Electrochemical Stability of Cu–10Al–10Zn, Cu–10Al–10Ni, and Cu–10Ni–10Zn Ternary Alloys in Simulated Physiological Solutions

H. Nady^{1,2} · M. M. El-Rabiei¹ · G. M. Abd El-Hafez¹

Received: 23 August 2016 / Revised: 19 September 2016 / Accepted: 28 September 2016 / Published online: 7 October 2016
© Springer International Publishing Switzerland 2016

Abstract Copper-based alloys are widely used in the consumer electronics industry for components such as connector contacts, shielding gaskets, and terminals. Nickel silver is a general term for alloys that contain copper, nickel, and zinc. Nickel silver first became popular as a base metal for silver-plated cutlery and other silverware, notably electro-plated nickel silver, jewelry and coins. In this article, the electrochemical stability of Cu–10Ni–10Zn alloy was compared with that of pure copper and two of copper ternary alloys, namely Cu–10Al–10Zn and Cu–10Al–10Ni in synthetic sweat solution, Hank's solution and in Ringer physiological solution. Corrosion behavior of the different electrodes was investigated using cyclic voltammetry, potentiodynamic polarization, and impedance spectroscopy techniques. The CVs showed peaks concerning the redox reactions for copper. These peaks were assigned to the formation and reduction of copper species. Furthermore, they showed that the copper

oxidation was suppressed to a large extent by the presence of Ni and zinc in the alloy composition than the presence of Al and Zn or the presence of Al and Ni elements. Also, the results showed that the Cu–10Ni–10Zn alloy exhibited good corrosion resistance due to the formation of a protective passive film. The electrochemical impedance spectroscopy results indicated that either a duplex film with an inner barrier layer and an outer porous layer or a single passive layer was formed on the surface. The formation of such passive film was discussed, and the different alloy surfaces examined by scanning electron microscopy and subjected to EDAX analysis. The surface analysis has shown the participation of the different alloying elements in the passive film according to the alloy constituents.

Graphical Abstract Addition of Ni decreases the rate of corrosion of the Cu, and the Cu–10Ni–10Zn was found to be the most corrosion-resistant alloy.

✉ H. Nady
hashem_nady@yahoo.com; nhm00@fayoum.edu.eg

¹ Chemistry Department, Faculty of Science, Fayoum University, Fayoum, Egypt

² Chemistry Department, Faculty of Science and Arts in Qurayate, Al Jouf University, Sakaka, Saudi Arabia

Cu-10Al-10Zn **Cu-10Al-10Ni** **Cu-10Ni-10Zn**

Keywords Copper alloys · Cyclic voltammetry · EIS · Potentiodynamic polarization · Physiological solutions

1 Introduction

Copper-based alloys are used in a wide variety of applications because of their good physical properties, excellent corrosion resistance, and reasonable price. Copper–nickel alloys are used as condenser tube materials in saline environments, as well as catalysts for hydrogenation and dehydrogenation. Copper–zinc alloys are important in civil engineering, as condenser and heat-exchange tubes in the power generation industry, and also as a decorative material in works of art. There are numerous publications on the electrochemical behavior and corrosion resistance of Cu–

Ni and Cu–Zn [1–7] alloys in different solutions. Recently, copper and many copper alloys have been used as antibacterial materials. The Copper Development Association (CDA) has shown that more than 90 % decrease in viable bacteria can be achieved using copper surfaces in place of plastic and stainless steel surfaces in hospital rooms [8]. Also, the copper alloys containing more than 65 % Cu were used for bedrails, chair arms, bedside tables, intravenous fluids stands, door knobs, and push-plates [8–13]. In order to minimize the spread of antibiotic resistant diseases in hospitals, there should be an increased utilization of the antimicrobial copper alloys. The corrosion of different metals caused by human hand contact has been studied by many researchers. Burton et al. described the problem of “rusters” in industry as the individuals whose hands tarnished the metals that they touched [14].

He provided an extensive review of the literature that attributed the cause of the corrosion by sweat to be due to the salt of NaCl. A similar result has also been observed by Lind et al. [15]. Lind et al. reported that the main cause of corrosion of metals in contact with synthetic sweat was 95 % attributed to the sodium chloride, while the lactic acid and urea contributed to only about 5 % of the corrosion loss [15]. Jensen et al. compared the corrosive action of palm hand sweat with “rusters” on two different steels and showed that corrosion rates increased with increased sweat rates, and he reported that the copper in steel was beneficial in reducing the corrosion of steel in presence of sweat [16]. Colin et al. focused on the composition of the corrosion layers on some of ternary copper alloys in synthetic sweat medium using Fourier transform mass spectrometer and laser microprobe mass analyser [17, 18]. Colin’s results showed that the corrosion product thickness layer increased with an increase in copper content. The objective of the present paper is to investigate the electrochemical stability of some copper ternary alloys in synthetic sweat, Hank’s solution, and in Ringer physiological solution. The alloys are Cu–10Al–10Zn, Cu–10Al–10Ni, and Cu–10Ni–10Zn. In this respect, polarization techniques and electrochemical impedance spectroscopy, EIS, were used. The surface morphology and chemical composition of the different alloys were examined by SEM and EDX.

2 Experimental Details

The working electrodes were made from commercial grade Cu–10Al–10Zn, Cu–10Al–10Ni, and Cu–10Ni–10Zn rods prepared in our metallurgical work shop. The prepared alloys are cast alloys without any special treatment. The metallic rods are mounted into glass tubes by two-component epoxy resin leaving a surface area of 0.2 cm^2 to contact the solution. The mass spectrometric analysis of the alloy electrodes is presented in Table 1. Electrochemical measurements studies were carried out in 100 ml glass cell having three-electrode system assembly. A saturated

calomel, SCE, electrode was used as a reference. The auxiliary electrode was a platinum rode. Before each experiment, the working electrode was polished using successive grades emery papers down to 2000 grit, washed thoroughly with distilled water, and then transferred quickly to the electrolytic cell.

Three types of solutions were used: Ringer physiological, Hank solution, and synthetic sweat. Preparation of 1 L of each of the solutions in which the electrodes were immersed was as follows: Hank’s solution (pH 7.4) NaCl 8.0 g/L; KCl 0.4 g/L; KH_2PO_4 0.6 g/L; CaCl_2 0.14 g/L; $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 0.1 g/L; NaHCO_3 0.35 g/L; $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ 0.06 g/L; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 0.06 g/L; and D-glucose 1.0 g/L [19]. Ringer physiological solution, NaCl 8.60 g/L; KCl 0.3 g/L; and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ 0.33 g/L, pH 7.4. Artificial sweat solution, NaCl 0.5 %; lactic acid 0.1 %; and urea 0.1 %, adjusted to pH 6.5 with ammonia [20]. All the solutions were prepared using distilled water and analytical grade reagents. Prior to all electrochemical measurements, the working electrode was immersed in the different test solutions for 1 h to attain a steady state open circuit potential. All experiments were performed using 100 mL of test solutions under naturally aerated and unstirred conditions. The polarization experiments and electrochemical impedance spectroscopic investigations were performed using a Voltalab PGZ 100 “All-in-one” Potentiostat/Galvanostat. The potentials were measured against and referred to the standard potential of the SCE [0.245 V vs. the standard hydrogen electrode (SHE)]. The polarization experiments were carried out at a scan rate of 5 mVs^{-1} and the cyclic voltammetry measurements were carried out using a scan rate of 10 mVs^{-1} in the potential range -800 to 600 mV . Electrochemical impedance spectroscopy measurements were made over a frequency range of 100 kHz – 100 mHz at the stable open circuit potential. The superimposed ac-signal amplitude was 10 mV peak to peak as assigned by the measuring system. The surface morphology and the constituent elements of the different electrodes were investigated by scanning electron microscope, SEM, equipped with energy dispersive spectroscopy, EDS, (model ISPECT S 2006, FEI Company, Holland).

Table 1 Mass spectrometric analysis for the different electrode materials in mass %

Sample	Cu	Al	Ni	Zn	Mn	Sn	Fe	Si	Mg
Cu	99.93	0.001	0.02	0.007	0.003	0.033	0.002	0.003	0.001
Cu–10Al–10Zn	79.14	10.40	0.00	10.20	0.01	0.02	0.21	0.01	0.01
Cu–10Al–10Ni	76.00	11.28	9.95	0.10	0.02	0.14	2.26	0.24	0.01
Cu–10Ni–10Zn	81.31	0.60	8.07	9.71	0.01	0.02	0.06	0.22	0.00

3 Results and Discussion

3.1 Cyclic Polarization Measurements

The cyclic voltammograms for the three Cu alloys under investigation were recorded in Ringer physiological solution at a scan rate of 10 mV s^{-1} . Figure 1 presents the results of potential cycling in the potential range -800 to $+600 \text{ mV}$. For studies, the effect of alloying elements on the stability of Cu in the test solution the CV of Cu is recorded and presented in Fig. 1. For the three different investigated alloys, the CV curve is characterized by a single anodic peak and one cathodic peak. Generally, cyclic voltammograms for copper and copper alloys often show two anodic peaks, the first is related to the formation of CuCl film on the metal surface. The breakdown of this film by the complexation–dissolution and copper oxidation results in the second peak [21, 22]. The presence of only one anodic peak for the three alloys can be explained by the formation of Al and/or Zn hydroxide/oxide layer along with the CuCl surface layer, which prevents its breakdown [21, 23]. The Al and/or Zn hydroxide layer prevents the direct copper-chloride reaction on the surface and shifts it to higher potentials, and so the first peak is inhibited and only one anodic peak in the CV diagram could be recorded. For Cu alloys containing Ni, the dissolution of copper is inhibited, especially in the presence of Zn. The shape of the anodic part of the voltammogram changes from a peak for Cu–10Al–10Zn and Cu–10Al–10Ni to a hump for a Cu–10Ni–10Zn alloy. The surface layer formed on the latter thus appears to be somewhat more protective in chloride media than that formed on the former alloys.

Fig. 1 Cyclic voltammograms at a scan rate 10 mV s^{-1} for Cu (solid line), Cu–10Al–10Zn (dashed line), Cu–10Al–10Ni (dotted line), and Cu–10Ni–10Zn (dashed dotted line) alloys in Ringer's solution

Figure 2 represents the CVs of the Cu–10Ni–10Zn alloy in naturally aerated synthetic sweat, Hank's, and in Ringer physiological solutions. The same curves also recorded for Cu–10Al–10Zn and Cu–10Al–10Ni but were not shown. For different alloys and in different solutions, only one anodic peak was observed. From Fig. 2, we can see that the low anodic current peak was recorded in synthetic sweat solution for the different alloys. This due to the lower chloride ion content (*cf.* solutions composition). In chloride-free solution at pH 6.5, this surface layer would consist of Cu_2O , formed according to the reaction [24]:

In solutions containing chloride ions, however, the formation of soluble species is thermodynamically preferred, due to the high stability of copper-chloride complexes. The tendency to form copper-chloride complexes is dominant, it destabilizes the formation of copper oxides, and extends the solubility range of copper in near-neutral solutions to higher pH values and lower potentials [25]. Copper dissolves anodically to form CuCl_2^- complexes according to the following reaction [26]:

The anodic peak thus denotes the formation of Cu_2O directly from Cu metal or by hydrolysis of soluble complexes in the vicinity of the electrode surface [2, 27]:

The formation of a partially protective surface layer leads to the passivation of the surface. In the reverse scan, a

Fig. 2 Cyclic voltammograms at a scan rate 10 mV s^{-1} of Cu–10Ni–10Zn alloy in Hank's (solid line), Ringer's (dashed line), and sweat (dotted line) solutions

Fig. 3 Cyclic voltammograms at a scan rate 10 mVs^{-1} for Cu-10Ni-10Zn alloy in sweat solution at 1 (solid line) and 40 h (dashed line)

cathodic peak appears and is related to the reduction of the surface layer formed in the anodic cycle.

The stability of Cu-10Ni-10Zn alloy in synthetic sweat solution also studied the cyclic voltammetry measurements. Figure 3 shows the cyclic voltammogram of Cu-10Ni-10Zn alloy after immersion for 1 and 40 h in synthetic sweat solution. It was noticed that the shape of the voltammogram did not change remarkably with time. This means that the stability of this alloy was high.

3.2 Potentiodynamic Polarization Curves

Figure 4 presents the potentiodynamic polarization behavior of Cu, Cu-10Al-10Zn, Cu-10Al-10Ni, and Cu-10Ni-10Zn alloys in Hank's solution, Ringer physiological solution, and synthetic sweat solution. The corrosion parameters i.e., corrosion potential, E_{corr} , corrosion current density, i_{corr} , the anodic, β_a and cathodic, β_c , Tafel slopes, and corrosion rate are calculated from polarization data and presented in Table 2. It is obvious that the addition of alloying elements (Al, Zn, and Ni) to Cu shifted the corrosion potential to positive direction in Ringer solutions, while in Hank's and synthetic sweat solution was shifted to negative direction. Also, the results show that the presence of Al and Zn in the Cu matrix did not improve the corrosion resistance of the material. In the contrary, the Cu alloys that contain Ni have higher corrosion resistance than that of Cu itself (cf. Table 2). The addition of Ni to Cu leads to an increase in the corrosion resistance of the alloy, especially in the presence of Zn. The Cu-10Ni-10Zn alloy has shown the lowest corrosion rate, especially in synthetic sweat solution. Oxides of Ni, Zn, and the corrosion products form a compact layer tightly bonded to the alloy

Fig. 4 Potentiodynamic polarization curves recorded for Cu (solid line), Cu-Al-Zn (dashed line), Cu-Al-Ni (dotted line), and Cu-Ni-Zn (dashed dotted line) alloys in Hank's (a), Ringer's (b), and sweat (c) solutions

surface, and so corrosion resistance of Cu-10Ni-10Zn alloy is improved. The remarkable difference in the corrosion current density values of the three different alloys measured under the same conditions means that the composition of the barrier layer formed on the three alloys is not identical. It has been generally accepted that the corrosion of Cu and Cu-based alloys in naturally aerated neutral solutions containing chloride ions involves the cathodic reduction of oxygen [28, 29]. The anodic reaction is the copper dissolution is shown in Eq. 2 [30]. It was suggested that the presence of CuCl_2^- at the metal surface

Table 2 Polarization parameters and rates of corrosion for Cu and the different Cu-ternary alloys in different physiological solutions

Solutions	E_{corr} (mV)	I_{corr} ($\mu\text{A cm}^{-2}$)	β_a (mVdec $^{-1}$)	β_c (mVdec $^{-1}$)	Corr (Rate/ $\mu\text{m y}^{-1}$)
Cu					
Hanks' solution	−389.7	16.9	114.8	−147.5	183.2
Ringer's solution	−684.7	13.6	134	−68.8	127.6
Synthetic sweat	−200.5	15.7	74.1	−158.1	130.2
Cu–10Al–10Zn alloy					
Hanks' solution	−389.7	16.9	114.8	−147.5	183.2
Ringer's solution	−429.3	25.2	100.8	−91.9	297.0
Synthetic sweat	−411.7	13.4	99.1	−109.2	145.7
Cu–10Al–10Ni alloy					
Hanks' solution	−455.6	7.0	150.2	−186.6	82.0
Ringer's solution	−365.1	6.5	93.9	−160.9	75.5
Synthetic sweat	−361.7	5.6	121.6	−140.4	60.8
Cu–10Ni–10Zn alloy					
Hanks' solution	−522.9	3.9	228.5	−119.8	42.3
Ringer's solution	−398.9	3.7	80.3	−78.6	40.6
Synthetic sweat	−358.4	2.5	95.0	−61.6	29.7

leads to a hydrolysis reaction and the formation of Cu_2O [19]. In the ternary, Al-containing alloys an additional passivation process is taking place in neutral solutions in which a layer of Al-oxide is formed as a result of the surface dissolution of Al [30, 31] according to:

Chloride is well-known to initiate pitting corrosion of Al and thereby destroy the passivating properties of the base metal [32, 33]. So, Al was unable to form a protective film on the alloys in the different solutions. Additionally, the presence of chloride ions in solution might enhance the solubility of copper since chloride is a weak complexing agent for the formation of monovalent complexes such as $\text{CuCl}(\text{aq})$, CuCl_2^- , CuCl_2^{2-} but also the divalent complex CuCl^+ . In the Zn-containing alloys, an additional passivation process is taking place due to the formation of Zn-oxide film during a dezincification process according to [34]:

In the presence of Ni, the dissolved nickel ions from alloy dissolution are incorporated into the crystal lattice of Cu_2O that is already formed as a barrier layer. The segregates of Ni into the Cu_2O layer occur via solid-state reaction and the Ni^{2+} interact with the mobile cation vacancies, which lead to a decrease in the ionic conductivity and an increase in the electronic conductivity of the film, and hence the corrosion resistance of the alloy increases [35, 36]. Also,

Dealloying is believed to be greatly dependent on the difference between the standard reversible potentials of major constituent elements, atomic percent composition, and on the kinetics of the solid-state diffusion of the alloyed elements. Dealloying of Cu alloys containing Al and Zn occurs in neutral to lower pH solutions as a result of selective dissolution of Zn and Al, respectively [37]. For dealloying in NaCl, the generally held view is that Cu–Al solid solution is less susceptible to dealloying than Cu–Zn solid solutions [38]. For Cu–Ni alloys, dealloying is more difficult since the difference between the standard reversible potentials for Cu and Ni are much lower and hence dealloying is very limited in this system. The calculated values of the rate of corrosion of the three different alloys in the same solution and under the same conditions show clearly that the Cu–10Ni–10Zn alloy is the most stable alloy in this medium. As presented in Table 2, it seems that the presence of Ni and Zn together in the copper alloy increases the corrosion resistance of the alloy to a large extent.

Figure 5 presents the potentiodynamic polarization curves of Cu–10Ni–10Zn in the Hanks, Ringer, and synthetic sweat solutions. The results show the similarity of the curves, and the corrosion current density of Cu–10Ni–10Zn in Hanks and Ringer solutions is more than that recorded in synthetic sweat solutions. The same trend was also observed with the two alloys. This is due to the concentration of chloride ions in Hank's and Ringer physiological solution, which is almost double in the artificial sweat. When cupronickel is subjected to prolonged anodic

Fig. 5 Potentiodynamic polarization curves of Cu-10Ni-10Zn alloys in Hanks' solution (solid line), Ringer's (dashed line), and sweat (dotted line) solutions

polarization, the dissolution of copper may give rise to CuCl_2^- which in turn becomes Cu_2O . The alloy surface is covered by the film. The copper ion concentration within the film thickness decreases gradually. The migration of monovalent copper ions away from the alloy surface generates cation vacancies [36] as

where $\text{Cu}_{\text{Cu}}(\text{ox})$ is a monovalent copper ion site inside the film; $V'_{\text{Cu}}(\text{ox})$ is vacancy of copper ions. When the electrode is made anodic, the cations move away from the electrode while cation vacancies travel towards it,

Fig. 6 Potentiodynamic polarization curves of Cu-10Ni-10Zn alloys in sweat solution at 1 (solid line) and 40 h (dashed line)

Fig. 7 Bode plots of Cu (filled triangle), Cu-Al-Zn (open square), Cu-Al-Ni (filled circle), and Cu-Ni-Zn (open diamond) alloys after immersion in Hanks' (a), Ringer's (b), and sweat (c) solutions at 37 °C

where $\text{Cu}_{\text{Cu}}(\text{M})$ is the cationic site in the alloy, $V_{\text{Cu}}(\text{M})$ is the vacancy created by the copper cation in the alloy. When nickel dissolution potential is reached, Ni^{2+} ions try to occupy the cation vacancies,

where $\text{Ni}_{\text{Cu}}(\text{ox})$ is the site where nickel divalent cation occupies the vacancy created by copper in the oxide. With the passage of time, outward diffusion of nickel ions occurs

Fig. 8 Nyquist plots of Cu (open square), Cu-10Al-10Zn (filled circle), Cu-10Al-10Ni (open triangle), and Cu-10Ni-10Zn (filled inverted triangle) alloys after immersion in sweat solution at 37 °C. (inset) Equivalent circuit model used for impedance data fitting. R_s solution resistance, R_{ct} charge-transfer resistance, C_{dl} double layer capacitance, R_{pf} passive film resistance, and C_{pf} passive film capacitance

from the alloy/film interface to the inside of the film. This generates additional cation vacancies in the alloy. As the formation of soluble NiCl_2 is more favorable than that of CuCl_2 , nickel ions leave faster from the oxide layer, which in turn generates further vacancies in the film,

Chloride ions adsorb on the surface of the film and try to occupy the vacancies created by the oxygen ions of Cu_2O

[39–42]. The inward diffusion from the solution/film interface inside the film is facilitated by anodic polarization,

As the chloride ion incorporation in the film increases, the number of oxygen vacancies occupied by chloride ions also increases. Chemical stability is decided by the copper and chloride ions ratio in this film.

The effect of immersion time on the stability of Cu-10Ni-10Zn in sweat solution was studied. Figure 6 shows the potentiodynamic polarization of Cu-10Ni-10Zn in sweat solution after 1 and 40 h of immersion. From Fig. 6, it is seen that two curves are the same and the corrosion rate is not changed. This means that the stability of this alloy is higher.

3.3 Electrochemical Impedance Spectroscopy (EIS)

The impedance data of Cu and the different alloys were recorded after alloy immersion in Ringer, sweat, and Hank's solutions and presented as Bode and Nyquist plots. Impedance spectra of Cu, Cu-10Al-10Zn, Cu-10Al-10Ni, and Cu-10Ni-10Zn alloys in three electrolytes at the E_{ocp} are presented as Bode and Nyquist plots in Figs. 7 and 8. It is clear from Fig. 7 that the Cu and the different investigated alloys exhibit different spectra in different solutions. This can be explained by the structural changes or changes in the ionic or electrical conductivity of the surface film. In Ringer, sweat, and Hank's solutions, the impedance spectra of Cu and Cu-10Al-10Zn alloy exhibit one time constant, while Cu-10Al-10Ni and Cu-10Ni-10Zn alloys exhibit two time constants (*cf.* Fig. 8). Those can be divided into

Table 3 Equivalent circuit parameters of the different Cu alloy indifferent physiological solutions

Solutions	R_s (Ω)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	α_1	R_f ($\text{k}\Omega \text{ cm}^2$)	C_f ($\mu\text{F cm}^{-2}$)	α_2
Cu							
Hanks	8.1	94.2	2670	0.96	—	—	—
Ringer	4.5	110.1	72.3	0.98	—	—	—
Synthetic sweat	8.7	122.6	2051	0.99	—	—	—
Cu-10Al-10Zn alloy							
Hanks	13.9	64.1	78.5	0.99	—	—	—
Ringer	9.7	185.7	270.8	0.99	—	—	—
Synthetic sweat	4.8	210.5	477.7	0.86	—	—	—
Cu-10Al-10Ni alloy							
Hanks	9.8	298.6	42.6	0.99	—	—	—
Ringer	12.6	369.7	68.0	0.99	1.7	372.5	1.0
Synthetic sweat	16.2	530.1	12.0	1.0	1.2	1032	1.0
Cu-10Ni-10Zn alloy							
Hanks	10.7	432.3	4.6	0.99	2.7	118.6	0.99
Ringer	13.3	468.6	10.7	0.99	3.1	51.5	0.99
Synthetic sweat	17.9	430.9	23.3	0.99	3.7	431.7	1.0

Fig. 9 SEM micrograph (a) and EDX results (b) of different alloys before electrochemical testing. a, b Cu-10Al-10Zn, c, d Cu-10Al-10Ni, e, f Cu-10Ni-10Zn

two distinct frequency regions: the time constant in the high-frequency part, which arises from the uncompensated ohmic resistance due to the electrolytic solution and the impedance characteristics resulting from the penetration of the electrolyte through a porous film, and the low-frequency part accounting for the processes taking place at the

substrate/electrolyte interface [43]. These behaviors imply the formation of a duplex film with an inner barrier layer and an outer porous layer on the surface of Cu-10Al-10Ni and Cu-10Ni-10Zn alloys. So these observed characteristics may indicate the films formed on these alloys in different solutions were corrosion resistant. While in case of

Fig. 10 SEM micrograph (a) and EDX results (b) of different alloys after immersion in sweat synthetic sweat solution. **a, b** Cu-10Al-10Zn, **c, d** Cu-10Al-10Ni, **e, f** Cu-10Ni-10Zn

Cu and Cu-10Al-10Zn, only one time constant was noticed in different solutions. From Bode phase plot, it can be noted that the phase angle drops toward zero degree at very high-frequency, and in the low-frequency region, it drops slightly again toward lower values; the former

indicated that the impedance is dominated by solution resistance in this frequency range and the latter demonstrated the contribution of surface film resistance to the impedance. It is clear that the Cu-10Ni-10Zn has the highest total impedance and the higher flat phase

maximum indicating its passive behavior [44]. The impedance data were analyzed using software provided with the impedance system where the dispersion formula was used [5, 45, 46]. For a simple equivalent circuit model consisting of a parallel combination of a capacitor, C_{dl} , and a resistor, R_{ct} , in series with a resistor, R_s , representing the solution resistance, the electrode impedance, Z , is represented by the mathematical formulation:

$$Z = R_s + [R_{ct} / \{1 + (2\pi f R_{ct} C_{dl})^\alpha\}], \quad (12)$$

where α denotes an empirical parameter ($0 \leq \alpha \leq 1$) and f is the frequency in Hz [28]. To account for the presence of a passive film, the impedance data were analyzed using the equivalent circuit model shown in Fig. 8 (inset), where another combination R_{pf} C_{pf} represent the passive film resistance, R_{pf} , and the passive film capacitance, C_{pf} , was introduced. The calculated equivalent circuit parameters for the different alloys are presented in Table 3. The passive film resistance, R_{pf} , of Cu–10Ni–10Zn alloy is remarkably, higher than that recorded for the other two alloys. The recorded high corrosion resistance of the Cu–10Ni–10Zn alloy can be attributed to the formation of a uniform passive layer on the alloy surface that is related to the complex metallurgical structure of alloys containing Ni and Zn. The lowest value of the film resistance, which is the highest corrosion rate, was found in Hank's solution and decreased in the following order: Hank's solution < Ringer physiological solution > synthetic sweat solution. The minor corrosion resistance of the different alloys in Hank's solution and Ringer physiological solution might be due to the high concentration of chloride anions, making them aggressive electrolytes. Another noticeable fact is that different alloys exhibited a major resistance to corrosion when immersed in synthetic sweat solution. This is in good agreement with results from the anodic polarization.

3.4 SEM and EDX Analyses

SEM and EDX analyses were used to define the morphology of surface attack and the chemical composition of corrosion products. The morphology of the different Cu-ternary alloy surfaces was investigated before and after 10 h immersion in synthetic sweat solution. Figure 9 presents the SE micrograph and EDAX analyses of mechanically polished Cu-ternary alloys. The SE micrographs for the Cu–10Al–10Zn, Cu–10Al–10Ni, and Cu–10Ni–10Zn alloys after the immersion in synthetic sweat solution are presented in Fig. 10. It turned out that the alloys containing Ni and Zn together possesses smoother surface, with respect to the SE micrograph before the immersion in synthetic sweat solution compared to that containing Al, where the surface becomes roughness and the corrosion sites

increases. Also, the Cu–10Al–10Zn alloys show more pits than the other two alloys indicating the higher corrosion rate of this alloy in synthetic sweat solution. The surface of the three alloys before and after immersion in synthetic sweat solution was subjected to EDAX analysis and the results of these investigations are presented in Figs. 9b, d, f and 10b, d, f. The data of the surface analysis are presented in the same figures. The data obtained reveal that surface of Ni-containing alloys is richer in Ni on the surface.

4 Conclusions

The corrosion rates of Cu, Cu–10Al–10Zn, Cu–10Al–10Ni, and Cu–10Ni–10Zn alloys in Hank's solution and Ringer physiological solutions higher than that recorded in synthetic sweat solution. Addition of Ni decreases the rate of corrosion of the Cu, and the Cu–10Ni–10Zn was found to be the most corrosion-resistant alloy. The EIS results have shown that the film resistance increased in the following order: Hank's solution > Ringer physiological solution > synthetic sweat solution.

Compliance with Ethical Standards

Conflict of Interest No conflict of interest

References

1. Milošev I, Metikoš-Huković M (1997) The behavior of Cu– x Ni ($x = 10$ to 40 wt%) alloys in alkaline solutions containing chloride ions. *Electrochim Acta* 42:1537–1548
2. Ismail KM, Fathi AM, Badawy WA (2004) Effect of the Ni content on the corrosion and passivation behaviours of Cu–Ni alloys in neutral sulphate solutions. *Corrosion* 60:795–803
3. Ismail KM, Fathi AM, Badawy WA (2004) The influence of Ni content on the stability of copper–nickel alloys in alkaline sulfate solutions. *J Appl Electrochem* 34:823–831
4. El-Sherif RM, Ismail KM, Badawy WA (2004) Effect of Zn and Pb as alloying elements on the electrochemical behaviour of brass in NaCl solutions. *Electrochim Acta* 49:5139–5150
5. Badawy WA, Ismail KM, Fathi AM (2005) Effect of Ni content on the corrosion behaviour of Cu–Ni alloys in neutral chloride solutions. *Electrochim Acta* 50:3603–3608
6. Badawy WA, Ismail KM, Fathi AM (2005) Environmentally safe corrosion inhibition of the Cu–Ni alloys in acidic sulfate solutions. *Appl Electrochem* 35:879–888
7. Badawy WA, Ismail KM, Fathi AM (2006) Corrosion control of Cu–Ni alloys in neutral chloride solutions by amino acids. *Electrochim Acta* 51:4182–4189
8. Sharpe PA, Schmidt MG (2011) Control and mitigation of healthcare-acquired infections: designing clinical trials to evaluate new materials and technologies. *J. Health Environ Res Des* 5:94–115
9. Noyce JO, Michels H, Keevil CW (2006) Potential use of copper surfaces to reduce survival of epidemic methicillin-resistant *Staphylococcus aureus* in the healthcare environment. *J Hosp Infect* 63:289–297

10. Mehtar S, Wiid I, Todorov SD (2008) The antimicrobial activity of copper and copper alloys against nosocomial pathogens and mycobacterium tuberculosis isolated from healthcare facilities in the western cape: an in vitro study. *J Hosp Infect* 68:45–51
11. Michels HT, Noyce JP, Wilks SA, Keevil CW (2005) Antimicrobial effects of cast copper alloy surfaces on the bacterium *E. coli* 0157:H7. In: American foundry society transactions, Schaumburg, pp 1–13
12. Weaver L, Michels HT, Keevil CW (2008) Survival of clostridium difficile on copper and steel: futuristic options for hospital hygiene. *J Hosp Infect* 68:145–151
13. Weaver L, Michels HT, Keevil CW (2009) Potential for preventing spread of fungi in air-conditioning systems constructed using copper instead of aluminium. *Lett Appl Microbiol* 50:1–6
14. Burton JL, Pye RJ, Brookes DB (1976) Metal corrosion by chloride in sweat. *Br J Dermatol* 95:417–422
15. Lind SE (1972) Corrosion of metals by human sweat and its prevention. *Corros Sci* 12:749–755
16. Jensen O, Nielsen E (1979) ‘Rusters’. The corrosive action of palmar sweat: II physical and chemical factors in palmar hyperhidrosis. *Acta Derm Venereol* 59:139–143
17. Colin S, Krier G, Jolibois H, Hachimi A, Muller JF, Chambert A (1998) Characterization of the corrosion layer of copper–nickel alloys in a synthetic sweat medium by FTMS and LAMMA laser microprobes. *Appl Surf Sci* 125:29–45
18. Colin S, Beche E, Berjoan R, Jolibois H, Chambert A (1999) An XPS and AES study of the free corrosion of Cu-, Ni-, and Zn-based alloys in synthetic sweat. *Corros Sci* 41:1051–1065
19. Schiffa N, Grosgeata B, Lissaca M, Dalard F (2002) Influence of fluoride content and pH on the corrosion resistance of titanium and its alloys. *Biomaterials* 23:1995–2002
20. British Standard, BS EN 1811:1999 (1999) Reference test method for release of nickel from products intended to come into direct and prolonged contact with the skin, British Standards Institution, London
21. Benedetti AV, Sumodjo PTA, Nobe K, Cabot PL, Proud WG (1995) Electrochemical studies of copper, copper–aluminium and copper–aluminium–silver alloys: impedance results in 0.5 M-NaCl. *Electrochim Acta* 40:2657–2668
22. Otmačić H, Telegdi J, Papp K, Stupnišek-Lisac E (2004) Protective properties of an inhibitor layer formed on copper in neutral chloride solution. *J Appl Electrochem* 34:545–550
23. Zhou Xiao-Zhong, Deng Chu-Ping, Yu-Chang Su (2010) Comparative study on the electrochemical performance of the Cu–30Ni and Cu–20Zn–10Ni alloys. *J Alloy Compd* 491:92–97
24. Bard AJ, Parsons R, Jordan J (eds) (1985) Standard potentials in aqueous solution, IUPAC. Marcel Dekker Inc, New York and Basel
25. Tromans D, Sun R-H (1991) Anodic polarization behavior of copper in aqueous chloride/benzotriazole solutions. *J Electrochem Soc* 138:3235–3244
26. Bacarella AL, Griess JC (1973) The anodic dissolution of copper in flowing sodium chloride solutions between 25 and 175°C. *J Electrochem Soc* 120:459–465
27. Deslouis C, Tribollet B, Mengoli G, Musiani MM (1988) “Electrochemical behaviour of copper in neutral aerated chloride solution. I: steady-state investigation. *J Appl Electrochem* 18:374–383
28. Vazquez MV, de Saez SR, Calvay EJ, Schiffrin DJ (1994) The electrochemical reduction of oxygen on polycrystalline copper. *J Electroanal Chem* 374:189–197
29. Cere S, Vazquez M, de Sanchez SR, Schiffrin DJ (2001) Surface redox catalysis and reduction kinetics of oxygen on copper–nickel alloys. *J Electroanal Chem* 505:118–124
30. Sury P, Otswald HR (1972) On the corrosion behaviour of individual phases present in aluminium bronzes. *Corros Sci* 12:77–80
31. Badawy WA, El-Rabee MM, Hilal NH, Nady H (2010) Effect of nickel content on the electrochemical behavior of Cu–Al–Ni alloys in chloride free neutral solutions. *Electrochim Acta* 56:913–918
32. Wharton JA, Barik RC, Kear G, Wood RJK, Stokes KR, Walsh FC (2005) The corrosion of nickel–aluminium bronze in seawater. *Corros Sci* 47:3336–3367
33. Badawy WA, El-Rabee MM, Nady H (2014) Synergistic effects of alloying elements in Cu-ternary alloys in chloride solutions. *Electrochim Acta* 120:39–45
34. Chen B, Liang C, Fu D, Ren D (2005) Corrosion behavior of Cu and the Cu–Zn–Al shape memory alloy in simulated uterine fluid. *Contraception* 72:221–224
35. Beccaria A-M, Crousier J (1989) Dealloying of Cu–Ni alloys in natural sea water. *Br Corr J* 24:49–52
36. Urquidí M, Macdonald DD (1985) Solute-vacancy interaction model and the effect of minor alloying elements on the initiation of pitting corrosion. *J Electrochem Soc* 132:555–562
37. Alfantazi AM, Ahmed TM, Tromans D (2009) Corrosion behavior of copper alloys in chloride media. *Mater Des* 30:2425–2430
38. Pryor MJ (1983) The dealloying of a Cu–8.9Al solid solution. *J Electrochem Soc* 130:1625–1627
39. Urquidí-Macdonald M, Macdonald DD (1989) Theoretical analysis of the effects of alloying elements on distribution functions of passivity breakdown. *J Electrochem Soc* 136:961–967
40. Chao CY, Lin LF, Macdonald DD (1981) A point defect model for anodic passive films: I. Film growth kinetics. *J Electrochem Soc* 128:1187–1194
41. Lin LF, Chao CY, Macdonald DD, Point A (1981) A point defect model for anodic passive films II. Chemical breakdown and pit initiation. *J Electrochem Soc* 128:1194–1198
42. Macdonald DD, Ben-Haim M, Pallix J (1989) Segregation of alloying elements in passive films. *J Electrochem Soc* 136:3269–3273
43. Souto RM, Laz MM, Reis RL (2003) Degradation characteristics of hydroxyapatite coatings on orthopaedic TiAlV in simulated physiological media investigated by electrochemical impedance spectroscopy. *Biomaterials* 24:4213–4221
44. Metikos-Hukovic M, Babic R, Škugor I, Grušć Z (2011) Copper–nickel alloys modified with thin surface films: corrosion behavior in the presence of chloride ions. *Corros Sci* 53:347–352
45. Badawy WA, El-Sherif RM, Shehata H (2007) Electrochemical behavior of aluminum bronze in sulfate-chloride media. *J Appl Electrochem* 37:1099–1106
46. Badawy WA, Al-Kharafi FM, El-Azab AS (1999) Electrochemical behaviour and corrosion inhibition of Al, Al-6061 and Al–Cu in neutral aqueous solutions. *Corros Sci* 41:709–727