning potential of the working electrode of ± 250 mV in relation to its open-circuit potential (E_{OCP}), at a speed of 0.5 mVs⁻¹. Investigation of corrosion was conducted in a corrosion cell according to the ASTM G5 (ASTM G5-94) standard, on a potentiostat/galvanostat instrument, Princeton Applied Research, model 263A-2, with PowerCORR® software, which is part of the Power Suite software package. The tests were performed at room temperature, 20±1°C. The results show that the corrosion rate of brass is higher in hydrochloric acid with oxidizing agent than the corrosion rate of brass in hydrochloric acid. Examining the effect of hydrochloric acid and the addition of oxidizing agent on the rate of general corrosion of brass, it was found that the corrosion of brass has caused the zinc contained in it. Corrosion of zinc is highest in 0.1 M HCl + 0.1 M H₂O₂ compared to corrosion of brass and copper in 0.1 M HCl + 0.1 M H₂O₂, where corrosion of copper is lowest in 0.1 M HCl + 0.1 M H₂O₂.

INTRODUCTION

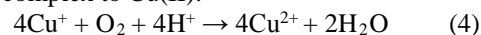
Brass is an alloy of copper and zinc containing 5-40% Zn as the main alloying element (Choucri *et al.*, 2019), other elements may be added to modify properties such as strength, machinability, or corrosion resistance (Francis, 2010). It has been used extensively in a variety of corrosive environment for many years (Akabueze *et al.*, 2012). Brass (along with bronze) are the oldest alloys used in marine technology (Feron, 2007).

Copper alloys with zinc can be double, triple and complex, with a copper content of at least 50% and zinc of not more than 44% (ordinary brass), as the main added element (Avramović *et al.*, 2006). Brass is commonly used as a condenser and heat exchanger (Gapsari *et al.*, 2018). Brass has characteristic colors. The color varies depending on the copper content (Avramović *et al.*, 2006).

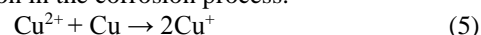
Brass undergoes an electrochemical process of selective corrosion which zinc dissolves in contact with the electrolyte (the dezincification process), leaving behind a porous layer of copper. The corrosion behavior of brass with respect to dezincification, de-alloying, and stress corrosion has been studied (El-Mahdy *et al.*, 2013). In oxygen-containing hydrochloric acid solutions, the corrosion rate of brass is increased because zinc and copper are dissolved by an oxygen reduction reaction:



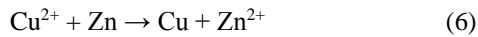
Dissolved oxygen from solution leads to oxidation of Cu(I)-complex to Cu(II):



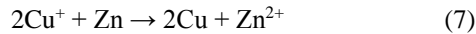
Increasing the concentration of Cu(II)-complex in the solution increases the participation of the following reaction in the corrosion process:



Copper can be redeposited from the solution on the brass surface:



and also:



Regardless of the type of corrosion reaction, autocatalytic dissolution and dissolution with the oxygen reduction reaction occurs, with repositioning. The process causes a relatively high concentration of zinc and a low concentration of copper in solution. In these investigation the redeposition process is the reason for dezincification (Avramović *et al.*, 2006).

In this paper, the influence of hydrochloric acid and the addition of oxidizing agents on the rate of general corrosion of brass were investigated. For comparison, the corrosion rate of copper and zinc in hydrochloric acid and in hydrochloric acid with oxidizing agent was also tested.

EXPERIMENTAL

Brass whose chemical composition is given in Table 1 was used for testing. For comparison, the corrosion rate of copper with a purity of 98.1% and zinc with a purity of 99.0% in hydrochloric acid and in hydrochloric acid with oxidizing agent was also tested. Chemical analysis of brass was performed at the Kemal Kapetanović Institute in Zenica. Standards JUS C.AI.185:1979 (Cu, Pb); JUS C.AI.159:1978; Analytical Methods for Atomic Absorption Spectrometry (Zn, Fe) were used to analyze the chemical composition of brass.

Table 1. Chemical composition of brass

Element	Cu	Zn
Mas. %	70,0	29,8

The tests were carried out in the following solutions: 0.1 M HCl; 0.1 M HCl + 0.1 M H₂O₂. The following chemicals were used in the preparation solutions: hydrochloric acid 35% (HCl, Lach-Ner, Czech Republic) and hydrogen peroxide 30% (GRAM-MOL, Zagreb, Croatia) all of p.a. purity.

The Tafel extrapolation method was used to examine general corrosion of brass. The Tafel extrapolation method involves scanning the potential of the working electrode of ± 250 mV in relation to its open circuit potential (E_{OCP}), at a speed of 0.5 mVs^{-1} . Investigation of corrosion was conducted in a corrosion cell according to the Standard ASTM G5 (ASTM G5-94), on a potentiostat/galvanostat instrument, Princeton Applied Research, model 263A-2, with PowerCORR® software, which is part of the Power Suite software package. The tests were performed at room temperature, $20 \pm 1^\circ\text{C}$.

RESULTS AND DISCUSSION

Figure 1. and Table 2. show the effect of adding an oxidizing agent to HCl solutions on the general corrosion rate of brass.

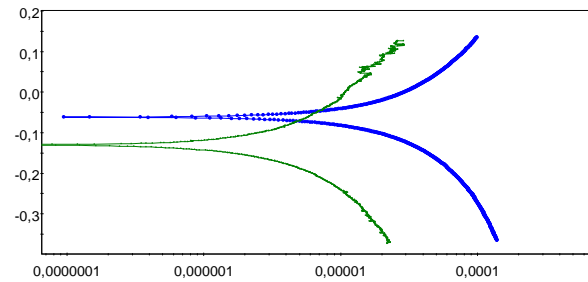


Figure 1. Tafel curves samples of brass
1 – sample treated in 0.1 M HCl;
2 – sample treated in 0.1 M HCl + 0.1 M H₂O₂

Table 2. The values of open circuit potential and corrosion current density of brass samples treated in HCl

The type of HCl solutions	E_{ocp} (mV)	Corrosion current density, i_{cor} (μAcm^{-2})
0.1 M HCl	-130,152	$1,067 \cdot 10^1$
0.1 M HCl + 0.1 M H ₂ O ₂	-61,692	$9,567 \cdot 10^2$

The results shown in Figure 1 and Table 2 show that the general corrosion rate of brass generally increases with the addition of H₂O₂. Table 2 shows that the addition of H₂O₂ increases the corrosion current density, a key parameter for estimating corrosion rate.

For comparison, the corrosion rate of zinc in hydrochloric acid and in hydrochloric acid with oxidizing agent was also tested. Figure 2. and Table 3. also show the corrosion rate of zinc in hydrochloric acid and in hydrochloric acid with oxidizing agent. The corrosion rate of zinc is higher in hydrochloric acid and in hydrochloric acid with oxidizing agent than the corrosion rate of brass in hydrochloric acid and hydrochloric acid with oxidant, as can be seen from the results of corrosion current density shown in Table 2 and Table 3.

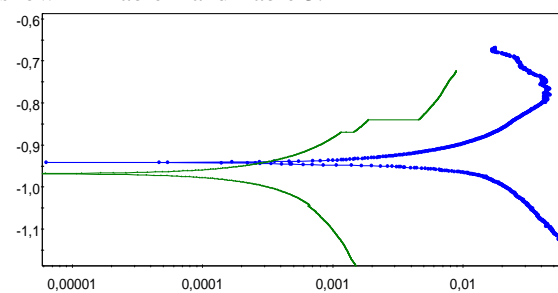


Figure 2. Tafel curves samples of zinc
1 – sample treated in 0.1 M HCl;
2 – sample treated in 0.1 M HCl + 0.1 M H₂O₂

Table 3. The values of open circuit potential and corrosion current density of zinc samples treated in HCl

The type of HCl solutions	E_{ocp} (mV)	Corrosion current density, i_{cor} (μAcm^{-2})
0.1 M HCl	-968.025	$1.447 \cdot 10^3$
0.1 M HCl + 0.1 M H ₂ O ₂	-941.531	$1.463 \cdot 10^4$

For comparison, Figure 3 and Figure 4 shows the corrosion rate of brass and zinc in hydrochloric acid and in hydrochloric acid with oxidizing agent.

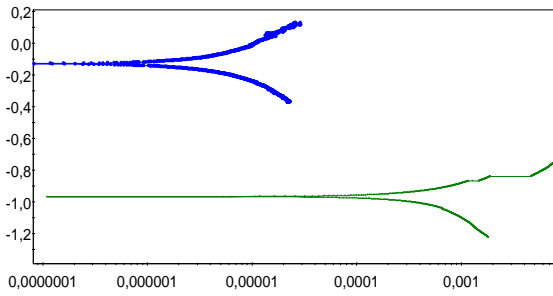


Figure 3. Tafel curves samples of brass and zinc
1 – sample of brass treated in 0.1 M HCl;
2 – sample of zinc treated in 0.1 M HCl

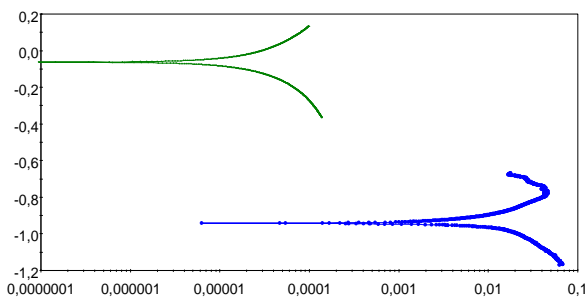


Figure 4. Tafel curves samples of brass and zinc
1 – sample of brass treated in 0.1 M HCl + 0.1 M H₂O₂;
2 – sample of zinc treated in 0.1 M HCl + 0.1 M H₂O₂

Figure 3 and Figure 4 show that the main cause of corrosion of the brass is zinc contained in it, and this is confirmed by the following Figure 5 corrosion of copper in hydrochloric acid and in hydrochloric acid with oxidizing agent.

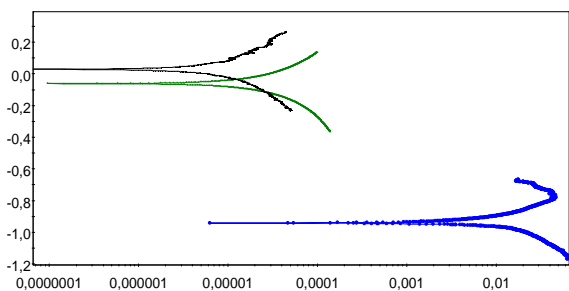
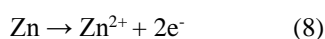
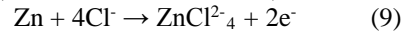


Figure 5. Tafel curves samples of brass, zinc and copper
1 – sample of brass treated in 0.1 M HCl + 0.1 M H₂O₂;
2 – sample of zinc treated in 0.1 M HCl + 0.1 M H₂O₂;
3 – sample of copper treated in 0.1 M HCl + 0.1 M H₂O₂

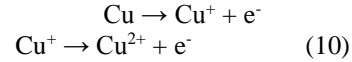
Figure 5. shows that the rate of general corrosion of copper is the lowest in 0.1 M HCl + 0.1 M H₂O₂. Since the standard electrode potential for zinc is at more negative potentials than that for copper, it is expected that zinc dissolution will occur before copper dissolution according to the following equation (Radovanovic *et al.*, 2018):



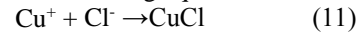
Furthermore, in chloride solutions there is also a reaction between zinc and Cl⁻ ions according to the following equation (Radovanovic *et al.*, 2018):



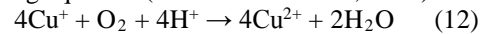
Moreover, copper dissolution occurs in acidic solution as shown by the following equations (Radovanovic *et al.*, 2018):



CuCl occurs in the reaction between Cu⁺ and Cl⁻ ions according to the following equation:



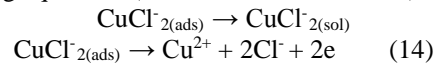
However, in the presence of atmospheric oxygen, oxidation of Cu⁺ to Cu²⁺ occurs according to the following equation (Radovanovic *et al.*, 2018):



The CuCl layer reacts with Cl⁻ and forms a soluble CuCl₂ complex according to the following equation (Radovanovic *et al.*, 2018):

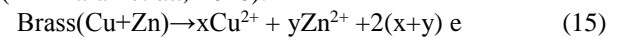


Based on the literature data, which refer to the conditions in the examined system, the formed CuCl₂ complex can be dissolved into the bulk solution. Also, in an acidic solution, CuCl₂ is oxidized to Cu²⁺ ions according to the following equations (Radovanovic *et al.*, 2018):

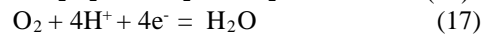
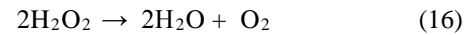


CONCLUSION

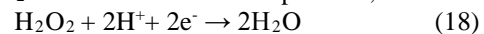
The alloy dissolution process begins with the simultaneous dissolution of both components of the alloy (Cu and Zn). The dissolution reaction occurs according to (Al Kharafi *et al.*, 2010):



where x and y are the fractions of dissolved copper and zinc, respectively. At the free corrosion potential, the electrons resulting from equation (15) are consumed in the cathodic reduction of hydrogen peroxide. A mechanism involving decomposition (or disproportionation) of H₂O₂ leading to O₂ formation, followed by electrochemical reduction of O₂, may be suggested.



Another mechanism that depends on the direct reduction of H₂O₂ in an acidic medium is possible, i.e.



Electroreduction of H₂O₂ can be considered to occur by generating adsorbed OH_{ad} species that receive an electron to give OH⁻ and finally combine with H⁺ to give H₂O (Al Kharafi *et al.*, 2010).

Thus, the results show that the corrosion rate of brass is higher in hydrochloric acid with oxidizing agent than the corrosion rate of brass in hydrochloric acid.

Examining the effect of hydrochloric acid and the addition of oxidizing agent on the rate of general corrosion of brass, it was found that the corrosion of brass has caused the zinc contained in it. Corrosion of zinc is highest in 0.1 M HCl + 0.1 M H₂O₂ compared to corrosion of brass and copper in 0.1 M HCl + 0.1 M H₂O₂, with copper corrosion lowest in 0.1 M HCl + 0.1 M H₂O₂.

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Summary/Sažetak

U ovom radu ispitan je uticaj hlorovodične kiseline i oksidacionog sredstva na brzinu opšte korozije mesinga. Poređenja radi, ispitivana je i brzina korozije bakra i cinka u hlorovodičnoj kiselini i hlorovodičnoj kiselini s dodatkom oksidansa. Za ispitivanje opšte korozije uzoraka mesinga, bakra i cinka upotrijebljena je Tafelova ekstrapolacijska tehnika. Navedena metoda podrazumijeva skeniranje potencijala radne elektrode ± 250 mV u odnosu na potencijal otvorenog kruga (E_{OCP}), brzinom od $0,5 \text{ mVs}^{-1}$. Istraživanja korozije provedena su u korozionoj ćeliji prema standardu ASTM G5, na instrumentu potenciostat/galvanostat, Princeton Applied Research, model 263A-2, koristeći softver PowerCORR®. Ispitivanja su provedena na sobnoj temperaturi, $20 \pm 1^\circ\text{C}$. Rezultati pokazuju da je brzina korozije mesinga veća u hlorovodičnoj kiselini s dodatkom oksidansa od brzine korozije u hlorovodičnoj kiselini. Ispitivanjem uticaja hlorovodične kiseline i dodatka oksidacionog sredstva na brzinu opšte korozije mesinga, ustanovljeno je da je koroziju mesinga uzrokovao cink koji se nalazi u njemu. Korozija zinka je najveća u $0.1 \text{ M HCl} + 0.1 \text{ M H}_2\text{O}_2$ u odnosu na koroziju mesinga i bakra u $0.1 \text{ M HCl} + 0.1 \text{ M H}_2\text{O}_2$, gdje je korozija bakra najmanja u $0.1 \text{ M HCl} + 0.1 \text{ M H}_2\text{O}_2$.