Tarnishing and Cu Ion release In Selected Copper-Base Alloys: Implications Towards Anti-Microbial Functionality

H. A. H., B. Indig, K. Williams* and J. R. Scully*
Center for Electrochemical Science and Engineering
Department of Material Science & Engineering
University of Virginia
395 McCormick Road, PO Box 400745, Charlottesville, Virginia, 22904
SAIC, 5971 Kingstowne Village # 410, Alexandria, Virginia, 22315
* nsdk@virginia.edu

Methcillin-resistant staphylococcus aureus (MRSA) is highly contagious and is spread mainly by hand-to-surface contact. In 2005, 94,650 patients in the United States contracted MRSA, and 18,650 of these patients died. MRSA is especially prevalent in hospitals, where patients are infected with MRSA touches surfaces that will, in turn, be touched by other patients whose immune systems may be compromised. This research is related to the goal of minimizing the spread of antibiotic-resistant diseases in hospitals enabled by corrosive release of Cu+ and Cu2+ from copper alloys in solutions such as human perspiration. At the same time it is desirable to maintain color stability on hospital surfaces by minimizing tarnishing. This creates a clearly contradictory situation. For instance, Nordic Gold, exposed in air for one week was still tarnished but not following one week of oxidation in air. However, the most efficacious copper alloys contain significant amounts of Zn, Ni, Al, and/or Sn. For instance, low brass (C24000) with 80% Cu and 19.1% Zn exhibits limited anti-microbial efficacy [4]. Other alloys containing the aforementioned alloying elements exhibit antimicrobial efficacy when freshly abraded but not following one week of oxidation in air. For instance, Nordic Gold, exposed in air for one week after abrasion exhibits limited antimicrobial function. In summary, the copper alloys with the best anti-microbial efficacy are often those that tarnish more readily. Conversely, the most corrosion resistant copper alloys often do not exhibit very good anti-microbial functionality especially when tested long after abrasion when oxide films have reformed.

The goals of this study were to first understanding tarnishing, copper release and color stability in a series of copper alloys. The second goal was to eventually identify a strategy for achieving a balance between optimal release, tarnishing, and antimicrobial function by tuning alloy composition. The first goal will be discussed in this talk.

This study investigated tarnishing, color stability and copper release from C11000 [99.95% Cu], C75200 [64.1% Cu; 18% Ni; 18% Zn; 0.32% Sn; 0.02% Al], Nordic Gold [89% Cu; 4% Al; 1% Sn; 5% Zn], Ecobrass [76% Cu; 12% Pb; 20.9% Zn; 3% Si], C70600 [86.55% Cu; 1% Zn; 1.4% Fe; 1% Mn; 0.05% Pb; 10% Ni], C51000 [94.52% Cu; 0.033% P; 5% Sn; 0.3% Zn; 0.1% Fe; 0.05% Pb], and C26600 [70% Cu; 29.88% Zn; 0.05% Fe; 0.07% P] (all composition in weight percentage). Nordic Gold is the “Euro” coinage material. These copper base alloys were exposed to the following environments: as ground, thermally oxidized in air at 170°C, exposed at OCP in aerated 0.5 M NaOH solution for 24 hours, as well as exposed at OCP in a standardized artificial perspiration solution for 130 hours. Exposed samples were analyzed for copper release, film thickness, tarnish identity, and color stability/reflectivity. A variety of techniques were used including cyclic voltammetry, galvanostatic reduction, optical microscopy and spectrophotometry, glancing angle X-ray diffraction (GXRD), and micro-focused Raman. ICP-OES and rotating ring disk methods were used to examine copper release.

GXRD and Raman spectroscopy showed that after 130 hours in artificial perspiration, Cu2+ and Cu2(OH)2Cl were present on all of the materials. C11000 was not color resistant and a thicker oxide compared to the other materials was found by GXRD and galvanostatic reduction methods. Other materials exhibited thinner oxides as corroborated by GXRD and galvanostatic reduction. Ecobrass was color resistant to thermal oxidation, but not to exposure in 0.5 M NaOH solution nor artificial perspiration. Nordic Gold was partially color resistant to thermal oxidation and sweat, but not resistant after exposure in 0.5 M NaOH solution. C75200 was color resistant after exposure in 0.5 M NaOH solution and thermal exposure, and was also, resistant to artificial perspiration. C51000 was color resistant to 0.5 M NaOH solution and thermal exposure, but was not resistant to artificial perspiration. C26600 was color resistant to thermal oxidation but not resistant to 0.5 M NaOH solution and artificial perspiration.

These results suggest that improved tarnish resistance in these copper alloys is brought about by either Ni or Zn alloying and possibly by Sn additions. Although 65% Cu is required for anti-microbial efficacy, this criterion alone is insufficient to define the details of tarnishing and Cu release tendencies. Nickel is indicated as one of the most effective alloying additions for anti-tarnishing ability in an alloy along with a small amount of Zn, Fe, and Mn (C70600). However, nickel cations were found to be released by corrosion along with Cu.

None of the alloying elements examined drastically suppressed the dissolution rate of Cu upon anodic polarization in artificial perspiration solution. However, Ni and Zn alloying additions suppressed open circuit potentials such that Cu dissolution occurred at lower overpotentials relative to the expected copper oxidation potentials. Thus, one of the roles of Ni and Zn was to retard Cu dissolution and tarnish film thickening during free corrosion by lowering the open circuit potential in artificial perspiration solution.

Ongoing work includes rotating ring disk studies to examine copper release in real time in alloys with both good and poor anti-microbial functionalities. Experiments will also be extended to artificial perspiration solutions containing trace sulfides additions.

Acknowledgements
This work was supported by Mr. James Michel and Dr. Harold Michels of the Copper Development Association. Alloys were supplied by CDA and by Olin Chemical Co. The NSF is thanked for supporting undergraduate researchers. The Zinc Development Association is also thanked for supporting the early stages of this work.

References