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Impact of oxidation of copper and its alloys in laboratory-simulated conditions on their antimicrobial efficiency

Monika Walkowicz[a,*], Piotr Osuch[a], Beata Smyrak[a], Tadeusz Knych[a], Ewa Rudnik[a], Łukasz Cieniek[b], Anna Różańska[c], Agnieszka Chmielarczyk[c], Dorota Romaniszyn[c], Małgorzata Bulanda[c]

[a] *AGH University of Science and Technology, Faculty of Non-Ferrous Metals, Department of Metal Working and Physical Metallurgy of Non-Ferrous Metals, al. A. Mickiewicza 30, 30-059 Krakow, Poland*
[b] *AGH University of Science and Technology, Faculty of Metals Engineering and Industrial Computer Science, Department of Surface Engineering & Materials Characterisation, al. A. Mickiewicza 30, 30-059 Krakow, Poland*
[c] *Jagiellonian University Medical College, Faculty of Medicine, Department of Microbiology, ul. Czysta 18, 31-121 Krakow, Poland*

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ABSTRACT

Copper and its alloys are known for their antimicrobial activity, which makes them appealing materials for various touch surfaces in public facilities. These materials are also known for being prone to tarnishing, especially in contact with human palm sweat. The paper describes investigations on tarnishing of copper and various copper alloys by oxidation at elevated temperatures. After evaluation of thickness and chemical composition of oxide layers, microbiological tests were carried out in order to determine the impact of oxidation on antimicrobial efficiency of copper alloys.

1. Introduction

Almost 500 types of copper and its alloys have been approved by EPA [1] on the basis of laboratory tests and clinical trials as materials for antimicrobial touch surfaces. The challenge in the application of copper-based materials as touch surfaces is that the most of them are getting covered with corrosive oxide layers when exposed to human palm sweat or disinfecting agents used in healthcare facilities. For this reason, copper alloys that have high corrosion resistance due to the presence of alloy additives (Al, Ni, Zn) are the preferred choice in this type of applications [2]. On the other hand, in several publications [3–5], efficiency of various copper alloys in the elimination of selected bacteria (Gram positive and Gram negative) during microbiological tests, based mainly on JIS Z 2801 standard [6], has been compared. Michels et al. [7] reported that antimicrobial efficiency of copper-based touch surfaces depends mainly on the copper wt. % content in copper alloys. The authors also shown that antimicrobial efficiency is strongly associated with the corrosion resistance of material, concluding that with the increase in the corrosion resistance of copper alloy, the antimicrobial efficiency decreases. This phenomenon can be explained by fewer copper ions present on surface of such alloys. Copper ions [8–11] are responsible for eliminating bacteria by causing disruption of external and/or internal membrane of the bacteria, accumulation of copper ions in bacteria's cell, and in consequence, decomposition of bacteria DNA.

In case of copper alloys containing less noble metals, the oxides of alloying elements can be found in the oxide layer. The composition of the oxide layer very often does not correspond to the share of elements in the alloy. Generally, the less noble metals oxidize easier, hence their content in the surface oxide layer is higher than it could be concluded from the alloy composition. On the other hand corrosion products of copper alloys containing nobler metals contain mainly copper oxides. Depending on the temperature and time of atmospheric oxidation, copper oxide (II) CuO and/or copper (I) oxide Cu_2O are formed on surface of pure copper [12–14]. The composition and thickness of the oxide layer on the copper or its alloys after contact with human sweat or with hospitals disinfectants depends mainly on the chemical composition of metallic material, composition and pH of the solution reacting with the surface, as well as on the temperature and corrosion rate. For example, Fredj et al. [15] reported that after prolonged and repeated contact with a human palm sweat, a film of Cu_2O with thickness of about 50–230 nm on the surface of copper and its alloys

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[*] Corresponding author.

E-mail addresses: monika.walkowicz@agh.edu.pl (M. Walkowicz), piotr.osuch@agh.edu.pl (P. Osuch), smyrak@agh.edu.pl (B. Smyrak), tknych@agh.edu.pl (T. Knych), erudnik@agh.edu.pl (E. Rudnik), lukasz.cieniek@agh.edu.pl (Ł. Cieniek), a.rozanska@uj.edu.pl (A. Różańska), agnieszka.chmielarczyk@uj.edu.pl (A. Chmielarczyk), d.romaniszyn@uj.edu.pl (D. Romaniszyn), malgorzata.bulanda@uj.edu.pl (M. Bulanda).

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Table 1
Compositions (wt. %) of the investigated commercial copper alloys.

Common name	UNS code*	Cu	As	Fe	Mn	Al	Ni	P	Pb	Sb	Si	Sn	Zn
Copper (Cu-ETP)	C11000	99.9	0.0	0.002	0.001	0.0	0.0	0.030	0.002	0.000	0.008	0.0	0.0
Yellow Brass (CuZn37)	C27400	63.2	0.001	0.001	0.001	0.001	0.06	0.001	0.004	0.001	0.008	0.0	36.7
Tin Bronze (CuSn6)	C51900	94.1	0.006	0.001	0.001	0.016	0.01	0.222	0.038	0.001	0.002	5.5	0.1
Nickel silver (CuNi18Zn20)	C75200	63.1	0.001	0.027	0.12	0.001	17.9	0.001	0.001	0.008	0.001	0.001	18.9

was formed. He also showed that the thickness of oxide layer depends on the content of Cu in the alloy, concluding the higher the content of copper in alloy, the thicker the oxide layer is. There are also papers, in which authors utilized various chemical compositions of synthetic sweat for oxidation of copper and its alloys. For example, Harvey et al. [16] used a solution corresponding exactly to the chemical composition of human sweat, and defined its chemical stability. Often composition of synthetic sweat is based on industry standards EN 1811 [17], or ISO 3160 [18], in which synthetic formulas differ in composition, concentration and pH. Milosey et al. [19], showed that for copper alloy 62Cu-18Ni-20Zn (wt%), after 30 days of immersion in artificial sweat, the oxides layer was around 1000 nm thick, and consisted mainly of Cu_2O and ZnO. Colin et al. [20] additionally claim that the layer formed on the surface of copper alloys, in addition to Cu_2O contains also compounds based on Cl, and on alloys with high nickel content also $Ni(OH)_2$ and NiO were found. He also showed that for alloys rich in Cu ($>$ 60%), chloride ions are present in the form of impurities in Cu_2O (copper chloride $CuCl_2$ and CuCl), while for alloys rich in Ni ($>$ 60%), the secondary compound $Cu_2(OH)_3Cl$ was also found. These observations were confirmed by Procaccini et al. [21]. Analysis of corrosive layers formed on surfaces of monetary copper alloys (coper-nickel, nickel brass) as a result of their contact with synthetic sweat, is also the subject of many papers, for example, Elhadiri et al. [22]. From a literature review it can be concluded that the corrosion products of copper in contact with the human palm sweat, are similar to those observed after oxidation at elevated temperatures.

Several authors describe the influence of a corrosion surface layer on antimicrobial effectiveness of copper alloys. For example, Yeh et al. [23] reported that such effects exist. On the other hand, Michels et al. [24] showed that such influence does not exist. It can be concluded that the effect of the surface corrosion on antimicrobial efficiency of copper alloys is still not clear. Hence the purpose of current investigation was to determine the antimicrobial efficiency of copper and selected copper alloys in contact with the bacteria: Staphylococcus Aureus, and *Escherichia* Coli, after atmospheric oxidation in various temperatures. The study includes also characterization of corrosion surface layer by coulometric method, and scanning microscopy.

2. Materials and methodology

2.1. Materials

Commercial, high-purity copper and three representative copper alloys were selected for the study. Table 1 shows a list of materials with chemical composition (in wt. %) and their UNS (Unified Numbering System) code. From metal sheets, tapes or flat bars of copper and copper alloys, samples with dimensions of 0.5 mm x 20 mm x 20 mm were cut out. In order to remove corrosion inhibitor from their surfaces, samples were subjected to mechanical polishing and then chemical polishing in a mixture of concentrated acids: orthophosphoric (V) H_3PO_4, nitric(V) HNO_3, and acetic CH_3COOH, by volume at 3:1:1, at 25 °C. The material was cleaned with acetone in an ultrasonic bath and rinsed in distilled water.

2.2. Heat treatment and cathodic reduction of oxide layers

Atmospheric oxidation in an annealing furnace at the temperatures in the range of 200–600 °C for a duration of 1–60 minutes for ETP copper, and 1–24 h for copper alloys was carried out. The objective was to create superficial layers of copper oxide (I) with a thickness of 50–230 nm. According to Fredj et al. [15] similar layers are formed in contact with human palm sweat during regular use of copper based hardware in real life conditions.

Qualitative and quantitative composition of oxide layers was determined by coulometric method. For the investigations samples were connected to the electrolysis circuit as a cathode (0.785 cm^2 working