RARE METALS

Antibacterial property, corrosion and discoloration resistance of pure copper containing Zn or Ni

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This study focused on the effects of Zn and Ni addition on the antibacterial properties and corrosion resistance of copper alloys. The antimicrobial properties of copper and copper alloys were evaluated using *Escherichia coli ATCC 8739* bacterial strain by employing the overlay and plate counting methods. X-ray photoelectron spectroscopy (XPS) was used to analyze the surface composition of the alloy after contact with bacteria. A salt spray method was used to simulate an artificial sweat contact environment to test the discoloration and corrosion resistance of the alloy, and scanning electron microscopy (SEM) was used to analyze the film layer and surface material composition of the corroded samples. The addition of Ni reduced the antibacterial performance of pure copper; however, the antibacterial performance of the alloy remained fast and

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efficient after the addition of Zn. Moreover, the addition of Zn and Ni significantly improved the corrosion resistance and surface discoloration of copper alloys in artificial sweat environments. This study provided support for the future application of copper alloys as antimicrobial surface-contact materials with safer public and medical environments in the face of diseases spread by large populations.

Several recent public health events worldwide, such as the COVID-19 pandemic, have caused millions of deaths and been detrimental to the safety of human life and the development of the world economy. These events are caused by close contact with pathogens. To provide a healthy and safe environment for human beings, it is critical to develop surface contact materials that yield good antibacterial effects and can control the spread of pathogens [1, 2]. Copper and copper alloys have attracted the attention of researchers due to their natural and efficient bactericidal ability [3–5]. The survival rates of food-borne pathogens and coronaviruses on the surfaces of copper and copper alloys are lower than those of current commonly used contact materials [6–9]. The copper content is generally considered to be the primary determinant of the antimicrobial properties of copper alloys [10–14], but the influence of the composition on the antibacterial properties remains unclear. Recent studies have shown that the antibacterial effects of copper-containing materials are dependent on the release of soluble copper or cupric ions [13–16]. It is widely accepted that free cupric ions generated from redox cycles between different states of copper (i.e., Cu(0), Cu(I), and Cu(II)) play a major role in bacterial inactivation [17–20], further research is required to determine which valence state of copper plays a major role in the deactivation of copper alloys after contact with bacteria for a short period. Additionally, as a surface contact material, copper alloy is used in hospitals and other

crowded environments where there is frequent contact with human skin. Artificial sweat tends to damage the surface of the alloy; this results in corrosion and discoloration at the damaged location that affects the aesthetics and service life of the alloy [21–23]. Therefore, in addition to good antibacterial properties, superior corrosion and discoloration resistance are required to sustain these materials in an artificial sweat environment. Zn and Ni are commonly added elements to copper alloys. Zn is low-cost and exhibits good antibacterial activity [24]; alternatively, Ni can improve the corrosion resistance of copper alloys and is mostly used in the field of marine antifouling. Therefore, in this study, high-purity copper (HPC), Cu-20Zn (wt%), and Cu-20Ni (wt%) samples were prepared to investigate the effects of Zn and Ni addition on the antibacterial properties of pure copper, as well as its corrosion and discoloration resistance to artificial sweat. This study can provide some data support and a theoretical basis for the composition optimization of antibacterial copper alloys for future applications. Photograph of microstructure of experimental alloy is shown in Fig. S1.

The antibacterial properties were evaluated in accordance with JIS/Z 2801–2000 using the *Escherichia coli ATCC 8739* (*E. coli*) strain by employing the overlay and plate counting methods [25]. Figure 1 shows the colony growth diagram and antibacterial rate results for the experimental material after contact with *E. coli* for 15 min. Several bacterial colonies were observed on the blank control, indicating good physiological activity of *E. coli*. No colony growth was detected on the surface of the HPC after the experiment, whereas a small number of colonies were gathered on the surface of Cu-20Zn and Cu-20Ni alloys. The antimicrobial activity of copper was reduced by the addition of Zn and Ni, but the antibacterial rate of the Cu-20Zn alloy was still able to reach 99% in 15 min, indicating strong and rapid bactericidal activity. However, the antibacterial rate of the Cu-20Ni alloy was only 76%. The strong antibacterial properties of the copper metal and Cu-bearing alloys have been widely confirmed; the antibacterial effects are related to the content of the ions released by the copper or the elements added during the process of electrochemical corrosion on the metal surface [26–28]. X-ray photoelectron spectroscopy (XPS) was used to analyze the surface composition of the alloys after contact with the bacteria. As shown in Fig. 2, there was no Cu(II) on the surface of the alloy as indicated by the Cu 2p orbital results; however, Cu(I) and Cu(0) in the Cu 2p orbitals had similar peak shapes, and their existences could not be distinguished from the 2p orbitals alone; thus, we measured the Cu LM2 orbitals. Two peaks with kinetic energies of 916.7–918.8 eV appeared in the auger electron spectrum; this could prove the existence of Cu(I) and Cu(0) on the surfaces of the alloys. The Cu $2p_{3/2}$ orbital fitting
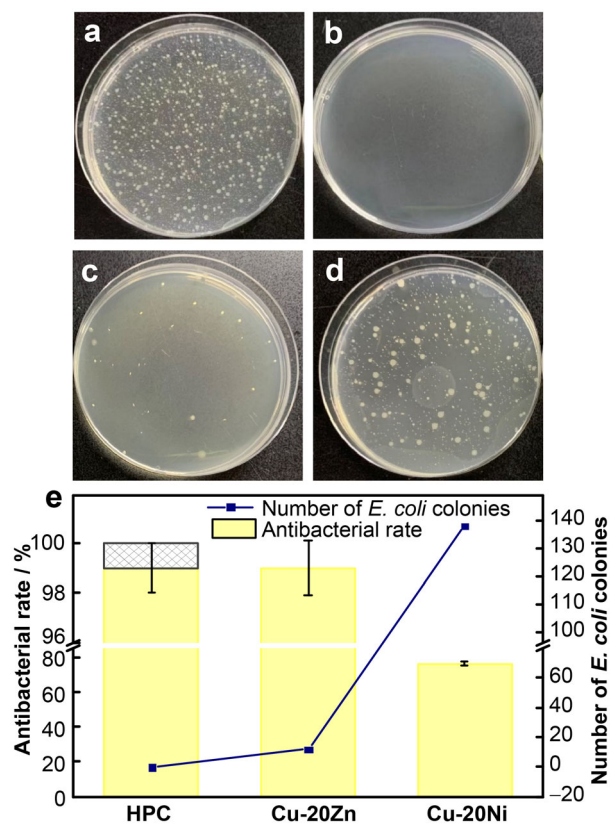

Fig. 1 Typical photographs of colonization by *E. coli* for 15 min of **a** blank group, **b** HPC, **c** Cu-20Zn, **d** Cu-20Ni, **e** antibacterial rate in 15 min (***$p < 0.001$)

results revealed that the binding energies of the materials were ∼ 932.60–932.30 eV, respectively, indicating that Cu(I) existed in Cu_2O. Zn existed in the form of ZnO on the surface of Cu-20Zn, and Ni existed as $Ni(OH)_2$ on the surface of Cu-20Ni. XPS and antibacterial test results revealed that Cu(I) was the main solution released during the period of contact between the copper and bacteria and that the presence of $Ni(OH)_2$ or Ni largely reduced the bacteriostatic effect of copper compared with the presence of ZnO. Utilizing the results of this study and the studies on microorganisms, the dynamic changes of the antibacterial mechanism on the surface of materials were clarified; the reaction process is shown in Fig. 3. The copper alloy underwent an electrochemical corrosion process, releasing positively charged Cu(I) to destroy the bacterial cell wall and enter the bacteria to induce bacterial death [29–31].

The salt spray method was used to simulate an artificial sweat contact environment to test the discoloration and corrosion resistance of the alloy. As shown in Fig. 4, the corrosion rates of the alloys decreased with corrosion time increasing. After 240 h, the corrosion rate of the HPC was the highest, reaching 0.030774 mm·year^{-1}. The addition of Zn and Ni reduced the weight loss rate and improved the corrosion resistance of the HPC. The surface color of copper was
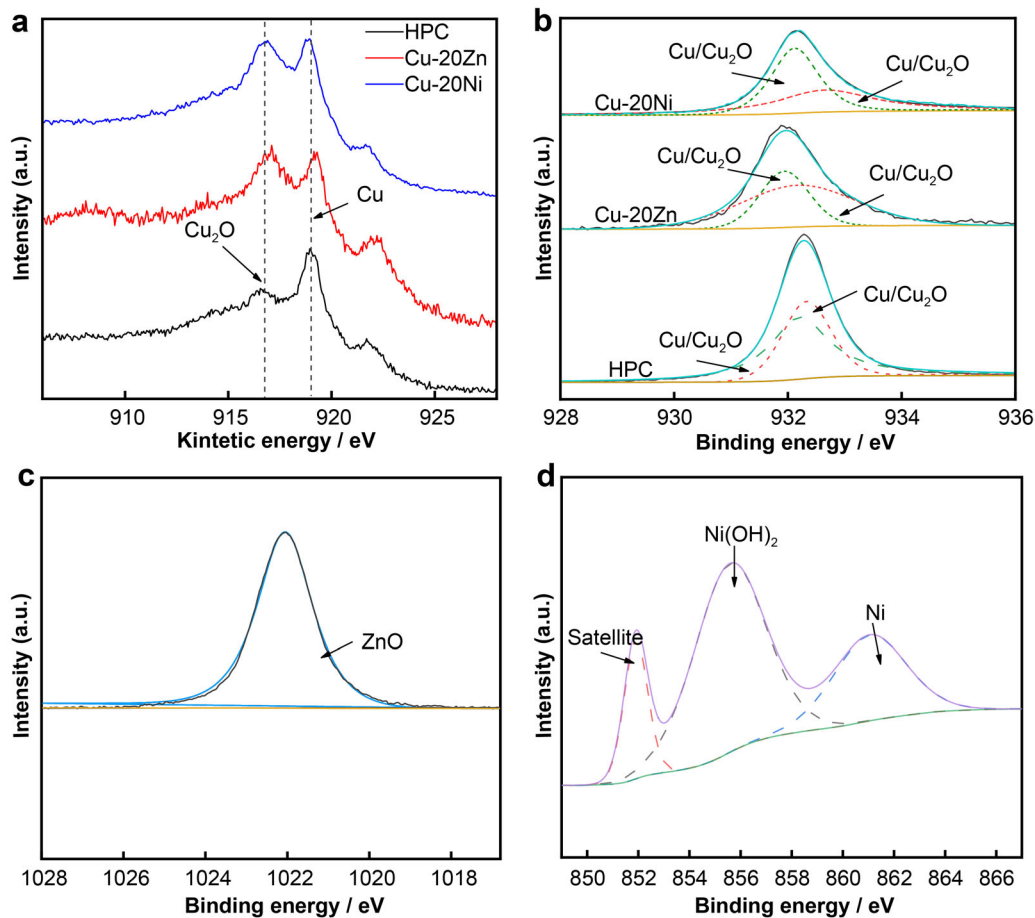
Fig. 2 High-resolution XPS spectra of **a** Cu LMM, **b** Cu 2p$_{3/2}$, **c** Zn 2p$_{3/2}$, and **d** Ni 2p$_{3/2}$
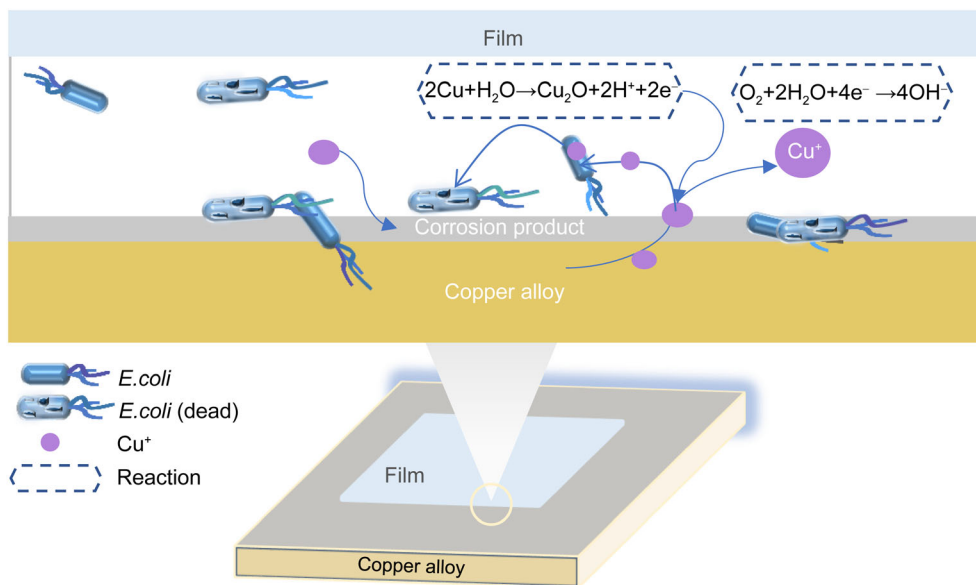

Fig. 3 Simulation of reaction process on surface of alloy during antibacterial action
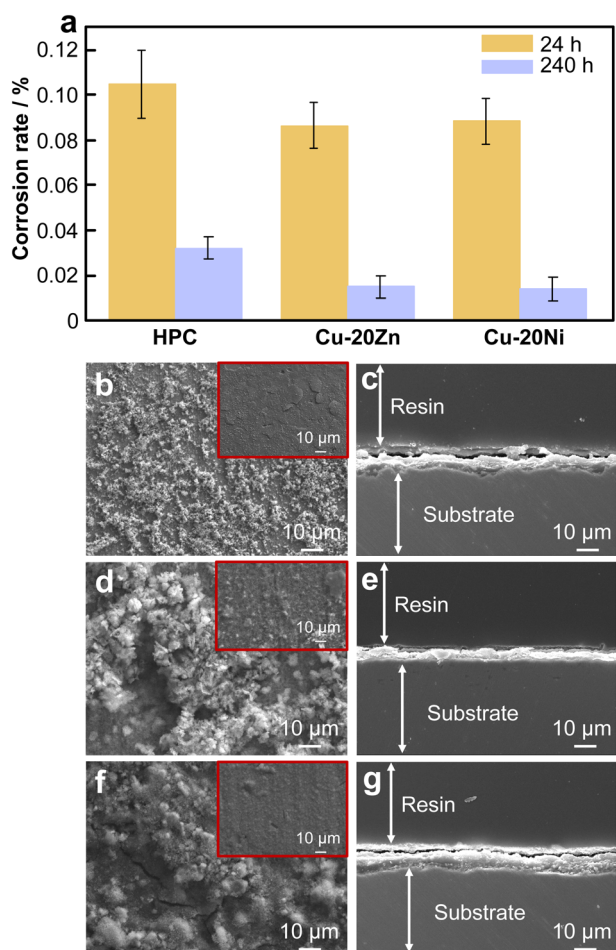
Fig. 4 a Corrosion rate; surface SEM images of b HPC, d Cu-20Zn, and f Cu-20Ni; cross-sectional SEM images of c HPC, e Cu-20Zn, and g Cu-20Ni

Fig. 5 a Color difference value and b discoloration of sample surface

found to be related to the state of the matrix; additionally, with the addition of these elements, the oxide formed after corrosion. Under the conditions of artificial sweat-induced accelerated atmospheric corrosion, the macroscopic surface discoloration results for the alloy after 1, 12 and 24 h were obtained, where ΔE is the change value of color difference before and after corrosion, as shown in Fig. 5. After 1 h corrosion, the surface of the HPC was uniformly corroded and discolored. A small part of the Cu-20Zn alloy was pitted and faded in color. The Cu-20Ni alloy was corroded along the grain boundary, and the corroded areas of all the experimental alloys were darker than the non-corroded areas. As the corrosion process progressed, the number of corrosion products increased, and the color change became more evident. Adding Zn and Ni changed the structure of the samples after corrosion, improving the discoloration resistance of the alloy. Cu_2O was first generated during the copper oxidation process, and other compounds continued to react as the process progressed, leading to a surface color change [32].
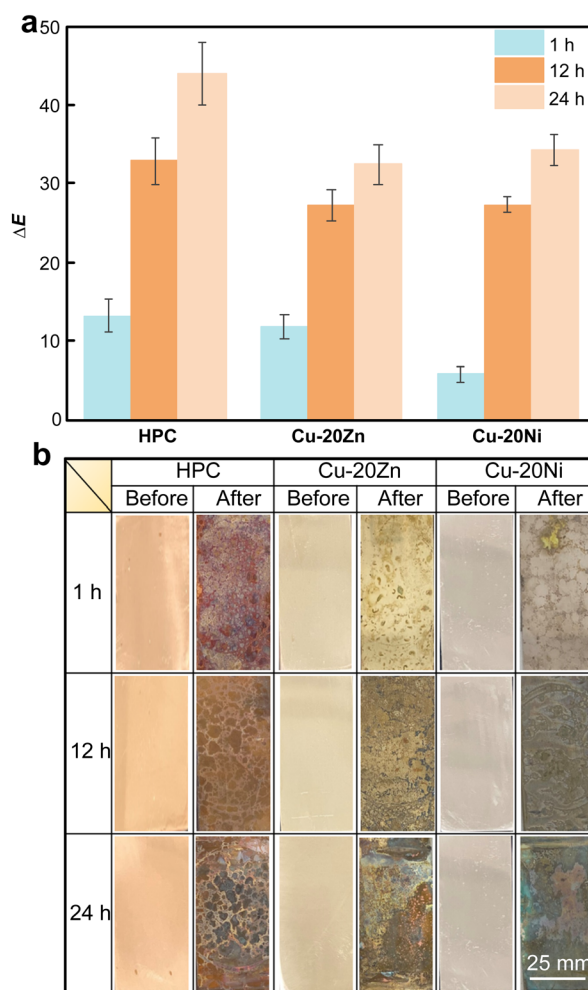
Scanning electron microscopy (SEM) was used to analyze the surface morphologies of the corroded samples. As shown in Fig. 4, the sample surfaces exhibited two morphologies. The top surface was a loose and rough layer, and the lower layer was relatively smooth and flat. However, the HPC surface film cracked and warped, and the corrosion product film was thick and rough. The bottom layers of Cu-20Zn and Cu-20Ni alloys were solid and firm without cracks. Analysis of the cross section of the membrane layer also revealed that the bottom layers of Cu-20Zn and Cu-20Ni were smoother and better integrated into the alloy matrix than HPC. The bottom layer of Cu-20Zn alloy had a honeycomb-like morphology. Cu-20Ni alloy had a dense, uniform film layer with a smooth cross-sectional morphology. The cross sections of the films of the two alloys were relatively flat, indicating that the two alloys had better corrosion resistance than HPC. During the acceleration of the corrosion process, the surface color changed rapidly. However, the addition of Zn and Ni promoted the formation of dense insoluble oxide products on

the surface during the reaction; this protected the surface and improved the corrosion and discoloration resistance.

In summary, we found that copper and copper alloys mainly released Cu(I) during the antibacterial process, significantly contributing to the antibacterial properties. The addition of different elements had varying effects on the antibacterial performance of copper. The antibacterial performance of the alloys remained fast and efficient after the addition of Zn; particularly, the antibacterial rate was maintained at 99% after 15 min contact with *E. coli*. However, the addition of Ni significantly reduced the antibacterial activity of copper, as the antibacterial rate of Cu-20Ni decreased by $\sim$ 24%. The addition of Zn and Ni was found to improve the discoloration and corrosion resistance of copper. The addition of Zn concurrently ensured strong and rapid antibacterial activity and improved the corrosion resistance of copper. Therefore, Zn can be used as the main additive element for antibacterial copper. This study may provide guidance for future composition designs and applications of copper alloys as antibacterial contact surface materials in public spaces.

Declarations

Conflict of interests The authors declare that they have no conflict of interest.

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