The Effect of Corrosion Conditions on Aging of Artificial Patina on Three Bronzes

Angela Kapitanović and Helena Otmačić Ćurković *

Research Laboratory for Corrosion Engineering and Surface Protection, Faculty of Chemical Engineering and Technology, University of Zagreb, HR 10000 Zagreb, Croatia; akapitano@fkit.hr
* Correspondence: helena.otmacic@fkit.hr

Abstract: The new bronze objects of art are almost always patinated before their exposure outdoors or indoors. Among the many patination methods used by practitioners, sulphide patination is one of the most common techniques. The aim of this work is to examine the corrosion behaviour of sulphide patinated bronzes under various aging conditions, including continuous immersion in simulated urban rain, alternating wet/dry cycles, and exposure to corrosion chamber with NO₂ gas. The study was conducted on three types of bronzes with varying tin content. Corrosion characterisation of patinated bronze samples was performed by the means of electrochemical impedance spectroscopy and polarization measurements. Chemical composition and morphology of sulphide patinated bronze surface was examined by infrared spectroscopy and scanning electron microscopy. Obtained results show that freshly patinated bronze surfaces exhibit low corrosion resistance that gradually improves over time. An increase in corrosion resistance strongly depends on aging conditions, and it appears to be the highest under continuous immersion conditions.

Keywords: artificial patina; bronze; corrosion resistance; electrochemical measurements

1. Introduction

Copper and bronze objects exposed to outdoor environments gradually become covered by a layer of corrosion product—patina. In the case of artistic or historical objects, the patina is considered to have an aesthetic value, which is why it is usually conserved together with the underlying bronze or copper. The colour of the patina depends on aging time and factors such as the presence of different pollutants and climatic conditions [1,2]. For new artistic objects made of bronze, it is general practice to conduct artificial patination prior to their exposure outdoors or indoors. In this way, a patina layer is formed that resembles the natural patina layer formed during prolonged exposure (several years) to the environment.

In Croatia, as well as in many other countries in the world, patination is often carried out with a sulphide solution, resulting in the formation of a dark or brown patina which resembles bronze covered by a layer of CuO. Sometimes, this patina is further treated with other chemical solutions to obtain an additional green or bluish layer of patina. Artificially patinated objects are then covered with a wax or varnish layer for corrosion protection [3,4]. Unfortunately, such coatings, which comply with the requirement of conservation ethics to be reversible and not change the appearance of the surface, do not provide long-term protection. With time, patinated bronze surfaces will become exposed to the environment. For that reason, it is important to perform corrosion studies on patinated bronzes in order to determine their corrosion resistance.

Many researchers have studied the formation of patina on bare bronze under various aging conditions, simulating processes that occur during outdoor exposure [5–8]. In addition, studies have been conducted on real artistic or historical objects covered by a decades- or centuries-old patina [9–12]. However, studies on freshly patinated bronzes...
are mainly conducted with the aim to evaluate different coatings used for their protection [3,13,14]. Very few studies are focused on examination of such patinated bronzes and their transformation during exposure to a corrosive environment. Furthermore, such studies mainly focus on green patinas and their spectroscopic characterization [15–19]. Kosec et al. performed Raman studies of artificial patinas on recent bronzes [15,16]. Among other types of artificial patinas, the brown sulphide patina was examined before and after 35-day exposure to urban acid rain [16] and after 12-week exposure to a climatic chamber with \( \text{SO}_2 \) and salt spraying [15]. Exposure to corrosive conditions in the climatic chamber led to significant changes in the appearance of the patina, which turned from brown to green. Spectroscopic investigation showed that the patina initially consisted of copper sulphide and some cuprite \((\text{Cu}_2\text{O})\), while chloride minerals were formed after 12 weeks, as well as some brochantite [15]. Exposure to urban acid rain led to transformation to a dark green-coloured patina composed of \( \text{Cu}_2\text{O} \), \( \text{SnO}_2 \), and copper hydroxyl sulphates, namely brochantite [16]. These results show that brown patina is very reactive and can undergo significant transformations when exposed to a corrosive environment. Moreover, sulphides are known to enhance corrosion of copper and its alloys [20]. Thus, further studies are needed in order to better understand the behaviour of freshly sulphide patinated bronze in various environments.

The aim of this work is to examine the aging of sulphide patinated bronzes under various conditions simulating an urban outdoor environment. The studies were conducted in a simulated urban rain solution with pH 5 (simulating acid rain) and pH 6 (simulating less aggressive urban rain). Patinated bronze aging was conducted either by continuous immersion or by alternating wet/drying cycles. Additionally, samples were aged in a corrosion chamber into which \( \text{NO}_2 \) (a corrosive pollutant typical of urban atmospheres) was introduced.

Our additional aim was to determine whether the bronze composition has an important influence on the stability of the sulphide patina. Tin is considered to have an important influence on bronze corrosion resistance [21]; as such, in this work, three types of bronze with different tin contents were examined. Two of these have been commonly used for recent sculptures in Croatia (CuSn6 and RG7); the third one has a higher tin content (CuSn12).

2. Materials and Methods

2.1. Sample Preparation

Experiments were performed on three kinds of bronze (CuSn6 (Cu 94%, Sn 6%), RG7 (Cu 83.25%, Sn 5.6%, Zn 4.58, Pb 5.85%) and CuSn12 (Cu 87.94%, Sn 11.02%, Zn 0.07%, Pb 0.54%)), received from Strojopromet Ltd., Zagreb, Croatia. The bronze was cut into 0.5 cm thick discs with upper surface 1.5 cm\(^2\) for CuSn6 and 1.33 cm\(^2\) for RG7 and CuSn12 bronze. On part of the samples, a copper wire was soldered and discs were embedded into an epoxy resin in order to serve as electrodes for electrochemical measurements. The rest was used for spectroscopic characterization. The bronze samples were polished with 80, 800, 1200, 2500 grade SiC paper; afterwards, they were degreased with ethanol in an ultrasonic bath and then rinsed with deionized water.

In order to obtain a brown sulphide patina, the bronze samples were preheated at 80 \(^\circ\)C. Hot samples were immersed for a minute in \( \text{K}_2\text{S}_2 \) solution in distilled water (1.25 g/50 mL), heated to 80 \(^\circ\)C [22]. Afterwards, the samples were washed with tap water and gently polished with a sponge in order to remove loosely attached patina. This procedure was repeated until the formation of stable patina. In principle, it was necessary to repeat the procedure three times. After preparation, the samples were left to dry for two days before further studies.

2.2. Sample Aging

The sulphide patinated samples were exposed to different forms of accelerated aging:
1. Continuous immersion in artificial urban acid rainwater with pH 5 (0.2 g/L Na₂SO₄, 0.2 g/L NaHCO₃, and 0.2 g/L NaNO₃ in redistilled water, with pH adjusted by 0.5 M H₂SO₄).
2. Continuous immersion in artificial urban rainwater with pH 6.5 (the same rainwater composition as above).
3. Alternating wet/dry cycles with wet cycles consisting of immersion in acid rainwater (pH 5).
4. Alternating wet/dry cycles with wet cycles consisting of immersion in acid rainwater (pH 6.5).

In the case of alternating wet/dry cycles, the samples were immersed in the solution for one hour and then left to dry for three days.
5. Accelerated aging was performed in a corrosion chamber with NO₂ for 14 days.

Aging was conducted in the corrosion chamber CON 300-FLAIR CWC KES (VLM GmbH, Bielefeld, Germany) with alternating wet (8 h at 40 °C) and dry (16 h at room temperature) cycles. One hour prior to wet cycles, NO₂ was evolved in the chamber by a reaction of 1.1 mg of copper and 100 µL of 14 M HNO₃ acid. The maximum obtained level of NO₂ was 1.4 ppm. The procedure for NO₂ evolution was developed according to the study of Dorhout et al. [23]. After each dry period, the corrosion chamber was completely aerated.

The summary of the aging procedures used is shown in Table 1.

### Table 1. Summary of aging conditions for sulphide patinated bronzes.

| Forms of Accelerated Aging | Corrosive Medium | Wetting Conditions | Dry Conditions | Total Duration |
|----------------------------|------------------|--------------------|---------------|---------------|
| Continuous immersion       | (1) Acid rain, pH 5  
(2) Urban rain, pH 6.5 | Immersion for 21 days | -             | 21 days       |
| Alternating wet/dry cycles | (3) Acid rain, pH 5  
(4) Urban rain, pH 6.5 | Immersion for 1 h  
3 days at room atmosphere | 18 days (6 cycles) |               |
| Corrosion chamber          | (5) 1.4 ppm NO₂, 1 h  
before wetting | 8 h at 40 °C, 100% humidity  
16 h at 24 °C | 14 days (14 cycles) |               |

2.3. Electrochemical Measurements

Electrochemical studies were performed by electrochemical impedance spectroscopy (EIS) and polarization measurements using a Bio-Logic SP-300 potentiostat (Bio-Logic, Seyssinet-Pariset, France). Measurements were conducted either in simulated acid rain at pH 5 (for samples described under points 1 and 3) or in simulated rain at pH 6.5 (for samples 2, 4 and 5). A conventional three-electrode electrochemical cell (~100 mL electrolyte volume) was used, where the sample was set as the working electrode while a saturated calomel electrode (SCE) and a Pt plate were used as the reference and counter electrodes, respectively. The cell was open to air, and all electrochemical measurements were performed at room temperature (23 ± 1 °C).

Electrochemical impedance spectroscopy measurements were conducted at $E_{ocp}$ in the frequency range of 100 kHz–10 mHz with a 10 mV amplitude. Polarization measurements were performed such that the samples were polarized ±150 mV vs open circuit potential. The obtained polarization curves were analysed through the Tafel extrapolation method, i.e., corrosion current density and corrosion potential were determined at the intersection of extrapolated linear sections of anodic and cathodic polarization curves.

2.4. Surface Characterization

To reveal the composition of artificial patinas, they were analysed by ATR-FTIR spectroscopy using a Shimadzu IR-Tracer100 (Shimadzu, Kyoto, Japan) with a scan range of 4000–400 cm⁻¹ and a resolution of 0.5 cm⁻¹. The results shown in this paper are averages of 45 scans.
Scanning electron microscopy (SEM) and X-ray energy-dispersive spectroscopy (EDS) were performed with VEGA 3 SEM TESCAN, Brno, Czech Republic. SEM measurements were conducted at 1000× magnification and 15 kV (initial state measurements) or 20 kV (final state measurements) acceleration voltage. Vertical distance was 9.5–15.2 mm. EDS imaging was conducted at an acceleration voltage of 10 kV and at a vertical distance of 15 mm.

3. Results and Discussion

3.1. The Effect of Aging Conditions on EIS Results

Firstly, the corrosion behaviour of patinated bronze was examined in artificial acid rain solution (pH = 5). Figure 1a,b shows the evolution of the EIS spectra for CuSn12 bronze after continuous immersion in artificial acid rain solution (pH 5) for three weeks. An increase in impedance modulus with time was observed. On the first day, the value of impedance modulus at the lowest frequencies was less than 1 kΩ·cm². Such a low value indicates that the patinated bronze surface was very reactive. On the second day of immersion, a small increase in impedance modulus was observed, while after one week, it increased significantly. Thus, it can be concluded that the corrosion resistance of the patinated CuSn12 bronze is improved with the exposure to acid rain solution. The phase angle plot initially shows the presence of a maximum at low frequencies. Moreover, the EIS spectrum for the second day reveals the existence of a poorly resolved capacitive behaviour at high frequencies.

![Figure 1. EIS spectra for CuSn12 for continuous immersion in simulated acid rain at pH 5. (a) Bode phase angle; (b) Bode impedance.](image)

In order to obtain more detailed information from the EIS results, the spectra were fitted to selected equivalent electrical circuits. For the spectra obtained on the first and the second day of immersion, it was necessary to use the equivalent electrical circuit with two time constants in order to obtain a good fit at medium and low frequencies. For high frequencies, it was not possible to obtain an accurate fit as the phase angle maximum was not well resolved. The selected model is shown in Figure 2a.

In this model, $R_{el}$ defines the electrolyte resistance between the working and reference electrode. $R_{ct}$ describes the charge transfer resistance, while $Q_{dl}$ is a constant phase element related to the double-layer capacitance, referring to the medium-frequency data. Lower-frequency data are represented by $R_{f}$—faradaic resistance associated with oxidation–reduction processes involving the reactive patina layer and $Q_{f}$—constant phase element representing faradaic capacitance. After a week of exposure, the maximum in the phase angle plot at high frequencies was expressed more. The evolution of this new maximum requires the addition of a new loop, developing the equivalent circuit presented in Figure 2b. The additional $R_{ox}$–$Q_{ox}$ loop represents the inner oxide layer (non-reactive patina layer) [13,24]. The presented model was previously used for describing EIS spectra of CuSn6 bronze covered with sulphate patina by Marušić et al. [13]. They found that the spectra of samples with sulphate patina exhibited an additional peak at the highest frequencies, which was not observed on bare bronze, thus indicating the presence of a new
layer: the non-reactive patina layer. Detailed explanations and mathematical descriptions of applied models can be found in the literature [15].

The parameters of EIS modelling of CuSn12 bronze are listed in Table 2. The parameters for the initial state show very low $R_{ct}$ and high $Q_{dl}$ values. Similar values were observed by Yuan et al. [20] when examining copper–nickel (70/30) corrosion in sulphide-containing seawater. It is possible that in contact with an acid rain solution, sulphide patina releases some corrosive $S^{2-}$ ions. It is also quite likely that the patination solution may have remained in the pores of patina layer. In general, it is known that copper and its alloys are sensitive to the presence of sulphides [25–28]. In our case, this would mean that the corrosion of the underlying bronze substrate is enhanced by the presence of sulphides. During exposure to rainwater, sulphides are removed from the surface, probably by diffusion into the solution or by forming stable corrosion products. The lower amount of aggressive compounds leads to an increase in charge transfer resistance and decrease in double layer capacitance values.

Table 2. EIS data for CuSn12 for continuous immersion in simulated acid rain at pH 5.

| Day  | $R_{ox}/k\Omega \cdot cm^2$ | $Q_{ox}/\mu C \cdot cm^{-2}$ | $n_{ox}$ | $R_{ct}/k\Omega \cdot cm^2$ | $Q_{dl}/\mu C \cdot cm^{-2}$ | $n_{dl}$ | $R_F/k\Omega \cdot cm^2$ | $Q_F/\mu C \cdot cm^{-2}$ | $n_F$ |
|------|-----------------|-----------------|--------|-----------------|-----------------|--------|-----------------|-----------------|--------|
| 1st  | -               | -               | 0.06   | 1863            | 0.62            | 2.69   | 2288            | 0.63            |        |
| 2nd  | -               | -               | 0.30   | 594.4           | 0.61            | 5.74   | 1297            | 0.63            |        |
| 7th  | 0.21            | 9.465           | 0.46   | 0.13            | 0.93            | 14.55  | 196             | 0.55            |        |
| 21st | 1.21            | 0.8787          | 0.73   | 4.42            | 26.92           | 0.50   | 25.03           | 52.34           | 0.58   |

A high $Q_F$ value, on the first day of measurement, indicates the presence of reactive patina compounds. Over time, a decrease in $Q_F$ and increase in $R_F$ values was observed. This can be ascribed to the transformation of the patina, where the amount of reactive species decreases while the patina layer becomes more stable. In addition, after a week of exposure, the formation of an internal oxide layer was observed; its resistance ($R_{ox}$) increased over time, showing that the oxide layer becomes more protective as well as thicker (decrease in $Q_{ox}$).

Similar behaviour was observed for the other two types of bronze. Their EIS spectra are shown in Figure 3 (CuSn6) and Figure 4 (RG7). The impedance modulus increased with immersion time for both alloys. Initial EIS spectra are quite similar for both alloys, whereas after the three weeks, the CuSn6 bronze exhibited higher impedance modulus values. The increase in impedance modulus is the result of a transformation and stabilization of the patina layer, which is also evident from the changes in the phase angle plots. For RG7, the transformation was slower, while the CuSn6 bronze had already shown clear maxima at medium and high frequencies on the seventh day of immersion.
Whereas after the three weeks, the CuSn6 bronze exhibited higher impedance modulus values. The increase in impedance modulus is the result of a transformation and stabilization of the patina layer, which is also evident from the changes in the phase angle plots. The EIS spectra for CuSn6 for continuous immersion in simulated acid rain at pH 5. (a) Bode phase angle; (b) Bode impedance.

The EIS spectra for RG7 and CuSn6 bronze were fitted to the same models used for the CuSn12 bronze shown in Figure 2. The obtained impedance parameters are given in Table 3 (CuSn6) and Table 4 (RG7). In general, the time evolution of the resistive and capacitive values is similar to that of the CuSn12 bronze, namely, increases in R values and decreases in Q occurs. Initially, the RG7 bronze showed the highest $R_{ct}$ value, which slightly decreased on the second day. The higher $R_{ct}$ value could be considered to be a result of the higher resistance of RG7 bronze towards the corrosion attack of sulphide ions, but it is also possible that release of sulphides from patina was slower such that this effect was not visible during the first measurement. On the 21st day of the immersion, the highest $R_{ox}$ and the lowest $Q_{ox}$ values were observed for CuSn12 bronze. This can be explained by the fact that this type of bronze contains the highest amount of Sn, which is known to easily form a stable oxide layer [29,30]. On the other hand, the resistance of the reactive patina layer ($R_F$) increased the most for CuSn6 bronze. Gianni et al. [21] made similar observations when examining the corrosion of bronzes in an urban environment, in that bronze with lower tin content exhibited a higher corrosion rate compared to high-tin bronze, but the patina that formed on the lower-tin bronze was more stable.

**Table 3.** EIS data for CuSn6 for continuous immersion in simulated acid rain at pH 5.

| Day  | $R_{ox}$/kΩ·cm$^2$ | $Q_{ox}$/µS·s$^{-1}$·cm$^{-2}$ | $n_{ox}$ | $R_{ct}$/kΩ·cm$^2$ | $Q_{dl}$/µS·s$^{-1}$·cm$^{-2}$ | $n_{dl}$ | $R_F$/kΩ·cm$^2$ | $Q_F$/µS·s$^{-1}$·cm$^{-2}$ | $n_F$ |
|------|-----------------|-----------------|------|-----------------|-----------------|------|-----------------|-----------------|------|
| 1st  | -               | -               | -    | 0.07            | 911.2           | 0.58 | 6.01            | 3741            | 0.64 |
| 2nd  | -               | -               | -    | 5.03            | 241             | 0.57 | 3.02            | 2456            | 0.83 |
| 7th  | 0.81            | 1.200           | 0.76 | 2.16            | 11.71           | 0.66 | 21.40           | 138.2           | 0.50 |
| 21st | 1.26            | 1.226           | 0.74 | 2.30            | 3.90            | 0.77 | 296.3           | 92.78           | 0.50 |
Table 3. EIS data for CuSn6 for continuous immersion in simulated acid rain at pH 5.

| Day | $R_{ct}/k\Omega \cdot cm^2$ | $Q_{ox}/\mu S \cdot s^n \cdot cm^{-2}$ | $n_{ox}$ | $R_{ct}/k\Omega \cdot cm^2$ | $Q_{dl}/\mu S \cdot s^n \cdot cm^{-2}$ | $n_{dl}$ | $R_F/k\Omega \cdot cm^2$ | $Q_F/\mu S \cdot s^n \cdot cm^{-2}$ | $n_F$ |
|-----|-----------------------------|--------------------------------------|---------|-----------------------------|--------------------------------------|---------|-----------------------------|--------------------------------------|---------|
| 1st | -                           | -                                    | -       | 1.60                        | 2115                                 | 0.67    | 2.04                        | 1619                                 | 1.00    |
| 2nd | 0.14                        | 32.64                                | 0.55    | 1.02                        | 340.9                                | 0.56    | 27.27                       | 404.3                                | 0.51    |
| 7th | 0.19                        | 24.65                                | 0.50    | 1.14                        | 22.89                                | 0.66    | 9.87                        | 91.07                                | 0.71    |
| 21st| 0.28                        | 10.38                                | 0.61    | 2.30                        | 13.01                                | 0.74    | 65.30                       | 139.60                               | 0.72    |

The second type of patina aging was conducted by alternating wet and dry conditions, as in the case of exposure to outdoor conditions. The EIS spectra of measurements for sulphide patinated CuSn12 bronze obtained during alternating wet/dry cycles are shown in Figure 5. An increase in impedance modulus in time is present, although with small changes between cycles. After six cycles, there are no significant changes in the shape of the phase angle curves, which are similar to those measured for short-term immersion during continuous exposure to acid rain solution. The equivalent electrical circuit in Figure 2a was used to fit EIS spectra. The obtained impedance parameters are shown in Table 5.

Figure 5. EIS spectra for CuSn12 for alternating wet/dry cycles in simulated acid rain at pH 5. (a) Bode phase angle; (b) Bode impedance.

Table 4. EIS data for RG7 for continuous immersion in simulated acid rain at pH 5.

| Day | $R_{ct}/k\Omega \cdot cm^2$ | $Q_{ox}/\mu S \cdot s^n \cdot cm^{-2}$ | $n_{ox}$ | $R_{ct}/k\Omega \cdot cm^2$ | $Q_{dl}/\mu S \cdot s^n \cdot cm^{-2}$ | $n_{dl}$ | $R_F/k\Omega \cdot cm^2$ | $Q_F/\mu S \cdot s^n \cdot cm^{-2}$ | $n_F$ |
|-----|-----------------------------|--------------------------------------|---------|-----------------------------|--------------------------------------|---------|-----------------------------|--------------------------------------|---------|
| 1st | -                           | -                                    | -       | 1.60                        | 2115                                 | 0.67    | 2.04                        | 1619                                 | 1.00    |
| 2nd | 0.14                        | 32.64                                | 0.55    | 1.02                        | 340.9                                | 0.56    | 27.27                       | 404.3                                | 0.51    |
| 7th | 0.19                        | 24.65                                | 0.50    | 1.14                        | 22.89                                | 0.66    | 9.87                        | 91.07                                | 0.71    |
| 1st | -                           | -                                    | -       | 1.60                        | 2115                                 | 0.67    | 2.04                        | 1619                                 | 1.00    |
| 2nd | 0.14                        | 32.64                                | 0.55    | 1.02                        | 340.9                                | 0.56    | 27.27                       | 404.3                                | 0.51    |
| 7th | 0.19                        | 24.65                                | 0.50    | 1.14                        | 22.89                                | 0.66    | 9.87                        | 91.07                                | 0.71    |
| 21st| 0.28                        | 10.38                                | 0.61    | 2.30                        | 13.01                                | 0.74    | 65.30                       | 139.60                               | 0.72    |

Table 5. EIS data for CuSn12 for alternating wet/dry cycles in simulated acid rain at pH 5.

| Cycle | $R_{ct}/k\Omega \cdot cm^2$ | $Q_{dl}/\mu S \cdot s^n \cdot cm^{-2}$ | $n_{dl}$ | $R_F/k\Omega \cdot cm^2$ | $Q_F/\mu S \cdot s^n \cdot cm^{-2}$ | $n_F$ |
|-------|-----------------------------|--------------------------------------|---------|-----------------------------|--------------------------------------|---------|
| 1st   | 0.14                        | 834.2                                | 0.68    | 5.29                        | 943                                  | 0.70    |
| 2nd   | 0.17                        | 386.4                                | 0.66    | 4.57                        | 1740                                 | 0.58    |
| 4th   | 1.11                        | 552.5                                | 0.62    | 9.82                        | 719.2                                | 0.57    |
| 6th   | 1.01                        | 341                                  | 0.56    | 12.26                       | 605.2                                | 0.50    |

Here, the increase in $R_{ct}$ and $R_F$ values in time is visible but not as pronounced as for continuous immersion conditions. The comparison of $R_F$ values with those obtained during continuous immersion shows that a longer wetting time leads to better stabilization and higher corrosion resistance. The high value of $Q_F$ indicates the presence of a large amount of reactive species (sulphides). It can be concluded that a longer wetting period enhances the removal of reactive species from the surface and transformation of the reactive patina into a more stable patina layer. These experiments were also performed on CuSn6 and RG7 bronze. The evolution of $R_{ct}$ and $R_F$ with number of aging cycles for these two bronzes is presented in Figure 6. A small increase in resistance values was observed for RG7 bronze, while for CuSn6 bronze, only some fluctuations were observed. Therefore, for all studied bronzes, more significant improvement in corrosion properties occurred under continuous wetting conditions.
The following experiments were also conducted under continuous immersion conditions but at a higher pH (6.5), simulating less corrosive rainwater. The EIS spectra for studied CuSn12 bronze during continuous immersion in simulated urban rain (pH 6.5) are shown in Figure 7, with those for CuSn6 bronze in Figure 8 and those for RG7 in Figure 9. As in the case of a more aggressive solution (pH 5), the impedance modulus increases over time for all samples. However, the increase between the first and the second day is more significant than in the pH 5 solution. This indicates that a less corrosive medium enhances the stabilization of sulphide patinated bronze. The evolution of phase angle plot is similar to that in the pH 5 solution, but with a more expressed phase angle maxima. For this reason, the same models were selected for fitting EIS data (Figure 2). The parameters obtained for CuSn12 bronze are given in Table 6, with those for CuSn6 in Table 7 and those for RG7 in Table 8. They indicate an increase in $R_{ct}$ values compared to more acid medium, but a more important difference was observed in $R_F$ values. For all studied bronzes, the $R_F$ values are higher than in the pH 5 solution. On the other hand, the $Q_F$ values are similar to those in the pH 5 solution. This implies that the amount of reactive patina is similar, but its resistance is probably higher due to the lower aggressiveness of the pH 6.5 medium.

![Figure 6](image-url)  
**Figure 6.** Evolution of charge transfer resistance ($R_{ct}$) and reactive patina resistance ($R_F$) with number of wetting cycles.

![Figure 7](image-url)  
**Figure 7.** EIS spectra for CuSn12 bronze for continuous immersion in artificial urban rain at pH 6.5. (a) Bode phase angle; (b) Bode impedance.
Figure 7. EIS spectra for CuSn6 bronze for continuous immersion in artificial urban rain at pH 6.5. (a) Bode phase angle; (b) Bode impedance.

Figure 8. EIS spectra for CuSn6 bronze for continuous immersion in artificial urban rain at pH 6.5. (a) Bode phase angle; (b) Bode impedance.

Table 6. EIS data for CuSn12 for continuous immersion in simulated urban rain at pH 6.5.

| Day  | R_{aO}/kΩ cm\(^2\) | Q_{ox}/μS s\(^{-1}\) cm\(^{-2}\) | n_{ox} | R_{dl}/kΩ cm\(^2\) | Q_{dl}/μS s\(^{-1}\) cm\(^{-2}\) | n_{dl} | R_{F}/kΩ cm\(^2\) | Q_{F}/μS s\(^{-1}\) cm\(^{-2}\) | n_{F} |
|------|-------------------|-----------------|--------|-------------------|-----------------|--------|-------------------|-----------------|--------|
| 1st  | -                 | -               | 0.16   | 765.40            | 0.69            | 6.11   | 737.6             | 0.68            | 0.68   |
| 2nd  | 0.44              | 0.740           | 0.44   | 1.15              | 30.10           | 0.60   | 168.1             | 59.58           | 0.69   |
| 7th  | 0.11              | 3.692           | 0.65   | 0.67              | 25.37           | 0.72   | 139               | 75.19           | 0.78   |
| 21st | 0.21              | 5.00            | 0.65   | 6.33              | 8.12            | 0.73   | 525.2             | 44.01           | 0.79   |

Table 7. EIS data for RG7 for continuous immersion in simulated urban rain at pH 6.5.

| Day  | R_{aO}/kΩ cm\(^2\) | Q_{ox}/μS s\(^{-1}\) cm\(^{-2}\) | n_{ox} | R_{dl}/kΩ cm\(^2\) | Q_{dl}/μS s\(^{-1}\) cm\(^{-2}\) | n_{dl} | R_{F}/kΩ cm\(^2\) | Q_{F}/μS s\(^{-1}\) cm\(^{-2}\) | n_{F} |
|------|-------------------|-----------------|--------|-------------------|-----------------|--------|-------------------|-----------------|--------|
| 1st  | -                 | -               | 0.45   | 1297              | 0.65            | 5.18   | 726               | 0.72            | 0.72   |
| 2nd  | 0.57              | 0.0284          | 0.72   | 0.73              | 114             | 0.58   | 75.46             | 215             | 0.72   |
| 7th  | 0.13              | 5.60            | 0.62   | 0.38              | 45.09           | 0.76   | 455.5             | 146             | 0.79   |
| 21st | 0.25              | 8.50            | 0.61   | 2.10              | 10.54           | 0.74   | 1492              | 146             | 0.76   |

Table 8. EIS data for CuSn6 for continuous immersion in simulated urban rain at pH 6.5.

| Day  | R_{aO}/kΩ cm\(^2\) | Q_{ox}/μS s\(^{-1}\) cm\(^{-2}\) | n_{ox} | R_{dl}/kΩ cm\(^2\) | Q_{dl}/μS s\(^{-1}\) cm\(^{-2}\) | n_{dl} | R_{F}/kΩ cm\(^2\) | Q_{F}/μS s\(^{-1}\) cm\(^{-2}\) | n_{F} |
|------|-------------------|-----------------|--------|-------------------|-----------------|--------|-------------------|-----------------|--------|
| 1st  | -                 | -               | 1.89   | 2832              | 1               | 6.26   | 657.3             | 0.57            | 0.57   |
| 2nd  | 0.58              | 0.0042          | 0.86   | 0.25              | 68.38           | 0.68   | 41.12             | 118.3           | 0.74   |
| 7th  | 0.39              | 1.0440          | 0.44   | 1.30              | 28.88           | 0.72   | 160.50            | 88.93           | 0.77   |
| 21st | 0.40              | 0.674           | 0.50   | 8.78              | 3.52            | 0.77   | 555.20            | 62.33           | 0.54   |

EIS spectra for alternating wet/dry cycles for CuSn6 bronze at pH 6.5 are shown in Figure 10. This type of aging resulted in negligible changes in impedance modulus.
over time, but impedance values are higher than at pH 5 (Table 6). In addition, sulphate patinated samples were exposed to the corrosion chamber with NO₂ for 14 days. The phase angle plots for such samples exhibit more expressed peaks at medium and high frequencies. All spectra were fitted with an electrical equivalent circuit in Figure 2b; parameters are shown in Table 9.

![Figure 10. EIS spectra for CuSn6 bronze for continuous immersion in artificial urban rain at pH 6.5. (a) Bode phase angle; (b) Bode impedance.](image)

| Cycle               | $R_{dl}/k\Omega \cdot \text{cm}^2$ | $Q_{dl}/\mu\text{S} \cdot \text{s}^n \cdot \text{cm}^{-2}$ | $n_{dl}$ | $R_{ct}/k\Omega \cdot \text{cm}^2$ | $Q_{ct}/\mu\text{S} \cdot \text{s}^n \cdot \text{cm}^{-2}$ | $n_F$ |
|---------------------|-------------------------------------|-------------------------------------------------|----------|-------------------------------------|-------------------------------------------------|--------|
| 6st after NO₂ chamber | 1.22                               | 20.58                                           | 0.46     | 0.25                                | 24.11                                           | 0.9    |

The patina exhibits higher $R_F$ values after exposure to a nitrogen dioxide atmosphere compared to alternating wet/dry cycles, indicating higher patina resistance ($R_F$). The lower $Q_F$ value indicates a lower amount of reactive species at the end of exposure, while lower $Q_{dl}$ and higher $R_q$ values are probably due to the lower amount of sulphide compounds on the surface. For cyclic exposure, a high $Q_{dl}$ value was obtained after the last cycle, indicating a high amount of sulphides was still present. This leads to the conclusion that transformation and stabilization of patinated samples occurred in all studied cases, but in a manner dependent on the wetting time. The longer the wetting time, the greater stabilization and corrosion resistance. Similar observations could be drawn for other types of studied bronzes.

3.2. The Effect of Test Conditions on the Polarization Behaviour

Potentiodynamic polarization measurements were also conducted in order to better understand the corrosion behaviour of studied patinated bronzes. The results obtained for CuSn12 are plotted in Figure 11. In pH 5 solution polarization curves obtained after sample aging (either under continuous or alternating conditions) show lower current densities than at the initial state. For alternating wet/dry conditions, the decrease in current densities was observed mainly in the cathodic part of the polarization curve, which might be explained either by improvement in barrier properties of the patina layer or a decrease in the amount of species that could be reduced at cathodic overpotentials. Taking into account the results of EIS measurements (small decrease in $Q_F$ values), a decrease in cathodic current densities could be mainly related to improved barrier properties of the patina layer.
3.2. The Effect of Test Conditions on the Polarization Behaviour

The comparison of the results obtained in solutions of different pH values shows a significant transformation, leading to a stabilized patina layer and better corrosion protection. The corrosion parameters obtained from the polarization curves by the Tafel extrapolation method are presented in Table 10. The highest corrosion current density of 1.32 µA cm$^{-2}$ was obtained initially in the more aggressive solution: acid rain (pH 5). In both media, the lowest corrosion current densities were obtained after continuous immersion, which confirms the previous conclusion that a longer wetting period enables a significant transformation, leading to a stabilized patina layer and better corrosion protection. The comparison of the results obtained in solutions of different pH values shows that regardless of the form of accelerated aging, the current density is higher in a more aggressive solution (pH 5).

Table 10. Corrosion parameters of sulphate patinated CuSn12 bronze obtained by Tafel extrapolation method.

| CuSn12                        | $E_{\text{corr}}$/V | $j_{\text{corr}}$/µA cm$^{-2}$ | $\beta_a$/V dec$^{-1}$ | $-\beta_c$/V dec$^{-1}$ |
|-------------------------------|---------------------|-------------------------------|------------------------|-------------------------|
| Initial state pH 5            | −0.001              | 1.32                          | 0.040                  | 0.076                   |
| Continuous immersion pH 5     | −0.002              | 0.38                          | 0.089                  | 0.659                   |
| Alternating wet/dry cycles pH 5| −0.015              | 0.81                          | 0.039                  | 0.080                   |
| Initial state pH 6.5          | −0.029              | 1.15                          | 0.043                  | 0.070                   |
| Continuous immersion pH 6.5   | −0.005              | 0.08                          | 0.009                  | 0.039                   |
| Alternating wet/dry cycles pH 6.5| −0.016             | 0.21                          | 0.037                  | 0.047                   |

Polarization measurements conducted on the other two bronzes show the same trends regarding the influence of medium pH as well as the wetting conditions, while the differences between studied bronzes are not significant.

3.3. Patina Composition Modification Characterized by Fourier Transform Infrared Spectroscopy

In order to analyse modifications in patina composition, the samples were characterized by ATR-FTIR spectroscopy and SEM. For freshly prepared patinated samples, there are no clearly visible peaks in the FTIR spectra. The FTIR spectrum shown in Figure 12 was obtained after continuous immersion of patinated samples in simulated acid rain (pH 5). The strongest peaks were observed for RG7 bronze. The band at 610 cm$^{-1}$ may be assigned with the presence of a bond between either copper or tin and oxygen [9,31], while the 1071 cm$^{-1}$ band can be attributed to SO$_4^{2-}$ vibration [32,33]. Both peaks indicate the formation of copper and tin oxides as well as sulphate patina, as observed by Kosec et al. [16]. They con-
cluded that sulphate compounds are formed by sulphide patina transformation. However, in their work, parts of the surface exhibited spectra with bands at higher wavenumbers that could be clearly ascribed to brochanite. Still, their experiment lasted for 35 days, which is longer than in our case. The transformation was less pronounced for CuSn6, and especially so for CuSn12 bronze.

On the other hand, the FTIR spectrum for alternating wet/dry cycles, shown in Figure 13, indicates the highest transformation for the CuSn12 bronze. One can clearly see a band at 608 cm\(^{-1}\) as well as bands indicating sulphate patina at 1113, 1149, and 1179 cm\(^{-1}\) or bands at 1362 and 1427 cm\(^{-1}\), which could be ascribed to carbonate patina [32]. The other two bronzes show bands at low frequencies, which represent oxides (629 cm\(^{-1}\)), while the bands that could be related to sulphate patina are not particularly distinguishable [32].

The FTIR spectra for cyclic and continuous immersion conditions are relatively similar, although EIS indicates bigger differences between these samples. As the ATR-FTIR spectra better reflects the composition of upper than inner patina layer, it can be concluded that for cyclic exposure of patina, the main transformations mainly occur in the upper patina layer.

The FTIR spectra of samples exposed to continuous immersion in simulated urban rain (pH 6.5) are presented in Figure 14. Patinated CuSn6 samples exhibited a band at 596 cm\(^{-1}\) related to the presence of oxides. The CuSn12 and RG7 bronzes exhibited similar FTIR spectra. The peak at 826 cm\(^{-1}\) is also assigned to the presence of oxides [31].

Figure 12. FTIR spectrum for continuous immersion of bronzes in acid rain at pH 5.

Figure 13. FTIR spectrum for alternating wet/dry cycles in acid rain at pH 5.

Figure 14. FTIR spectrum for continuous immersion of bronzes in acid rain at pH 6.5.
wider bands can be observed at higher wavenumbers, which could possibly be the result of sulphate patina formation.

Figure 13. FTIR spectrum for alternating wet/dry cycles in acid rain at pH 5.

In the case of alternating wet/dry cycles performed in urban rain, a band at 610 cm\(^{-1}\) is visible in the FTIR spectra of all bronzes. After exposure to the corrosion chamber with NO\(_2\) atmosphere, the most intensive peak appears at 604 cm\(^{-1}\). In addition, the formation of sulphate patina is possible based on the appearance of small peaks at 1000 and 1396 cm\(^{-1}\) [32].

The results of FTIR investigations show that in all studied aging conditions, there are some changes in patina layer composition, including the formation of oxides and/or sulphate compounds. However, the differences between examined aging conditions are not as clear as those observed by electrochemical measurements. In the case of the continuous immersion, the transformations are probably more intense in the inner patina layer and thus less visible in the FTIR spectra.

3.4. Patina Composition Modification Characterized by Scanning Electron Microscopy

SEM images of prepared sulphide patina samples are given in Figure 15 (upper part). The patina layer on the RG7 bronze appears to be the most heterogeneous, while the most uniform and the smoothest layer was observed on the CuSn12 bronze. The complex morphology of the RG7 patina is probably the result of the fact that RG7 bronze has the most heterogeneous composition.

The EDS analysis of multiple points on the surface revealed the presence of Cu and S for all bronzes. A high amount of Cu was obtained for all bronzes (54 at.%–64 at.%), reflecting the composition of the patina but also that of the substrate. The S content is highest in the case of CuSn6 at 25 at.%–32 at.%, with RG7 at 24 at.%–26 at.% and CuSn12 bronze at 24 at.%–27 at.%. It is only for RG7 that some O was observed, while Sn was not detected in the case of RG7.

The SEM results depend on the measurement point due to some differences in the thickness of the prepared patina. Figure 15 (below) presents patinated samples after continuous immersion in simulated urban rain (pH 6.5). The changes in morphology can be observed by the formation of precipitations and cracks. EDS results show that the amount of Cu is decreased (to around 40%) due the thickening and transformation of patina layer. An increase in O content and a decrease in S content was measured for all studied bronzes (an example for CuSn6 bronze is given in Figure 16). These results are in accordance with FTIR spectra showing formation of oxides and sulphates.
3.4. Patina Composition Modification Characterized by Scanning Electron Microscopy

An increase in O content and a decrease in S content was measured for all studied bronzes (an example for CuSn6 bronze is given in Figure 16). These results are in accordance with FTIR spectra showing formation of oxides and sulphates. The EDS examinations show that the aging process leads to the formation of oxide and sulphate compounds. The EDS analysis of multiple points on the surface revealed the presence of Cu and S in all studied bronzes. A high amount of Cu was obtained for all bronzes (54 at.%–64 at.%), while Sn content was lower than 15 at.% for RG7 and CuSn6, and higher in the case of CuSn12 at 25 at.%–32 at.%. It is only for RG7 that some O was observed, while Sn was not detected in the case of RG7.

Based on these results, it can be concluded that the longer the wetting time, the faster the transformation of patina and reaching the higher corrosion resistance state. The choice of aging conditions has a more important influence on patinated bronze properties than the bronze composition, as similar results were obtained for all studied bronzes.

The SEM results depend on the measurement point due to some differences in the complex morphology of the RG7 patina. This is probably the result of the fact that RG7 bronze has the most heterogeneous composition. The patina layer on the RG7 bronze appears to be the most heterogeneous, while the most uniform and the smoothest layer was observed on the CuSn12 bronze. The patina layer on the CuSn6 bronze appears to be intermediate between RG7 and CuSn12. The patina thickness on CuSn12 bronze was 7 μm, while on RG7 bronze it was 10 μm. The SEM images of RG7 after continuous immersion show more cracks in the patina layer, which indicates a decrease in patina thickness.

Studies on patina composition conducted with FTIR measurements indicate the formation of oxides and sulphates in all considered aging conditions. The changes in morphology can be observed on the SEM images of RG7 bronze after continuous immersion (pH 6.5). The patina layer appears to be more heterogeneous and less uniform compared to the initial state. The changes in electrochemical properties as well as in the composition of patinated bronze results in the appearance of oxygen in EDS spectra, while the S:O ratio decreases with increased wetting time and acidity of corrosive media.

The electrochemical studies show that the corrosion of freshly patinated samples is faster than for wet/dry cycles, which also confirms that in the former case, more significant formation of oxides and sulphates occurred. By comparing continuous immersion and wet/dry cycles, it is evident that the former case leads to more significant formation of oxides and sulphates compared to the latter case. This is in accordance with EIS and FTIR results showing more intense corrosion resistance with time was observed, which is mainly related to the improved corrosion resistance of the patina layer. The strongest improvement in corrosion properties was obtained for continuous immersion conditions followed by NO2 corrosion chamber exposure, while the lowest increase in corrosion resistance was observed for alternating wet/dry cycles.

Figure 15. SEM images of (a) RG7, (b) CuSn6, and (c) CuSn12 bronzes before (upper image) and after (lower image) continuous exposure to urban rain. Scale bare in each image represents 20 μm.

Figure 16. EDS spectra for CuSn6 bronze: (a) initial state; (b) after continuous immersion (pH 5); (c) after continuous immersion (pH 6.5); (d) after alternating wet/dry cycles at pH 6.5.
For alternating wet/dry cycles at pH 6.5, the amount of S was lower than at the initial state, while more O was detected. For continuous immersion, the atomic ratio S:O was higher than for wet/dry cycles, which also confirms that in the former case, more significant formation of oxides and sulphates occurred. By comparing continuous immersion in acid rain (pH 5) with the initial state, once again, a decrease in S and increase in O content was observed. In comparison to the less aggressive medium, the S:O ratio was similar for CuSn12 bronze, while for the other two bronzes, the oxygen content was higher for pH 5, which is in accordance with EIS and FTIR results showing more intense transformation of patina in more acid solution.

4. Conclusions

This work examines the aging of sulphide patinated bronzes under various corrosion conditions. The changes in electrochemical properties as well as in the composition of the patina were studied.

The electrochemical studies show that the corrosion of freshly patinated samples is significant, especially in a more acidic solution, which is ascribed to the corrosive attack of sulphide ions present in the patina layer. In all studied aging conditions, an increase in corrosion resistance with time was observed, which is mainly related to the improved resistance of the patina layer. The strongest improvement in corrosion properties was obtained for continuous immersion conditions followed by NO$_2$ corrosion chamber exposure, while the lowest increase in corrosion resistance was observed for alternating wet/dry cycles.

Studies on patina composition conducted with FTIR measurements indicate the formation of oxide and sulphate compounds. The EDS examinations show that the aging of patinated bronze results in the appearance of oxygen in EDS spectra, while the S:O ratio decreases with increased wetting time and acidity of corrosive media.

Based on these results, it can be concluded that the longer the wetting time, the faster the transformation of patina and reaching of the higher corrosion resistance state. The choice of aging conditions has a more important influence on patinated bronze properties than the bronze composition, as similar results were obtained for all studied bronzes.

Author Contributions: Conceptualization, H.O. ´C. and A.K.; methodology, H.O. ´C.; validation, H.O. ´C. and A.K.; formal analysis, A.K.; investigation, A.K.; resources, H.O. ´C.; data curation, A.K.; writing—original draft preparation, H.O. ´C. and A.K.; supervision, H.O. ´C.; funding acquisition, H.O. ´C. All authors have read and agreed to the published version of the manuscript.

Funding: This work was fully funded by the Croatian Science Foundation under the project IP-2019-04-5030.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Leygraf, C.; Chang, T.; Herting, G.; Odnevall Wallinder, I. The origin and evolution of copper patina colour. Corros. Sci. 2019, 157, 337–346. [CrossRef]
2. FitzGerald, K.P.; Nairn, J.; Skennerton, G.; Atrens, A. Atmospheric corrosion of copper and the colour, structure and composition of natural patinas on copper. Corros. Sci. 2006, 48, 2480–2509. [CrossRef]
3. Kosec, T.; Novak, Ž.; Fabjan, E.Š.; Škrlep, L.; Sever Škapin, A.; Ropret, P. Corrosion protection of brown and green patinated bronze. Prog. Org. Coat. 2021, 161, 106510. [CrossRef]
4. Letardi, P. Testing new coatings for outdoor bronze monuments: A methodological overview. Coatings 2021, 11, 131. [CrossRef]
5. Bureš, R.; Klajmon, M.; Fojt, J.; Rak, P.; Jílková, K.; Stoullil, J. Artificial patination of copper and copper alloys in wet atmosphere with increased content of SO$_2$. Coatings 2019, 9, 837. [CrossRef]
6. Masi, G.; Esvan, J.; Josse, C.; Chiavari, C.; Bernardi, E.; Martini, C.; Bignozzi, M.C.; Gartner, N.; Kosec, T.; Robbiola, L. Characterization of typical patinas simulating bronze corrosion in outdoor conditions. *Mater. Chem. Phys.* 2017, 200, 308–321. [CrossRef]

7. Bernardi, E.; Chiavari, C.; Lenza, B.; Martini, C.; Morselli, L.; Ospitali, F.; Robbiola, L. The atmospheric corrosion of quaternary bronzes: The leaching action of acid rain. *Corros. Sci.* 2009, 51, 159–170. [CrossRef]

8. Rosales, B.M.; Vera, R.M.; Hidalgo, J.P. Characterisation and properties of synthetic patina on copper base sculptural alloys. *Corros. Sci.* 2010, 52, 3212–3224. [CrossRef]

9. Mikić, D.; Ćurković, H.O.; Kosec, T.; Peko, N. An electrochemical and spectroscopic study of surfaces on bronze sculptures exposed to urban environment. *Materials 2021*, 14, 2063. [CrossRef]

10. Chang, T.; Odnevall Wallinder, I.; de la Fuente, D.; Chico, B.; Morcillo, M.; Welter, J.-M.; Leygraf, C. Analysis of historic copper patinas. Influence of inclusions on patina uniformity. *Materials 2017*, 10, 298. [CrossRef]

11. Morcillo, M.; Chang, T.; Chico, B.; de la Fuente, D.; Odnevall Wallinder, I.; Jiménez, J.A.; Leygraf, C. Characterisation of a centuries-old patinated copper roof tile from Queen Anne’s Summer Palace in Prague. *Mater Charact.* 2017, 133, 146–155. [CrossRef]

12. Chiavari, C.; Rahmouni, K.; Takenouti, H.; Joiret, S.; Vermout, P.; Robbiola, L. Composition and electrochemical properties of natural patinas of outdoor bronze monuments. *Electrochim. Acta* 2007, 52, 7760–7769. [CrossRef]

13. Marušić, K.; Ćurković, H.O.; Takenouti, H. Inhibiting effect of 4-methyl-1-p-tolylimidazole to the corrosion of bronze patinated in sulphate medium. *Electrochim. Acta* 2011, 56, 7491–7502. [CrossRef]

14. Otmačić Ćurković, H.; Kosec, T.; Marušić, K.; Legat, K. An electrochemical impedance study of the corrosion protection of artificially formed patinas on recent bronze. *Electrochim. Acta* 2012, 83, 28–39. [CrossRef]

15. Ropret, P.; Kosec, T. Raman investigation of artificial patinas on recent bronze—Part I: Climatic chamber exposure. *J. Raman Spectrosc.* 2012, 43, 1578–1586. [CrossRef]

16. Kosec, T.; Ropret, P.; Legat, A. Raman investigation of artificial patinas on recent bronze—Part II: Urban rain exposure. *J. Raman Spectrosc.* 2012, 43, 1587–1595. [CrossRef]

17. Bongiorno, V.; Campodonico, S.; Caffara, R.; Piccardo, P.; Carnasciali, M.M. Micro-Raman spectroscopy for the characterization of artistic patinas produced on copper-based alloys. *J. Raman Spectrosc.* 2012, 43, 1617–1622. [CrossRef]

18. Constantinides, I.; Adriaens, A.; Adams, F. Surface characterization of artificial corrosion layers on copper alloy reference materials. *Appl. Surf. Sci.* 2002, 189, 90–101. [CrossRef]

19. Di Carlo, G.; Giuliani, C.; Riccucci, C.; Pasucci, M.; Messina, E.; Fierro, G.; Lavorgna, M.; Ingo, G.M. Artificial patina formation onto copper-based alloys: Chloride and sulphate induced corrosion processes. *Appl. Surf. Sci.* 2017, 421, 120–127. [CrossRef]

20. Yuan, S.J.; Pehkonen, S.O. Surface characterization and corrosion behavior of 70/30 Cu-Ni alloy in pristine and sulphide-containing simulated seawater. *Corros. Sci.* 2007, 49, 1276–1304. [CrossRef]

21. Gianni, L.; Cavallini, M.; Adriaens, A. Corrosion behaviour of bronze in urban environments: Influence of tin content. *Corros. Eng. Sci. Technol.* 2013, 48, 334–339. [CrossRef]

22. Richard, H.; Rowe, M. *The Colouring, Bronzing and Patination of Metals*; Thames&Hudson: London, UK, 1991.

23. Dorhout, J.M.; Anderson, A.S.; Batista, E.; Carlson, R.K.; Currier, R.P.; Martinez, R.K.; Clegg, S.M.; Wilkerson, M.P.; Nowak-Lovato, K. NOx speciation from copper dissolution in nitric acid/water solutions using FTIR spectroscopy. *J. Mol. Spectrosc.* 2020, 372, 111334. [CrossRef]

24. Marušić, K.; Otmačić-Ćurković, H.; Horvat-Kurbegović, Š.; Takenouti, H.; Stupnišek-Lisac, E. Comparative studies of chemical and electrochemical preparation of artificial bronze patinas and their protection by corrosion inhibitor. *Electrochim. Acta* 2012, 57, 7106–7113. [CrossRef]

25. Xie, X.; Du, L.; Pan, L.; Cao, S.; Yan, M.; Yang, W. Effect of sulphide in water on corrosion of copper alloys. *Anti-Corros. Methods Mater.* 2007, 54, 34–36. [CrossRef]

26. Liang, K.; Xu, Y.; Lu, Q.; Zhang, S.; Tan, Y. Investigation of copper corrosion behavior in various sulfide solutions. *Adv. Eng. Res.* 2017, 125, 457–462.

27. Jacobs, S.; Edwards, M. Sulphide scale catalysis of copper corrosion. *Water Res.* 2000, 34, 2798–2808. [CrossRef]

28. Zhang, F.; Ornek, C.; Liu, M.; Müller, T.; Lienert, U.; Ratia-Hanvy, B.; Carpen, L.; Isathdon, E.; Pan, J. Corrosion-induced microstructure degradation of copper in sulphide-containing simulated anoxic groundwater studied by synchrotron high-energy X-ray diffraction and ab-initio density functional theory calculation. *Corros. Sci.* 2022, 184, 109390. [CrossRef]

29. Lyon, S.B. Corrosion of tin and its alloys. *Shreir’s Corros.* 2010, 1, 2068–2077.

30. Nam, N.D.; Kim, M.J.; Jang, Y.W.; Kim, J.G. Effect of tin on the corrosion behavior of low-alloy steel in an acid chloride solution. *Corros. Sci.* 2010, 52, 14–20. [CrossRef]

31. Catelli, E.; Sciutto, G.; Prati, S.; Jia, Y.; Mazzero, R. Characterization of outdoor bronze monument patinas: The potentials of near-infrared spectroscopic analysis. *Environ. Sci. Pollut. Res.* 2018, 25, 24379–24393. [CrossRef]

32. Chukanov, N.V. *Infrared Spectra of Mineral Specie*; Springer: New York, NY, USA; London, UK, 2014.

33. Secco, E.A. Spectroscopic properties of SO4 and (OH) in different molecular and crystalline environments. I. Infrared spectra of Cu2(OH)2SO4, Cu4(OH)4SO4, and Cu3(OH)4SO4. *Can. J. Chem.* 1988, 66, 329–336. [CrossRef]