

COMPARATIVE CORROSION BEHAVIOR OF PURE COPPER AND BRASS IN 3.5% NaCl SOLUTION

Lidia BENEĂ, Eliza DĂNĂILĂ

Competences Center: Interfaces-Tribocorrosion-Electrochemical Systems (CC-ITES), Faculty of Engineering, Dunarea de Jos University of Galati, 47 Domneasca Street, RO-800008 Galati, Romania
e-mail: lidia.benea@ugal.ro

ABSTRACT

Copper and brass are used in many economic sectors as electrical, construction, transport and others. From common household electrical wiring to boat propellers and from photovoltaic cells to saxophones, copper and its alloys are employed in a variety of end-uses. Copper tubing is now the standard material for potable water and heating systems in most developed countries. This is in part due to its bacteriostatic properties, or in other words due to the ability of copper to inhibit the growth of bacterial and viral organisms in water. Therefore, the corrosion resistance of copper and brass are important in defining the field of use as construction parts. This paper aims at investigating the comparative corrosion behavior of pure copper and brass in 3.5 % NaCl solution. The corrosion behavior of both type samples in 3.5% NaCl solution was investigated by the use of electrochemical methods as open circuit potential and linear polarization resistance measurements. The results show an improved corrosion resistance of pure copper sample in 3.5 wt. % NaCl solution as compared with brass sample.

KEYWORDS: copper, corrosion rate, cyclic voltametry

1. Introduction

Corrosion process is certainly one of the most common causes of failure of engineered components and structures. The corrosion phenomenon leads to deterioration of the material (usually a metal) and its properties, being caused by the reaction of the metal with the environment. The corrosion behavior of the material depends on the environment to which it is subjected, and the corrosive action of an environment depends on the material exposed to that environment [1]. Therefore, it is very important to know the corrosion resistance of a material before being designed for a specific application.

Copper tubes are used for plumbing, heating, air-conditioning and refrigeration systems which can be found in the residential, industrial or commercial installations. For several decades, copper has been used as a plumbing material for potable water distribution systems [2]. Also, copper alloys like brass are widely used in domestic water-distribution systems in valves, heat exchangers, pumps, heating components, plumbing fittings and plumbing fixtures [3]. Localized or pitting corrosion is recognized as one of the major problems, with copper tubing or

brass failure in tap water being a major and ongoing problem in many countries [2].

The aim of the present work is to systematically study the comparative corrosion behavior on pure copper and brass. Different electrochemical techniques were explored and complemented by surface optical microscopy.

2. Materials and methods

An VoltaLab PGZ 100 potentiostat / galvanostat controlled by VoltaMaster software was used for electrochemical measurements. A conventional three-electrode setup was used for electrochemical studies, in which a Pt-Rh grid served as the auxiliary electrode and an Ag/AgCl with KCl saturated solution ($E = 200$ mV vs. standard hydrogen electrode – SHE) as the reference electrode. The copper electrode and brass respectively served as the working electrode. The chemical composition of tested samples was 99.97 % for pure copper and the following Cu-57.8%, Zn-39.02%, Pb-2.99%, Fe-0.19% for brass. Prior to the corrosion tests, the surfaces of the samples exposed to the solution were mechanically polished to a mirror finish by using SiC

grinding paper (320-2000 μm), degreased with acetone and dried with hot air. The exposure surface area of the working electrode was 6.25 cm^2 . As the corrosive electrolyte was selected 3.5 % NaCl aqueous solution and electrochemical measurements were conducted at room temperature. The pH of this solution was 6.43. The volume for each experiment was 135 mL of 3.5 % NaCl aqueous solution.

3. Results and discussion

3.1. Open Circuit Potential (OCP)

The open circuit potential measurements give the information about thermodynamic stability of the sample surface to electrochemical oxidation in a particular corrosive environment [4]. This potential may vary with time due to change in the oxidation tendency of the surface (oxidation, formation of the passive layer or immunity) [4-5]. Figure 1 shows the variation of the open-circuit potential (E_{OC}) with time, for copper and brass electrodes immersed in 3.5 % NaCl aqueous solution, over a period of 60 minutes. The E_{OC} of the pure Cu electrode stabilizes at a more positive value as compared with that of brass electrode reaching a mean value of -189 mV versus Ag/AgCl. On the other hand, the E_{CORR} of the brass electrode reached a more negative steady state value, revealing an average value of -205 mV versus Ag/AgCl.

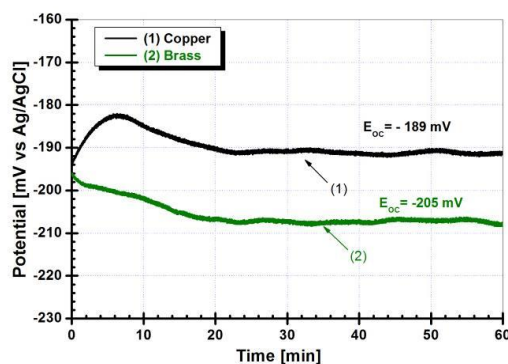


Fig. 1. Open circuit potential (E_{OC}) for: (1) pure copper and (2) brass electrodes over a period of 60 minutes, immersed in 3.5 % NaCl aqueous solution

The both type of studied samples reach the steady states after approximately 22 minutes from immersion and did not exhibit potential drops associated with surface activation during 60 minutes exposure in the 3.5 % NaCl solution. This kind of behavior strongly suggests that the native oxide films from the both studied surfaces are thermodynamically

resistant to chemical dissolution in 3.5 % NaCl solution.

Since the difference between the steady states revealed by both electrodes (pure copper and brass) is not so big, of only 16 mV, it could be assumed that the processes which occur, on the brass surface are mainly governed by copper. Similar observations have been made earlier for Cu–16%Zn–6.5%Al alloy as compared with pure copper and pure zinc immersed in borate buffer solution [6]. In other words, it can be said that Zn element has a little influence in defining the potential of the brass/solution interface.

3.2. Linear polarization resistance (LPR)

Linear polarization resistance (LPR) is a rapid response testing technique commonly used in material corrosion studies which allow the calculation of the corrosion rate. For this method, the tested material was polarized with a small overvoltage in the range of $\pm 40\text{ mV}$, relative to its Open Circuit Potential (OCP) and the resulting ("linear") current response was measured. The measured resistance is inversely related to the corrosion rate. The linear polarization resistance measurements were carried out at a scan rate of 5 mV/sec.

The polarization resistance values of the both tested surfaces studied in 3.5 % NaCl solution are shown in Fig. 2.

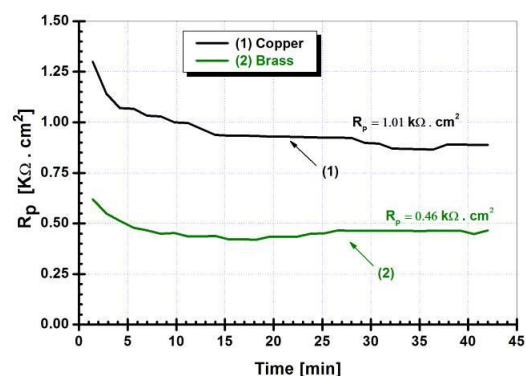


Fig. 2. The evolution of R_p values during immersion time of: (1) pure copper and (2) brass electrodes

From Fig. 2 it can be seen that the lowest polarization resistance (R_p) value is attained by the brass electrode being equal to 0.46 kohm cm^2 , while the pure copper electrode reveals a mean value of polarization resistance equal to 1 kohm cm^2 . An increased value of polarization resistance for pure copper electrode means lower corrosion current density and therefore a lower corrosion rate, as

compared with brass electrode as it can be seen in Fig. 3.

Corrosion rate can be defined as the amount of corrosion loss per year in thickness. From Fig. 3 it can be seen that the lowest corrosion rate value is attained by the pure copper electrode being equal to 0.082 mm/year, while the brass electrode reveals a mean value of corrosion rate equal to 0.164 mm/year. According with the data presented in Fig. 3 it can be clearly seen that the corrosion rate of brass shows a double value as compared with pure copper electrode. The higher corrosion rate corresponding to brass as compared with copper can be attributed to the presence of zinc as an alloying element, which leads to the incorporation of ZnO (as the main oxidation product on Zn metal) in the passive layer. Similar results were reported earlier by Kosec *et al.* [7] who studied the electrochemical behaviors of copper, Cu-10Zn and Cu-40Zn alloys and zinc in inhibited and uninhibited 0.5 M NaCl solution and by Valcarce and collaborators [8] who investigated the susceptibility to pitting corrosion of copper and 70/30 brass in artificial tap water with or without *Pseudomonas fluorescens*.

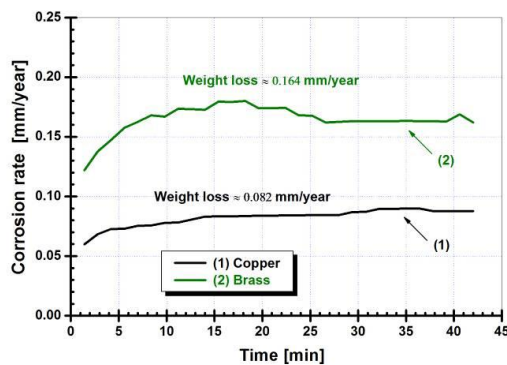


Fig. 3. Variation of corrosion rate vs. exposure time for: (1) pure copper and (2) brass electrodes

Corrosion resistance is certainly an important consideration in constructive parts as automotive screw machine components. Despite exposure to corrosive conditions, the constructive parts must continue to function, threads and fittings must continue to fit properly, and an image of quality should be maintained. Affected by corrosion, many constructive parts can conduct to system failure.

3.3. Cyclic voltammetry diagrams (CV)

The cyclic voltammetry was initiated from negative direction (-1.0 V vs. Ag/AgCl) to positive direction (+0.3 V vs. Ag/AgCl) with the sweep rate of

5 mV/s. The scan direction was reversed after the anodic current reached + 0.3 mV vs. Ag/AgCl to form a complete cycle and the recorded diagrams for both copper and brass are presented in Fig. 4.

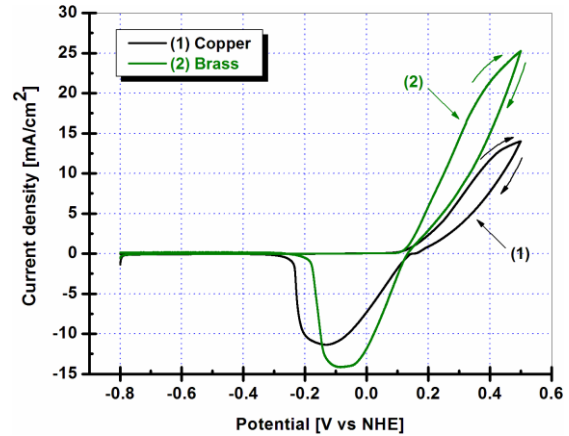


Fig. 4. Cyclic voltammograms of (1) copper and (2) brass performed at 5mV/sec sweep rate during immersion in 3.5 % NaCl aqueous solution expressed versus Normal Hydrogen Electrode (NHE)

As it is shown in Fig. 4 the shape of both voltammograms are similar, but the anodic current for brass is higher as compared with anodic current for copper.

The reversed diagrams from positive to negative potentials is drawn under the direct diagram from negative to positive direction for copper as well for brass confirming the repassivation of both surfaces. The reactions taking place at specific potentials for copper and copper corrosion compounds (products) are presented in Fig. 5.

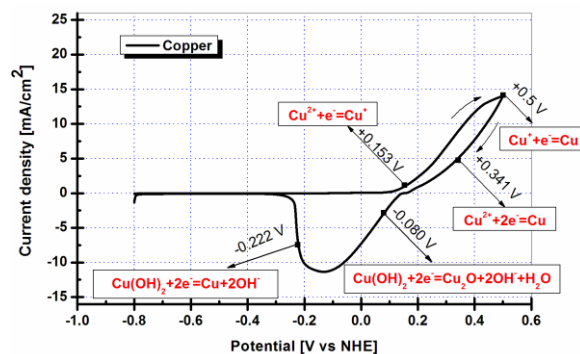


Fig. 5. Specific corrosion reactions of copper on cyclic voltammograms of copper at different potentials expressed versus Normal Hydrogen Electrode (NHE)

The shape of cyclic voltammograms for brass is similar with those of copper explained by the fact that the corrosion process of brass is dominated by copper corrosion reactions.

For zinc corrosion in brass on cyclic voltammograms we did not identify the specific reactions of zinc in the measured potentials range, confirming that the entire corrosion process of brass

in sodium chloride solution is dominated by copper reactions.

3.4. Optical Microscopy

The optical micrographs of copper and brass surfaces performed before and after the corrosion tests are shown in Figures 6 and 7.

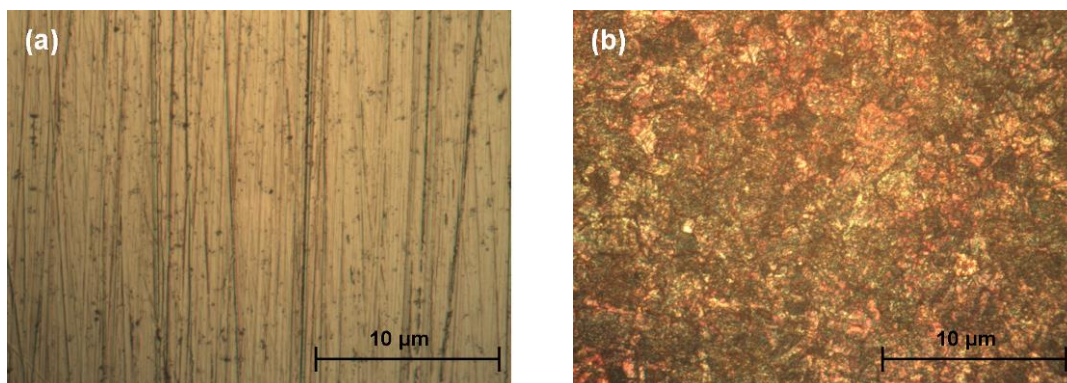


Fig. 6. Optical microscopy images of pure copper (a) before and (b) after corrosion experiments

In Fig 6 (a) it is shown copper surface before corrosion with some polished tracks. After corrosion, the surface of copper is uniformly covered with a thin

layer of copper corrosion products (oxides with different colors.

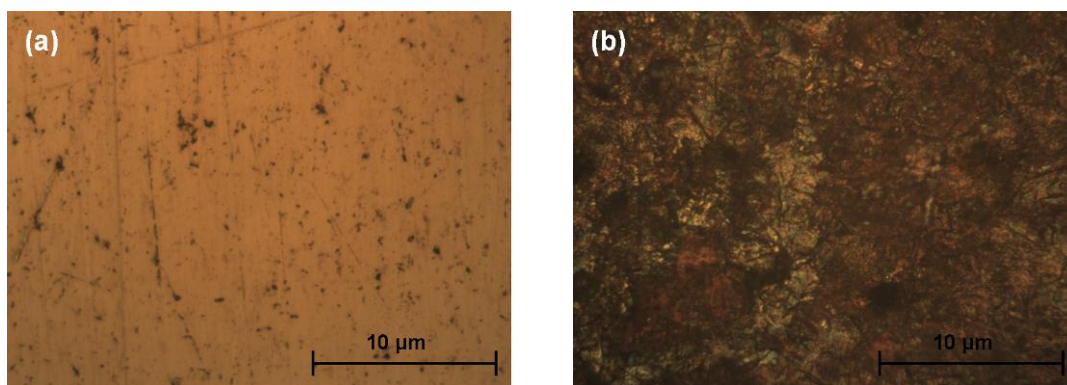


Fig. 7. Optical microscopy images of brass (a) before and (b) after corrosion experiments

The surface of brass from Fig 7 (a) before corrosion tests presents some polishing tracks but also some inclusions. After corrosion tests, Fig. 7(b) the surface of brass shows mainly a corrosion film product very similar to copper. The corrosion products of zinc are easily soluble, and being white, it is difficult to distinguish from other colored oxides of copper.

4. Conclusions

Corrosion of materials is a very important issue to consider when choosing a material that must operate in a specific environment.

After evaluating the results of laboratory research work on the two types of materials, the following have been drawn.

The free potentials values of pure copper are nobler than that for their alloy with zinc (brass), according to evolution of potential at immersion in 3.5% NaCl solution.

By assessing polarization resistance through 30 linear polarization measurements and dimensional mass loss (mm / year) it was observed the same trend of best corrosion resistance of copper compared with brass.

From cyclic voltammograms and specific corrosion reactions identified at specific potentials, it

was shown that even on brass surface the corrosion process is dominated by copper reactions.

The optical microscope micrographs before and after corrosion tests confirm the above-mentioned conclusions.

References

- [1]. **Davis J. R.**, *Corrosion: Understanding the basics*, ASM International, p. 1-17., 2000
- [2]. **Burstein G. T., Bia H., Kawaley G.**, *The Persistence of Inhibition of Copper Corrosion in Tap Water*, *Electrochimica Acta*, 191, p. 247-255, 2016.
- [3]. **Yohai L., Vázquez M., Valcarce M. B.**, *Brass corrosion in tap water distribution systems inhibited by phosphate ions*, *Corrosion Science*, 53, p. 1130-1136, 2011.
- [4]. **Santana Jiménez Y., Tejera Gil M., Torrado Guerra M., Baltés L. S., Mirza Rosca J. C.**, *Interpretation of open circuit potential of two titanium alloys for a long-time immersion in physiological fluid*, *Bulletin of the Transilvania University of Brasov*, vol. 2, (51), p. 197-204, 2009.
- [5]. **Choudhary S., Garg A., Mondal K.**, *Relation between open circuit potential and polarization resistance with rust and corrosion monitoring of mild steel*, *Journal of Materials Engineering and Performance* vol. 25(7), p. 2969-2976, 2016.
- [6]. **Blanco M., Barragan J. T. C., Barelli N., Noce R. D., Fugivara C. S., Fernández J., Benedetti A. V.**, *On the electrochemical behavior of Cu-16%Zn-6.5%Al alloy containing the β -phase (martensite) in borate buffer*, *Electrochimica Acta*, 107, p. 238-247, 2013.
- [7]. **Tadeja Kosec, Ingrid Milošev, Boris Pihlar**, *Benzotriazole as an inhibitor of brass corrosion in chloride solution*, *Applied Surface Science*, 253, p. 8863-8873, 2007.
- [8]. **Valcarce M. B., de Sánchez S. R., Vázquez M.**, *Localized attack of copper and brass in tap water: the effect of Pseudomonas*, *Corrosion Science*, 47, p. 795-809, 2005.