Tailor the antibacterial efficiency of copper alloys by oxidation: when to and when not to

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ABSTRACT

Copper and its relevant species, such as oxides and many alloys, have been recognised as potential antibacterial surfaces. Despite the relatively low antibacterial efficacy of cuprous oxide ($\text{Cu}_2\text{O}$) compared to pure copper, it is still worth consideration in some scenarios. Taking copper-nickel co-sputtered thin films with two copper contents (55 and 92 at.%) as examples, this work investigated the potential of oxidation in altering the antibacterial behaviour of copper alloy surfaces. By heat treatment at 200–250 $^\circ\text{C}$ for 20–24 h, a layer mainly composed of $\text{Cu}_2\text{O}$ was successfully fabricated on the top of the Cu-Ni alloys. Antibacterial efficiency against $\text{Escherichia coli}$ in 1 h was obtained by the droplet method and further compared. The coupons with 92 at.% copper became less effective after oxidation: the reduction rate declines from 97.0 to 74.3%; whereas the coupons with 55 at.% copper showed a large increase after oxidation, rising from 15.0 to 66.8%. The experiments described herein reveal a promising concept of oxidation in enhancing the less effective copper alloy surfaces for antibacterial applications.
Introduction

Copper and copper alloys have been extensively investigated in recent years in terms of their antibacterial activity [1–3]. These metallic copper surfaces are excellent candidates in many scenarios, amongst which frequently touched surfaces have been highlighted, as they can be contaminated and further transmit deadly pathogens [4–7]. In our daily lives, antibacterial surfaces installed in public environments such as in transportations and buildings would be extremely helpful since timely cleaning is not always available. For the same reason, there is high expectation and demand in health care facilities, as it could become the decisive factor in combating with healthcare-associated infections (HAIs) that are strongly related to cross-contamination on surfaces.

The knowledge regarding antibacterial mechanisms of copper is being developed, which most of the time, is linked with the ionic copper released from the surfaces. Cuprous ions (Cu⁺) could directly damage enzymes by replacing iron in their iron-sulphur clusters [8] or exhibit antibacterial effect indirectly by forming reactive oxygen species (ROS) [9]. Therefore, the antibacterial efficiency presented by the metallic copper surfaces, to a considerable degree, depends on how efficiently copper ions are released from the surfaces. This efficiency is certainly environment-dependent, for example, it can be evidently enhanced in a relatively corrosive environment in the existence of chloride [10]. Nevertheless, the chemical composition of the surfaces also plays an important role, as some alloying elements are originally designed to reduce the global corrosion tendency [11]. As a result, a phenomenon has been frequently observed on copper alloys: their antibacterial efficiency is poorer than the one of pure copper [12]. A huge range of metallic copper surfaces prepared with antibacterial properties have been assessed, including pure copper [13], Cu-Sn [14], Cu-Ag [15], Cu-Zr [16], Cu-Zr-Ag [17, 18], etc.

In addition to the metallic copper surfaces, copper oxides, regardless of their oxidation state: cupric oxide (CuO) or cuprous oxide (Cu₂O), have both shown antibacterial activity, although usually being considered less effective than pure copper [19–21]. As copper oxides can also release copper ions, even though by dissolution instead of corrosion, they do share similar antibacterial mechanisms as the metallic copper surfaces. Besides, extra amount of ROS could be produced via photocatalytic effect introduced by their semiconductor characteristics [22], assisting the antibacterial process. Copper oxide surfaces with antibacterial activity have been successfully synthesised by various methods, e.g. chemical vapour deposition [20], sputtering [21], wet chemical method...
Apart from depositing an extra oxide layer on the pre-existing objects, such oxides can be obtained by directly transforming the metallic copper surfaces through specific oxidation processes. Several attempts have been recently reported, in order to evaluate the impacts of such sort of oxidation on the metallic copper alloys as well as their antibacterial efficiency [26, 27]. More precisely, it is usually the potential undesirable degradation of antibacterial efficiency that draws the attention of researchers. However, considering that the antibacterial efficiency of copper alloys could actually vary on a quite large scale [1], there might be several copper alloys that own poorer antibacterial efficacy than copper oxides. In these cases, oxidation of these surfaces would not necessarily become an unwelcome phenomenon. Instead, it can be the key to improve the antibacterial activity of those copper alloy surface, meanwhile preserving the advantage of metallurgical processing or mechanical properties introduced by alloying elements.

Consequently, we designed a scenario to verify this hypothesis. Copper-nickel thin films were produced by co-sputtering method, with two different copper contents, representing copper alloys with antibacterial efficiency in two ranges: intrinsically better or worse than Cu2O. These thin films were thermally oxidised, aiming to form a layer of Cu2O on the surface. Their antibacterial efficacy against E. coli was analysed, confirming the potential of this strategy.

Materials and methods

Thin film deposition

Copper-nickel thin films were deposited on microscope glass slides by magnetron co-sputtering technique. Before being transferred into the sputtering chamber, the substrates were cleaned with ethanol in an ultrasonic bath. During deposition, the sputtering pressure was maintained at 0.4 Pa, whilst the flow rate of argon was 50 sccm. The distance between the substrate and the Cu target (2" diameter and 99.99% purity) and Ni target (2" diameter and 99.99% purity) were 59 and 66 mm, respectively. The Cu content was controlled by adjusting the sputtering current of the Cu target by a DC generator (MDX-1.5 K, Advanced Energy): it was 0.20 A for high Cu content coupons (hereafter “High Cu”) and 0.05 A for low Cu content coupons (hereafter “Low Cu”). Sputtering of Ni target was performed with a constant current 0.10 A for both sets, by a pulsed-DC generator (Pinnacle, Advanced Energy), whose frequency and off time were 50 kHz and 4 ms, respectively. The total deposition time was 10 min for the High Cu and 20 min for the Low Cu. These thin films were deposited without intentional heating of the substrate holder.

Heat treatment

Formation of oxides on the above-mentioned thin films were processed in a heating oven (UT 6120, Heraeus). Coupons were placed in the oven at room temperature, and the heat treatment was counted from the time the oven reached the specific temperatures. There were two sets of heat treatment parameters: (1) 200 °C for 20 h and (2) 250 °C for 24 h. At the end of this time, the oven was shut down and the coupons were taken out after the oven reached room temperature. The ventilation of the oven was maintained at the lowest level before the oven was shut down. According to their original copper contents, they are called “High Cu HT” and “Low Cu HT” hereafter.

Solutions

Phosphate-buffered saline (PBS) was prepared using NaH2PO4. 1H2O (Merck, Germany, final concentration 0.01 M), NaCl (VWR, Germany, final concentration 0.14 M) and pure water for analysis, and its pH value was adjusted by adding NaOH to 7.4. It was sterilised after preparation.

Surface characterisation

High resolution grazing incidence X-ray diffractometer (GIXRD, Cu Kα source with a wavelength of 1.54 Å at 1° grazing angle, PANalytical X’Pert PRO-MPD) was used to determine the phases of as-deposited and heat-treated thin films. The following diffraction data are used to index: JCPDS#04-0836 for Cu, JCPDS#75-1531 for Cu2O, and JCPDS#04-0835 for NiO. Different functions of scanning electron microscope (SEM, Helios NanoLab600, FEI) were employed at 5 kV: both Everhart-Thornley detector and Through-the-Lens detector were applied to
examine the top-surface of the coupons, whilst their
global or local chemical composition was obtained by
energy-dispersive X-ray spectroscopy (EDS). Image
classification and analysis was processed with Fiji
[28], with which the “Find Maxima” algorithm was
applied.

Antibacterial efficiency determination

The antibacterial activity on the coupon surface was
tested via the droplet method [29]. E. coli WT K12
(BW25113) strain were grown overnight aerobically
in Lysogeny broth (LB) medium at 37 °C in a water
bath with a speed of 220 rpm. Next day, the bacterial
culture was taken out and centrifuged at 5000 × g to
separate the stationary cells. The centrifugation pro-
cess was repeated three times with PBS using the
same parameters. Finally, the stationary cells were
resuspended in PBS to prepare the bacterial suspen-
sion. Following this, 20 µL of the suspension was
applied on the tested surfaces in the form of droplet.
The test was carried out in a high humid environ-
ment at room temperature for a 1 h duration. At the
end of this time, 10 µL of the suspension was
retreated from the droplet after repetitive pipetting,
then serially diluted in PBS and finally spread on LB
agar plates. The plates were stored in an incubator at
37 °C for 24 h. Finally, the colony-forming units (cfu)
were counted to enumerate the bacteria of the sus-
pension taken. For negative control, the cfu/ml value
from the test on the stainless steel was chosen for the
section “Heat treatment at 200 °C is only successful
for the High Cu” and the original cfu/ml value of the
susension for the section “Heat treatment at 250 °C
turned the Low Cu to Cu2O”. Reduction rate is cal-
culated by dividing the number of deactivated bacte-
ria (i.e. difference of the cfu between the values of
negative control and the values obtained in 1 h) by
the values of negative control.

Results and discussion

Characterisation of as-deposited Copper-
nickel thin films

Prior to investigating the effects of heat treatment, it
is important to understand the features of the as-de-
posited thin films. Figure 1a presents the elemental
analysis of the Cu-Ni co-sputtered thin films
prepared with two currents applied to the Cu target.
In the spectrum obtained from the High Cu, the CuL
peak dominates the X-ray distribution, whilst the NiL
peak can hardly be distinguished. On the other hand,
the NiL peak becomes obvious in the case of the Low
Cu. Quantification of these two elements after ZAF
 correction can be found in the inset: 92 at.% for the
High Cu and 55 at.% for the Low Cu. However, it
must be noticed that, these values may not precisely
represent the actual composition because of the
overlap of these two peaks, especially in the case of
the High Cu (find detailed explanation in SI Fig. 1).

X-ray diffractograms shown in Fig. 1b further
reveal the phase composition of the coupons. The
broad diffraction peaks located from 15 to 40° origi-
nate from the amorphous glass substrate. This peak
was less obvious for the High Cu, simply due to the
greater thickness of the thin film (SI Fig. 2). For the
same reason, the other diffraction peaks that can be
indexed to Cu, are more intense in the diffractogram
of the High Cu. Besides, on the diffractogram of the
Low Cu, shift of the Cu diffraction peaks to higher
angle can be observed as highlighted in the inset.
This phenomenon is associated to the substitution
of Cu atoms by Ni atoms in the fcc solid solution.
Because the metallic Ni atoms is smaller than the Cu
ones, an increase of Ni content leads to a decrease of
the fcc lattice constant, causing a shift towards higher
diffraction angle according to Bragg’s law.

Figure 1c–e further compare the morphology of the
as-deposited thin films. It is clear that a larger grain
size is observed on the High Cu, whereas that shown
on the Low Cu already reaches the limit of resolution
at that operating conditions. For the same reason, the
statistics from image processing indicate a relatively
high fraction in the ultrasmall region, which could
come from the inevitable error introduced by the
blurry boundaries. The discrepancy of two thin films
could be attributed to the thickness, i.e. the growth
process of thin films, where the Low Cu could be
closer to its nucleation regime and therefore with a
finer microstructure.

To conclude, the Cu content is not the sole differ-
ence existing between two set of Cu-Ni thin films.
However, it can be seen from the following sections
that the influence of other parameters is not con-
cerning in the present study.
Heat treatment at 200 °C is only successful for the High Cu

Heat treatment in ambient atmosphere at 200 °C has been demonstrated to form a layer of Cu₂O on top of pure Cu samples [19]. As a result, heat treatment at this temperature was firstly applied on Cu-Ni co-sputtered thin films, aiming to oxidise their outermost part and to obtain a layer mainly composed of Cu₂O.

Phase analysis of the heat-treated thin films can be found in Fig. 2a. For the High Cu HT, heat treatment introduces three extra and distinct peaks in its diffractogram, namely the (110), (111), and (220) diffraction peaks of Cu₂O. However, it has to be admitted that the formation of nickel oxide (NiO) should not be ruled out, based on the greater affinity of Ni atoms for oxygen [30]. The fact that it is hardly detectable can be attributed to the low Ni concentration in the alloy.

On the other hand, the attempt to form Cu₂O on the Low Cu HT seems to be unsuccessful: no additional diffraction peaks can be identified clearly or indexed to Cu₂O (or NiO). The reason why the current heat treatment parameters might not be effective enough to form an observable amount of Cu₂O could be associated with the addition of Ni. Previous research performed at elevated temperature (around...
450 °C) has observed a prolonged nucleation period for Cu₂O as the concentration of Ni rises in the low copper content regime [31]. In addition, in both cases, the diffraction peaks from Cu can still be easily recorded, meaning that a substantial portion of these heat-treated thin films is still in the unreacted metallic state. These Cu diffraction peaks exhibit a shift to higher angle. As discussed in the above section, the shift of these metallic diffraction peaks corresponds to the shrinkage of fcc lattice. It is true that annealing tends to enhance diffusion, remove defects, improve the crystallinity, and thus results in relaxation of the internal stress. But if the shrinkage of glass substrate

Figure 2 High resolution GIXRD results (a) of 200 °C heat-treated coupons (“High Cu HT” and “Low Cu HT”) and their original as-deposited coupons (“High Cu” and “Low Cu” that have been shown in Fig. 1) for comparison. Cu₂O (JCPDS#75-1531) was applied to index the additional peaks. Enlarged spectra at the right side compare the positions of (111) and (200) diffractions with pure copper (JCPDS#04-0836). Representative SEM image (b) and high resolution SEM images (c, d) of two different regions found on the High Cu HT. EDS spectra (e) were collected from the regions that marked by squares in (b), with inset indicating the average quantitative results based on the data shown in SI Fig. 3. The label of Ni is marked with star in order to remind the readers of the likely overlap between NiL and CuL.
due to annealing is more significant than that of thin films, then an external compressive state would still be introduced on the thin films. Alternatively, this compressive state can be related to the formation of oxides. The Pilling–Bedworth ratio of Cu$_2$O and NiO are both greater than 1, implying that an increase in volume is expected once Cu or Ni transforms to its oxide. It could therefore introduce compressive stress to the unreacted metallic thin films.

Although the formation of Cu$_2$O on the High Cu HT was successful, interestingly, the oxidation is not homogeneous. Figure 2b–e compare the evident morphological features: there are some (mostly round) regions owning coarser and upheaved particles, whereas the other regions are finer and flatter. Besides, stronger X-ray signal of oxygen can be found in the former region, representing the formation of thicker or denser oxide. It has to be noted that the atomic percentages calculated (as well as those to be shown in the following section) do not represent the chemical composition of any phases in any regions. This is because the X-ray signal could originate from both the oxide layer and the underneath co-sputtered thin films, and it therefore does not satisfy the premise of quantification under ZAF correction. Although these micron-scale features are not going to be further discussed with the global antibacterial activity, recent studies from different research groups did imply their possible roles in assisting bacteria deactivation [32, 33].

As for the antibacterial behaviour, previous studies have shown the significant effect of oxide formation on pure copper surfaces [19, 27]. Similar tests were now conducted on both Cu-Ni thin films, both the as-deposited state and the heat-treated state. Figure 3 shows the survival and reduction rate of E. coli after 1 h contact time compared to stainless steel. The results show that the High Cu killed bacteria most efficiently (96.8%), whilst its heat-treated state, the High Cu HT became less efficient (77.9%). This can be attributed to the formation of Cu$_2$O on the High Cu HT: the intrinsic antibacterial efficiency of the High Cu is higher than that of Cu$_2$O, thus the oxide coverage on the surface compromises the antibacterial behaviour.

The Low Cu, on the other hand, exhibits a relatively poor antibacterial efficacy: the reduction rate increases from 33.7% to 44.2% after heat treatment. This could be a neglectable enhance, given that the standard deviations are relatively huge. This can be attributed to the insufficient oxidation of the surface: if the surface was completely transformed into Cu$_2$O only (as in the case of the High Cu HT), then an antibacterial efficiency or reduction rate similar to the High Cu HT should have been observed. That being said, other modifications in terms of microstructural or surface properties introduced by the thermal oxidation process (i.e. annealing process) could also contribute to this neglectable change in antibacterial efficiency. To sum up, it is still necessary to find another approach that can lead to a sufficient Cu$_2$O formation on the Low Cu, in order to accomplish verification of the concept proposed.

**Heat treatment at 250 °C turned the Low Cu to Cu$_2$O**

Since the heat treatment parameters described in the above section failed to oxidise the Low Cu (even with prolonged period, see SI Fig. 4), thermal oxidation at a slightly high temperature (250 °C) was proceeded as it often increases the tendency to form oxides [34, 35], meanwhile avoiding the formation of less-desirable CuO [36]. Although it is unnecessary to carry out this heat treatment on the High Cu (as the designed Cu$_2$O was already obtained at 200 °C and served its purpose), it was still included here for better comparison.

The diffractograms in Fig. 4a demonstrate the efficacy of this heat treatment at 250 °C on both coupons. Cu$_2$O oxide still dominates the oxide species formed on the High Cu HT, but most excitingly, the very same oxide finally appears on the Low Cu HT. Additionally, a relatively tiny and broad diffraction peak was recorded and can be assigned to (220) diffraction of NiO. And again, such an annealing process introduces a shift of Cu diffraction peaks to higher angle for similar reasons discussed in the previous section.

Similarly, Fig. 4b–d show the localised strong oxidation phenomenon observed on the Low Cu HT (and the High Cu HT as well, see SI Fig. 6). The regions outside are also oxidised, but less in amount. Since in the case of the Low Cu HT, X-ray radiation of CuL and NiL can be easily differentiated, it is thus clear that a drop of NiL intensity can be recognised inside the strong oxidation regions. This revealed the preferred oxidation of Cu in these regions.

Regarding the antibacterial behaviour shown in Fig. 5, similar to the results in the previous section,
the High Cu shows the best antibacterial efficiency (97.0%) amongst the tested coupons, whilst the High Cu HT endures a decrease (to 74.3%) due to surface oxidation. On the other hand, unlike the heat treatment at 200°C/176°C, the number of surviving bacteria on the Low Cu HT decreases significantly this time. The reduction rate thus mounts from 15.0% to 66.8%, which is very close to that obtained from the High Cu HT. This trend is exactly as expected, as it reflects the successful Cu₂O formation on the surface of the Low Cu HT, which thus should show a comparable antibacterial efficiency as the High Cu HT. Formation of NiO could be a contributory factor of the slight difference between two heat-treated coupons, because it has not been considered to share comparable antibacterial property as Cu₂O. Besides, the antibacterial efficiency of the heat-treated coupons from this study and the sputtered Cu₂O coating (around 50% in 1 h) from our previous study [21] are just comparable but not entirely identical. This once again suggests that the antibacterial property does not depend on chemical/phase composition only, but possibly also on the minor effects of the microstructural or surface parameters, which may still require further investigation.

It is true that there are some discrepancies compared to the reduction rates obtained in the first heat treatment trial, e.g. the same Low Cu showed only 15% in this trial but 33.7% in the first trial. This could be introduced by the selection of the negative control (stainless steel or the original suspension), or the possible difference in the original concentration of the bacterial suspension [37, 38], etc. The slight decrease obtained from the High Cu HT (74.3% in this trial but 77.9% in the first trial) could be attributed to the same reason, or other slight intrinsic differences between two High Cu HT surfaces. Nevertheless, none of these affects the concept to be verified: oxidation on certain metallic copper alloy surfaces can truly improve their antibacterial efficiency.

**Discussion on this promising strategy and practical insights**

From the above comparison, it is clear that oxidation opens a powerful and simple pathway to tailor the antibacterial performance of the metallic copper alloy surfaces. This is summarised in Fig. 6, where antibacterial efficiency of pure copper and Cu₂O are set as benchmarks. For the alloys that already show a better reduction rate than Cu₂O (grouped as “Copper Alloys Type I”), oxidation should be avoided as it impairs their intrinsic antibacterial efficiency, although whether it can be effectively avoided is another issue. On the contrary, for those intrinsically less potent than Cu₂O (grouped as “Copper Alloys Type II”), measures that lead to surface oxidation should be considered. By transforming the metallic surfaces into Cu₂O, their antibacterial efficiency can be replaced by that of Cu₂O.
It should be noted that, although in the present work, Copper Alloys Type I is represented by the High Cu whilst Copper Alloys Type II by the Low Cu, alloys with relatively lower copper contents do not necessarily always exhibit a poorer antibacterial efficacy \([26, 39]\). In other words, whether to oxidise an alloy or not should rely on its intrinsic antibacterial efficiency (which can be measured from trials), but not simply on its chemical composition (e.g. how high the copper content is).

The proof of concept presented in this work was accomplished by Cu-Ni co-sputtered thin films, because sputtering is without a doubt one of the most effective and effortless methods to obtain a defined...
surface with certain chemical composition or crystallinity. Many recent studies have applied this method to design functional surfaces and explored their antibacterial potentials [14, 17, 18]. But the very same idea is certainly applicable or even more meaningful in bulk copper alloys that can be fabricated in conventional metallurgical ways, no matter whether it is with commercial alloying elements or newly developed compositions [40, 41]. Its adaptability to a wide range of existing commercial copper alloys is worth being emphasised in the future studies.

Meanwhile, exclusive formation of Cu$_2$O could be a challenge, just like the formation of NiO on the Low Cu HT shown in this study. One could also imagine as more/different alloying elements are included, undesirable by-products could form during oxidation process [42], undermining the coverage of antibacterial Cu$_2$O or even suppressing its formation. Extensive investigation is thus needed in the selection of alloy composition in each applying scenario, even though coexistence of oxides might be inevitable subject to the oxygen affinity. Suitable temperature (as already shown in the present work) together with ambience composition might be two important parameters in guiding a desirable oxidation process. Nevertheless, apart from thermal oxidation, there are also other feasible approaches to introduce oxide that might be adapted accordingly, e.g. anodic oxidation [43] or laser surface treatment [32, 44, 45].

No matter which oxidation method is selected, there are other features of the oxidised layer that are essential to application and therefore should also be examined if possible. One of them is the horizontal homogeneity of oxidation. Localised strong oxidation spots that are observed in this work, however, did not introduce too much concern in antibacterial efficiency test, as it actually represents inhomogeneity in depth whilst the droplet method for 1 h is an evaluation based on the global antibacterial performance of the outermost surface in short term. Moreover, only if the amount of copper released into the droplet is sufficient to deactivate the microbes, the locations where release occurs could be less important. But this may not always suit the actual scenarios: there might be no aqueous environment covering the entire surface, and therefore it is important to ensure every position that is contaminated by microbes can present equally excellent antibacterial effect. In addition to chemical composition, homogeneity could be required in other aspects such as microstructure and micro/nano-roughness. To better investigate the localised antibacterial behaviour, recently developed tests with dry or quasi-dry inoculum [46, 47] are certainly important alternatives.

On the other hand, inhomogeneity in depth, namely the effective oxidation depth is still an important variable. Usually, one advantage of applying copper and its alloys in daily touched surfaces is their quasi self-healing properties: abrasion-corrosion introduced by touching or cleaning [48].
could help releasing the topmost layer as well as the adhered microbes. This exposes the “new” surface underneath, maintaining the similar antibacterial efficacy. However, when surface oxidation is applied, the desired antibacterial effect only exists in the oxidised part, meaning within a certain depth. It is therefore important to evaluate the loss rate of the oxides in each specific circumstance in order to determine the desired depth of oxidation for an aimed lifespan. Along with this perspective, adhesion of the oxidised layer should be assessed or improved when necessary, since weak adhesion might cause early failure of the antibacterial layer.

Furthermore, adoption of oxidation strategy also shifts the mechanism of antibacterial copper ion release: from corrosion of the original metallic phases [49] to dissolution of Cu₂O [21], which can be influenced by temperature, pH value, etc. [50]. As a result, specifying the environmental factors in the evaluations will ensure much applicable implication and persuasive conclusion. Given that the outermost surface will be oxidised on purpose, the deterioration induced by atmospheric corrosion might not be as troublesome as that on the metallic copper surfaces [10, 42], but it could still be worthwhile tracking the stability of the oxidised surface, e.g. together with daily disinfection events [51].

Last but not the least, although it was only the antibacterial efficiency against *E. coli* that was investigated in the present study, copper surfaces have actually shown capability against a very broad range of bacteria [3, 7, 52], viruses [53–55], and fungi [25, 52, 56]. Therefore, the strategy proposed here is also encouraging in many scenarios where the general antimicrobial property is needed.

**Conclusion**

Thermal oxidation of Cu-Ni co-sputtered thin films are served as examples to illustrate the potential roles of oxidation on antibacterial copper alloy surfaces. Some concluding remarks are listed as follows:

- Critical oxidation temperature depends on the copper content of the thin films. To form a layer of Cu₂O on the surface in 20–24 h, thin films with higher copper content (92 at.%) require only 200°C, whilst a relatively higher temperature (250°C) is required for those with lower copper content (55 at.%).
- Although the atomic percentage of oxygen increased globally, some relatively strongly oxidised regions are found on both oxidised thin films, together with distinct sub-micron topography.
- Successful oxidation of the investigated thin films introduces dramatic changes in their antibacterial performance against *E. coli* evaluated by the droplet method: the high copper content thin films get degraded (reduction rate in 1 h declines from 97.0% to 74.3%) whilst the low copper
content ones get significantly improved (from 15.0% to 66.8%).

- The concept of enhancing antibacterial efficiency of less effective copper alloy surfaces by means of surface oxidation is verified.

Acknowledgements

The authors would like to thank Johannes Webel for the meaningful introduction in SEM image classification, and Dr. Christoph Pauly for constructive discussion in interpretation of EDS results.

Author contribution

JL contributed to conceptualization, investigation, validation, visualization, and writing – original draft. AA contributed to investigation, validation, visualization, and writing – original draft. J-FP contributed to funding acquisition, resources, supervision, and writing – review and editing. FM contributed to funding acquisition, resources, and supervision.

Funding

This study was supported by Erasmus Mundus Joint European Doctoral Programme in Advanced Materials Science and Engineering (DocMASE, 512225-1-2010-1-DE-EMJD, European Commission) and the PhD-Track-Programme (PhD02-14, Franco-German University). A.A. has been funded by the German Aerospace Center—Space Administration (DLR) within the project “Investigation of antimicrobial metal surfaces under space conditions—An effective strategy to prevent microbial biofilm formation” (Project Number 50WB1930), and German Research Foundation (DFG) within the project “Controlled bacterial interaction to increase the antimicrobial efficiency of copper surfaces” (Project Number 415956642). Open Access funding enabled and organized by Projekt DEAL.

Data availability

The data that support the findings of this study are available from the corresponding author on request.

Declarations

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

Supplementary Information: The online version contains supplementary material available at http://doi.org/10.1007/s10853-022-06879-5.

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