All that glitters is not gold: Unraveling the material secrets behind the preservation of historical brass

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Highlights

- Non-degraded centuries-old brass objects are rare.
- Brass sequins appear pristinely preserved in a series of 16th-century altarpieces.
- Key information on the factors affecting the reactivity of brass has been obtained.
- The manufacturing process has a central role on the stability of these objects.

Abstract

Brass is a relatively stable alloy but it tends to tarnish over time due to the interaction with the atmosphere. Thus, it is rare to observe centuries-old brass objects untouched by the passing of time. For this reason, the pristine appearance of hundreds of brass sequins in the Enclosed Gardens of Mechelen (reliquary altarpieces produced between 1530 and 1550) is remarkable. In this study, the chemical and metallographic characterization of such unexpectedly well-preserved objects is presented. The results revealed the reason for their stability to be a combination of high-quality materials (i.e. medium Zn content, low impurities) and optimal surface properties (i.e. high homogeneity, low roughness), indicating the high level of expertise of the craftsmen who produced them. Novel fundamental insights on the historical manufacturing method of metallic sequins were also obtained.

Keywords: Alloys, Brass, Copper, Degradation, Cultural heritage

1. Introduction

Brass is a relatively stable alloy but it tends to tarnish over time due to the interaction with the atmosphere. Thus, it is rare to observe centuries-old brass objects untouched by the passing of time. The Enclosed Gardens of Mechelen Hospital sisters, seven Masterpieces in the collection of the Museum Hof Van Busleyden (Mechelen, BE), are one of the few exceptions [1,2]. Upon visual observation, one of the predominant features in these artworks is the presence of hundreds of round and leaf-shaped brass pieces (the so called sequins) with an extremely reflective appearance (except for a very small number of completely corroded pieces, described in detail in a previous publication [3]). Such a pristine state is in striking contrast with the high degree of degradation observed for the other materials constituting the artworks (e.g. faded and embrittled textiles, corroded glass beads and tarnished metals). This generally poor conservation state is likely a result of non-ideal conservation conditions. The objects were in fact stored for over 400 years in the convent of Mechelen's Hospital Sisters in non-climatized (likely high-humidity) conditions, before being stored in the museum in the first half of the 20th century. This makes the reflective appearance of the sequins even more remarkable.

An enclosed garden is a retable offering complex representations of an ideal, paradisiacal garden, often enclosed by painted side panels. These are unique form of mixed-media devotional art produced between 1530 and 1550 that appeared in the late medieval Low Countries [1,2]. The central section is an impressive combination of narrative sculptures, relics, hand-worked textiles, metallic elements and all kind of adornments. Although common in the past, only few of these stunning multi-material artefacts survived the test of time.

Metallic sequins appear as clothes ornaments and symbols of wealth throughout ancient history. In the middle ages, they were extremely popular as fashion accessory among nobility as well as decoration in religious art and liturgical fabrics [4], [5], [6], [7], [8]. Both in ancient and early medieval times, the sequins were usually made of gold or of gilded metal [9]. The use of gold granted both the characteristic reflective appearance and a certain exclusivity to the sequins. Between the 13th and the 14th century, cheaper metals, such as copper alloys, started being used for the production of sequins as well [8]. Initially linked to counterfeit, the mass production of cheaper shiny sequins likely turned into a parallel industry of its own [8]. Due to the low prestige of these objects compared to their gold counterparts, however, only very few clear mentions exist in the literature [10,11].

Apart from the sequins, the most common type of metallic objects found in the Enclosed Gardens are wires. These are used, alone or in combination with silk, to structure decorative elements and hang sequins and other adornments. If the sequins are in a pristine conservation state, the wires show an opposite situation, with heavy tarnishing and a complete loss of their metallic appearance. Despite the extreme differences in appearance, in-situ p-XRF analyses (discussed later in this work) showed that both sequins and wires are made of a brass alloy similar in composition.

Although brass was a valuable material in ancient history [12], it was widely spread during later periods becoming an cheap material used in daily life objects [13,14]. Brass is a relatively stable alloy of copper and zinc but it is sensitive to oxidation, tarnishing over time due to the interaction with the atmosphere [15], [16], [17], [18], [19], [20]. It is therefore unusual to observe centuries-old brass objects which appear almost completely untouched by the passing of time. Several factors, including changes in the composition and in the metallographic structure of the alloy, can have a significant positive or negative influence on the stability of brass [21], [22], [23]. In particular, the alloying with Zn increases the corrosion resistance compared to pure copper, but Zn percentages higher than ∼15% can induce a higher risk of dealloying, leading to a loss of mechanical and aesthetical properties [19,23,24]. The minor components of brass can also significantly affect the resistance to degradation. Among others, Ni, Sn, As and Al, in concentrations below 0.2–0.3%, can increase the stability of the alloy, while Fe and Pb might favor its degradation [21]. Clear information on the link between metallographic features and reactivity of brass are limited in the literature, however, an effect of average grain size and residual strain on the tendency of the alloy to undergo oxidation reactions can be expected. A smaller grain size and higher residual strain, in particular, can lead to an increased reactivity [21,25]. In a similar fashion, the surface morphology also plays a role in the corrosion of metal alloys, with an increase in roughness being linked to a higher tendency to corrode [26], [27], [28]. This is particularly evident in metals prone to passivation (similar to Cu alloys), especially when unidirectional roughness [27] or deep scratches [28] are present. Furthermore, different types of surface coatings (e.g. tinning, gilding, silvering) [20,[29], [30], [31] were also used since antiquity to improve and preserve the esthetic properties of Cu-alloy surfaces.

When it comes to metal sequins in particular, the information in the literature is sparse, and mostly limited to historical sources and few archeological findings [10,32,33]. Despite their popularity throughout human history, little is known about composition, metallography and stability of these objects. This study, therefore, represents a unique occasion to investigate and shed light on the material properties of this previously overlooked type of metallic ornament and, in general, on the stability of stamped brass elements.

Based on these premises, several fundamental research questions arise: why is the conservation state of wires and sequins so different even though they are made of a similar alloy and they were preserved in exactly the same environment? What is the secret behind the pristine appearance of the brass sequins even after five centuries of exposure to the environment?

Three possible reasons for the different conservation state were investigated in particular: 1) differences in the chemical composition of the alloy (Zn concentration and minor elements); 2) presence of a surface coating on the sequins (metallic or organic); 3) differences in the metallographic structure and surface morphology of the objects (role of the manufacturing process).

2. Research aim

In order to explain the main reasons of the exceptional preservation of historical brass pieces, an in-depth historical research was performed in combination with a multifaceted analytical approach to investigate the chemical composition (SEM-EDX, pXRF, FTIR and µ-Raman spectroscopy), metallographic structure (alcoholic ferric chloride etching followed by OM and SEM observation) and surface morphology (OM, SEM and AFM) to 65 non-degraded sequins and 19 degraded wires found in the same historical objects. Our results demonstrated how the manufacturing process, strongly affecting metallographic structure and surface morphology of the objects, ultimately determined the different conservation state of the analyzed pieces.

3. Materials and methods

Non-invasive p-XRF analysis were first performed in-situ on a total of 84 metallic objects (65 sequins and 19 wires) from 5 different Enclosed Gardens (Enclosed Gardens of Mechelen Hospital sisters, Museum Hof Van Busleyden, Mechelen, BE). A selected number of objects (21 sequins and 19 wires), representative of the different stylistic groups and chosen because easily removable from loose decorative elements, was then further studied in the laboratory by means of FTIR and µ-Raman spectroscopy, AFM, OM and SEM-EDX both on a surface level and in cross section. Metallographic analyses were also performed on these samples.

The portable X-Ray Fluorescence instrument Olympus-InnovX Delta Professional was used to perform in-situ measurements. This device generates primary X rays by means of a Rh-tube with a maximum acceleration voltage of 40 kV and a maximum beam current of 200 µA. All the analyses were performed at 40 kV with a 90 s Live Time. The software used for the qualitative and quantitative analysis was Innov-X Delta Advanced PC Software. The accuracy of the software for quantitative analysis was verified by analyzing the CHARM set of certified reference copper alloys. [34] The level of accuracy observed allows a meaningful comparison between the two groups of brass objects in exam (Table S1).

The FTIR spectra were collected with a spectrometer Bruker Alpha II equipped with a DTGS detector and a diamond ATR accessory. A total of 128 scans have been accumulated in each sample, using a resolution of 4 cm^{-1} and a wavenumber range between 4000 and 400 cm^{-1}. The spectra showed have not been corrected in order to avoid any kind of distortion.

Raman spectroscopy measurements were performed by means of a Xplora Plus Microscope (Horiba) under a 785 nm laser, considering the effective range of 150–1000 cm^{-1}. At each point, 5 accumulations were collected during 10 s each one. The spectra showed have not been corrected in order to avoid any kind of distortion.

The OM images were collected with an Olympus DSX510 digital microscope. Both bright field and polarized light modes at different magnifications were employed. The specific conditions for the single images are specified throughout the manuscript.

The samples were examined with a Field Emission Gun – Environmental Scanning Electron Microscope (FEG-ESEM) equipped with an Energy Dispersive X-Ray (EDX) detector (FEI Quanta 250, USA; at AXES and EMAT research groups, University of Antwerp), using an accelerating voltage of 20 kV, a take-off angle of 30°, a working distance of 10 mm and a sample chamber pressure of 10^{-4} Pa. Imaging was performed based upon secondary electrons (SE), back-scattered electrons (BSE). EDX point spectra were acquired, using a beam current of ~0.5 nA and a dwell time of 60 s per spectrum. The same beam current was used for EDX mapping. Different maps were collected at different resolution, with pixel size values from 18 to 420 nm and dwell time from 1 to 4 ms/pixel. The line scans analyses were performed with a spatial resolution of 500 nm.

The AFM instrument used during all experiments is the nanowizard 4™ with a manual stage (JPK BioAFM, Bruker). All imaging experiment were performed using a beam shaped cantilever on the AIO chip (cantilever D) which has a nominal spring constant of 40 N/m and a nominal tip radius of <10 nm (Budget sensors, Bulgaria) All images were acquired in the Quantitative Imaging® mode using a setpoint of 200 nN. Calculation of RMS roughness and processing of the images were performed in the JPK SPM DP software (v 6.1.163).

Selected fragments of the metallic objects in analysis were prepared for the metallographic analysis by first embedding them in acrylic resin (ClaroCit) since no infiltration of the resin inside the sample is expected [35]. The surface was then polished with silicon carbide discs, followed by diamond and alumina pastes.

The samples were then cleaned and chemically etched with an alcoholic ferric chloride solution (240 ml of ethanol - Supelco, ref. 8.18760 -, 60 ml of HCl - Sigma Aldrich, ref. 320,331 - and 20 g of $FeCl_3 \cdot 6H_2O$. The cross sections were immersed during 2 s in the etching solution and afterwards rinsed gently with water. They were then inspected with OM (Bright Field and Polarized light) and SEM.

4. Results and discussion

In order to facilitate the design of the experiments and the discussion of the results, the 65 sequins were divided in eight groups based on their macroscopic appearance (Fig. 1a-h). Some examples of metallic wires encountered in the Enclosed Gardens are also presented in Fig. 1i-k. All 19 wires and a selection of 21 sequins (taken from each group) were investigated both in- and ex-situ (Fig. 1l).

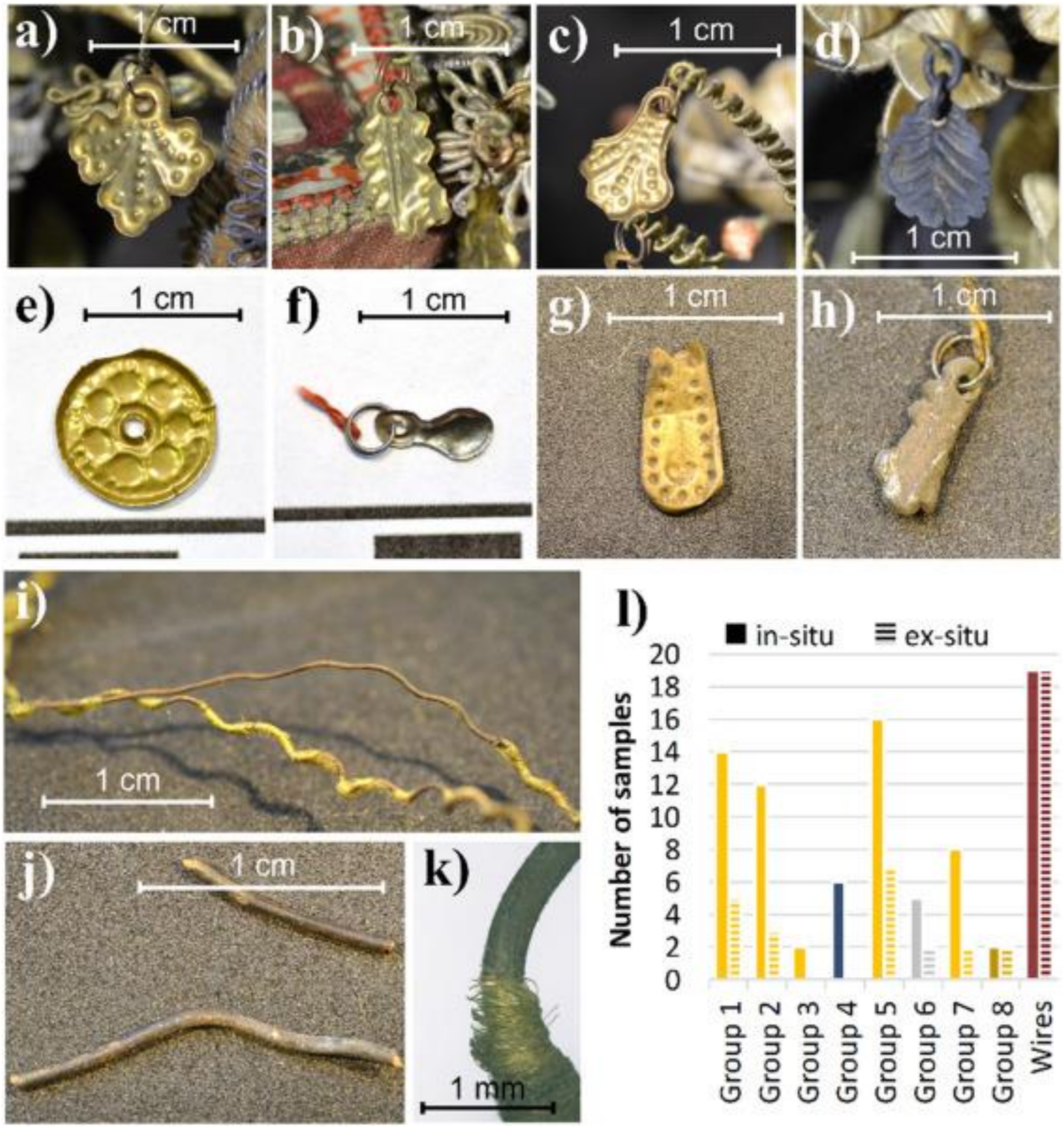

Fig. 1. Overview of the type of metallic objects in exam. Categories of sequins: a) Group 1, b) Group 2, c) Group 3, d) Group 4, e) Group 5, f) Group 6, g) Group 7 and h) Group 8. i), j) and k) examples of brass wires. l) Samples selected per category for in-situ and ex-situ analyses.

4.1. Chemical composition of the alloy and presence of surface coatings

The thorough elemental characterization performed in this study demonstrated that, despite the clearly different conservation state, no substantial systematic difference exists in the composition of brass sequins and wires (see SI Section S1 and Fig.S1). Both are made of an α-brass alloy with a medium-high Zn content (~20%), but always lower than 30%. This is in agreement with the composition normally encountered in historical brass (pre-19th century) produced with the cementation process [36]. The Zn content and the low impurity levels indicate a high-quality metal alloy, most likely produced starting directly from copper and zinc ores, and not by recycling existing brass objects [11]. Such an alloy, due to the complex and very technical nature of its production technique, would have been relatively expensive compared to other copper alloys or more impure brasses. For this reason, as seen in other late-medieval European findings, it was used mostly to produce liturgical and more luxurious objects [11,15]. However, when compared to gold, whose appearance was likely supposed to imitate, this would have been a much cheaper option.

The elemental and molecular analyses also demonstrated that neither gilding nor any other organic surface finishing observed in other historical metallic objects [37] is present on the sequins (see SI Section S2 and Fig. S2-S6). The only exception is a small group of sequins (3 objects) with a silver-like appearance, which showed residues of a tinning treatment. The use of brass and the complete absence of gold is in agreement with the choice of materials usually encountered in these shrines. Normally these are not, in fact, luxurious/exotic materials such as precious metals, but rather common and in some cases recycled [1,2].

In conclusion, the pristine conservation state of the sequins in the Enclosed Gardens cannot be explained by a difference in the chemical composition of the alloy nor by the presence of a protective coating.

4.2. Metallographic structure and surface morphology

Metallographic features, such as grain size, homogeneity and orientation [22], and surface properties, such as average roughness and the presence of deep scratches [26], [27], [28], can significantly affect the resistance to corrosion of metallic objects.

The metallographic analysis and microscopy investigations performed in this study highlighted striking differences in grain size, surface roughness and morphology for sequins and wires. The surface properties in particular, direct consequence of the distinct production processes for the two types of objects, are the ultimate reason for the differences observed in their conservation state.

In detail, the metallographic analysis of the wires (Fig. 2a and Fig. S7) showed recrystallized and twinned grains (average size from 9.3 µm to a maximum of 43.8 µm), with no clear elongation in the direction of drawing and no residual strain (see SI Section S3 and Fig. S7). In the sequins, on the contrary, the α-brass alloy is finely divided in micro-sized grains which are always smaller than in the wires (average size=5.4 µm). An extremely high amount of strain lines is also observed throughout the whole volume. Smaller grains and higher strain are often linked to an increased reactivity for metals susceptible to oxidation [21,25]. In this case, however, the smallest grains and the highest strain are encountered in the pristinely preserved sequins and not in the tarnished wires. It is true that, in an alloy prone to passivation, an enhanced reactivity would translate into a faster and more efficient passivation [25]. Nevertheless, no clear passivating layer is observed in the sequins. Therefore, the metallographic structure of the alloy does not seem to play a preeminent role in the conservation state of the objects. If this was the case, in fact, a higher level of tarnishing would be expected for the sequins rather than for the wires.

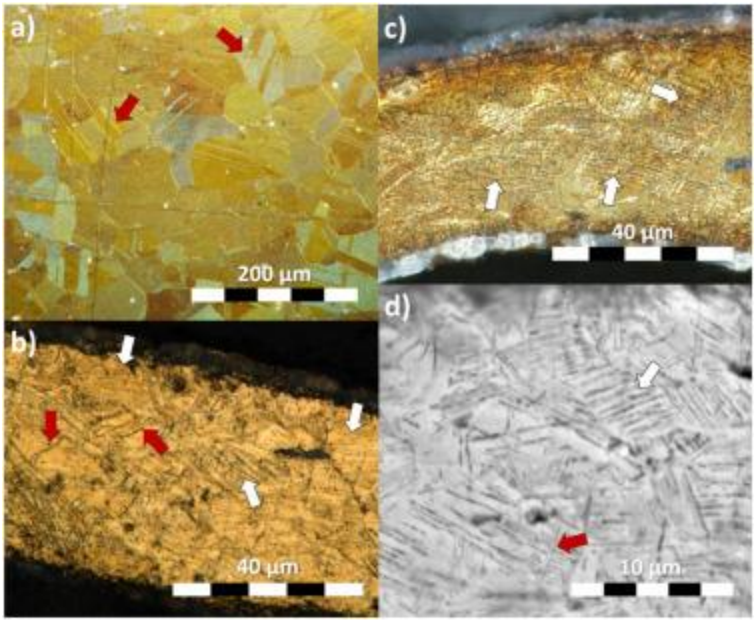

Fig. 2. Photomicrographs of the transversal cross-section of the samples after metallographic etching: a) wire, polarized light; b) Sequin (Group 5), bright field; c) Sequin (Group 1), polarized light; d) Sequin (Group 2), SEM secondary electron imaging. The main metallographic features are highlighted (red=twin lines; white=strain lines).

The microscopy analysis of the sequins showed that, on a microscopic level, the surface is not always as pristine as it appears macroscopically (Fig. 3a-c), although a clear difference remains when compared with the heavily tarnished surface of the brass wires (Fig. 3d-f). Furthermore, a connection between surface morphology and degradation can be noted in both cases. On the surface of the sequins, in fact, the distribution of the few corrosion products appeared linked to the few microscopic imperfections. In a similar fashion, on the wires the tarnishing clearly follows the direction of drawing (yellow arrows), which is also the direction along which most imperfections and irregularities are distributed [38].

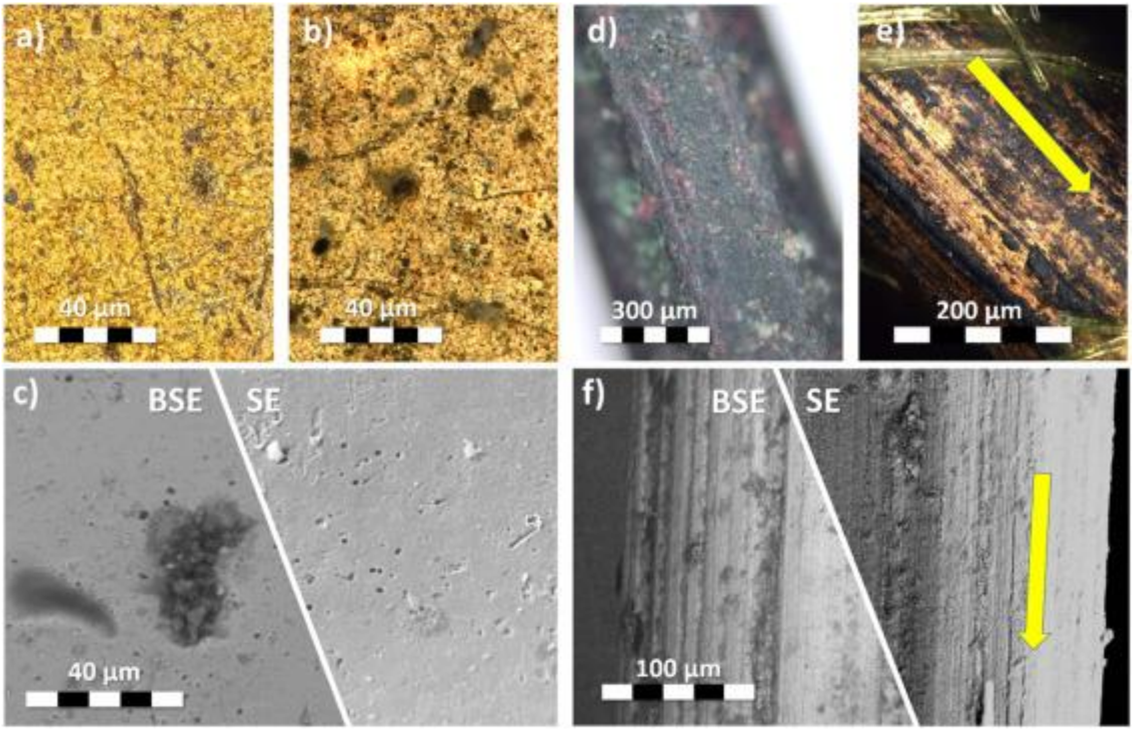

Fig. 3. Photomicrographs of the surface of some of the metallic samples in analysis. OM (a, b) and SEM (c) of macroscopically non-degraded sequins; OM (d, e) and SEM (f) of heavily tarnished wires. The direction of drawing of the wires is highlighted in yellow. BSE=back-scattered electrons, SE=secondary electrons.

In addition to the similarities in the spatial distribution, the degradation products on sequins and wires show also a similar composition (see SI Section S4 and Fig. S5-S9). In both cases, in fact, Cu, C, S, O and/or Cl, are mainly observed in the degraded areas (Fig. S5 and Fig. S6). These are elements normally encountered in the degradation products on the surface of historical copper alloys due to the interaction with environmental agents [16,17,39,40]. The presence of mostly oxides, chlorides and hydroxy-chlorides of copper on both sequins and wires is confirmed by Raman spectroscopy (Fig. S9). Al and Si containing dust is also observed (Fig. S5 and S8). These similarities suggest that the mechanisms responsible for the degradation of sequins and wires are likely the same, but on a significantly different scale.

The link between surface defects and tarnishing should be considered in conjunction with the different roughness and homogeneity of the surfaces of wires and sequins, highlighted by the AFM analysis (Fig. 4). These two factors together, in fact, substantiate a clear connection between the different surface morphology (Fig. 4a,b,c) and roughness (Fig. 4d) and the differences observed in the conservation state of the objects. The surface of the non-degraded sequins is smooth, non-porous and shows only few tiny imperfections (as seen in Fig. 3a,b,c, Fig. 4a and Fig. S6a). Such a smooth surface is different from the one the wires would have shown after being drawn, even before any oxidation process took place. The very act of drawing, in fact, often produces defects and imperfections developed in the direction of drawing [38]. The edge of the drawplates used to shape the wire tends to develop microscopic defects and imperfections as a consequence of usage [38]. These imperfections are transferred onto the wires while they are drawn, thus affecting the regularity of the circumference and the homogeneity of the surface. Such deep unidirectional scratches are clearly visible in the 3D-imaged surface of the samples in analysis (Fig. 4b,c). Their presence creates preferential spots for the degradation process to start [27,28], negatively affecting the overall stability of the wires. This clearly confirms the link between these imperfections and the longitudinal distribution of the corrosion products (Fig. 3e,f). It is important to notice that scratches with nanometric thickness were observed also on the surface of the sequins (Fig. 4a). However, these are much more superficial than in the wires and show no preferential orientation, hinting towards the handling and usage of the objects rather than their production.

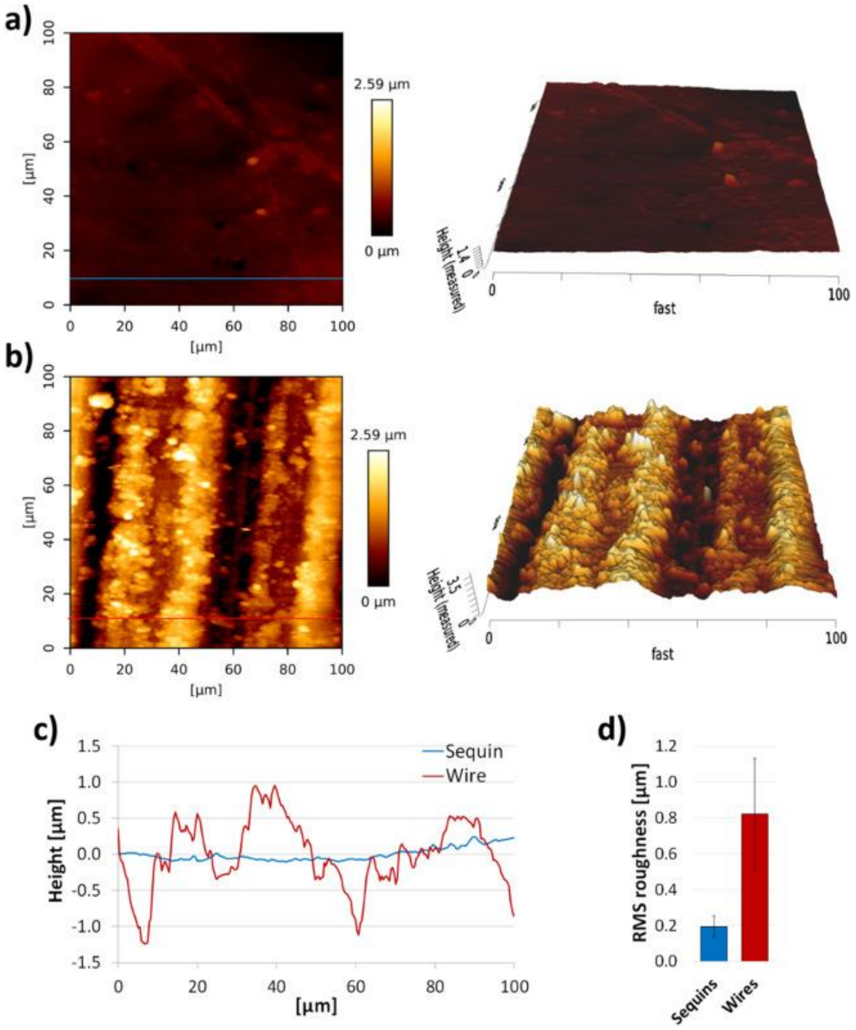

Fig. 4. AFM analysis. Representative height and 3D images for a) sequins and b) wires (the drawing direction is vertical); c) height profile along two lines (highlighted in a and b); d) average surface roughness (RMS) for all the areas considered (six for sequins and three for wires).

All things considered, the striking differences observed in the surface morphology of sequins and wires, which translate into a higher roughness and therefore a higher reactivity for the latter, justify the different appearance of the two types of objects despite their similar composition. The good surface properties alone, however, are not enough to explain the pristine appearance of the brass sequins. This is clear when we consider the conservation state of the small group of sequins made of silver (Fig. 1d). Despite being likely produced in a similar way as their brass counterparts, in fact, these appear completely tarnished. This is a result of the higher reactivity of silver in the conservation environment: large amounts of silk and other sulfur-containing proteinaceous textiles in a partially enclosed environment likely lead to a build-up of H_2S [41] and to the consequent formation of dark Ag_2S. Therefore, rather than by the mere surface morphology, the pristine conservation state of the sequins in the Enclosed Gardens of Mechelen is better described by a combination of relatively stable materials (brass with low Pb and impurities) and optimal surface properties. Both factors are needed to ensure such outstanding results.

It is important to mention that the difference in conservation state of sequins and wires might have also been intensified by the presence of textiles (mostly silk [1]) wrapped around the latter. The fibers in contact with the metal, in fact, could have negatively affected its stability due to the off-gassing of aggressive pollutants [41,42] or by increasing the retention of humidity [43]. However, since some of the heavily tarnished wires considered in this study were not wrapped in textile, this mechanism might have had a negligible effect on the degradation. The similar composition of the degradation products found on sequins and wires, both in contact and not in contact with silk (Fig. S5, S6, S8 and S9), confirms this hypothesis.

4.3. Historical manufacturing process of metallic sequins: uncovering the past

Ultimately, the optimal surface properties of the metallic sequins are undoubtedly a result of the way they were produced. On the basis of the experimental evidence just discussed, novel fundamental insights on the historical production method of these objects were obtained.

Different hypotheses on the manufacturing methods of metallic sequins exist in the literature. A first hypothesis, based on the interpretation of 15th century Italian notary deeds, describe a complex procedure involving several steps, including casting in specific molds, piercing and finishing through the use of hammers and plies [10]. In an opposite fashion, the only material analysis conducted on historical metallic sequins (from a 14th-century French copper-smith workshop) [33] suggests a much simpler process, involving a stamping step out of hammered metal sheets. This second process is also supported by historical sources, with a clear representation of such a practice in an illustration from the end of the 16th century in the House books of the Nuremberg Twelve Brothers Foundation [44].This technique presents interesting resemblances with a similar and better studied type of object: the thin, uni-faced medieval silver coins called bracteates [45]. Extremely diffuse in central and northern Europe, these coins were hammer-struck using only one coin die and pre-cutting a round flan from a thin metal sheet. A piece of soft material, such as leather or lead, placed on top or below the flan allowed to impress the design without using a two-part die.

Sequins were in high demand in Europe in the 15th-century [9,32,46] and were sold for low prices compared to the metals used to produce them [47], which supports the idea of a stamping process, fast and simple enough to allow a large scale production. The material evidence collected on the sequins described in this work confirms this hypothesis. In the first place, the micro size of the α-brass grains observed (Fig. 2b,c,d) suggests that several cold working/annealing steps were alternated in the process [48]. This indicates that the first phase was the battering of the metal to form thin sheets, as opposed to the casting mentioned in the Italian sources [10]. To obtain such a thin foil, in fact, an excessive hardening of the alloy should be prevented by annealing it [38]. This hammering/annealing step, followed by the pickling with an acidic solution, might have also caused a loss of Zn from the metal [23], justifying the slight dezincification observed on the surface of the otherwise pristinely preserved sequins. The use of a thermal treatment is confirmed also by the twin lines in several grains (Fig. 2b,d). The fact that these twin lines are frequently bent and that a high amount of strain lines is present in the grains through the whole volume, however, shows that the last step in the production of the sequins was some heavy cold-working [20,48]. This confirms that the sequins were produced by embossing the three-dimensional decors applying a strong pressure to the metal sheet, in a similar fashion to what observed for the bracteates. The much higher precision in the centering of the design observed for the sequins (Fig. 1) than for bracteates [49], however, suggests that in this case the embossing and cutting were realized in one single step. Such a procedure is normally referred to as blanking, and the sharp-edged punches needed to stamp out these three-dimensional forms are called blanking punches [38]. The use of this technique is confirmed also by the thinner and curved edges of the sequins (Fig. 1 and Fig. S10a,b), since the brass at the edges would have been strongly compressed between the die and the lead anvil just prior to fracture, and the presence of residual fragments of uncut metal sheet at the edge of some of the sequins (Fig. S10c).

A similar blanking process is proposed by Thomas et al. [33] for the medieval French sequins considered in their work. However, there is a significant difference in the thickness of these objects (≈ 200–400 μm) and the 16th-century sequins analyzed in the present work (≈ 25–50 μm). This suggests that the production process for sequins evolved over the centuries, not only towards an increasing complexity of the three-dimensional designs, but also towards a reduced thickness of the metal sheet used for the stamping, thus significantly decreasing the amount of metal needed to produce a single sequin. Such technological improvements possibly helped making the manufacture of brass sequins into a more profitable profession than in 15th-century Italy, where the manufacturers strove to make ends meet probably also due to the more complex and less efficient production process [10].

This production process played a fundamental role in determining the mechanical and surface properties of the objects. On one hand, despite the limited thickness, the stamping process and lack of a final annealing step granted the objects a certain residual strain and rigidity, fundamental for them to be hung in the altarpieces and to maintain their shape over time. On the other hand, the pressure needed to impress the three-dimensional design and shear the sequin out of sheet metal produced the smooth homogenous surface behind their pristine appearance.

5. Conclusions

The multifaceted analytical approach discussed in this manuscript allowed to expose the material properties behind the extraordinarily pristine conservation state of the brass sequins in the 16th century Enclosed Gardens of Mechelen.

The main reason why these objects survived so surprisingly well the test of time is a combination of good quality materials (low Pb and impurities) and optimal surface properties (low roughness and no scratches or imperfections). These qualities are a direct consequence of their manufacturing process and a clear manifestation of the high level of expertise of the craftsmen who produced them.

It is a widely accepted concept that late- and post-medieval craftsmen were well-aware of the effect the composition of the brass alloy would have on its mechanical and aesthetical properties [11]. This clearly emerges also from the results of the present study. The composition of the brass alloy, in fact, is ideal when it comes to the plastic properties needed for the stamping of sequins and the drawing of wires, as well as to obtain a material resembling gold. Evidently, the artisans who produced the objects in analysis were skilled and had a great knowledge of the properties of brass, and this likely played a key role in the history of sequins. Such mastering of brass technology, in fact, allowed to optimize the manufacturing process, making the use of brass more profitable and thus offering a concrete, cheaper but high-quality alternative to gold. This transition from more expensive towards cheaper materials is historically extremely relevant, since it represents a first fundamental step towards sequins becoming the universal fashion accessory they are nowadays.

The key role played by the final steps of the manufacturing process on the long-term stability of the brass alloy is revealed. It cannot be inferred, however, whether or not the craftsmen were fully aware and concerned with the effect of the production process on the stability of the objects. The sequins were stamped out of a very thin sheet of metal, much thinner than for the only sequins previously studied in depth (produced in Paris in the 14th-century). The heavy cold work needed to obtain such a thin material, together with the pressure involved in the stamping process, produced a highly strained structure, but also an extremely smooth and homogenous surface with few to no imperfections. The compositionally similar brass wires, on the other hand, shaped through several drawing/annealing cycles, show defects and deep scratches developed in the direction of drawing that created preferential points for the degradation to start, negatively affecting the overall stability of the objects. In this context, the choice of manufacturing process was most likely subordinated to the achievement of specific mechanical and aesthetical properties. Therefore, the effect these methods had on the surface properties and long-term stability of the alloy, positive in the first case and negative in the second, were probably not the main concern of the artisans that produced them. This means that, although the composition of the alloy and the expertise of the craftsmen undoubtedly played a fundamental role, the exceptional long-term stability of the sequins might not have been fully foreseeable at the time of their production.

Additionally, this work represents a significant step towards a deeper understanding of the long-term behavior of α-brass, in particular in an indoor environment. The results show how historical brass can still present unaltered aesthetical properties after a five-century long exposure to the environment, even when the Zinc content is above the arbitrary 15% limit that conventionally defines alloys at high risk of dezincification. Such information has a clear relevance well beyond the field of conservation science and cultural heritage.

Furthermore, the novel insights obtained on the historical manufacturing process of metallic sequins, shed light on a key-moment in the evolution of this preeminent fashion accessory recurring throughout human history.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Acknowledgments

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Appendix.

Supplementary Material for

All that glitters is not gold: unraveling the material secrets behind the preservation of historical brass.

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This file includes:

- Supplementary text
- Figures S1 to S10
- Table S1
- Supplementary References

Supplementary Text

S1_Chemical composition of the alloy. The in-situ p-XRF analysis confirmed that the large majority of sequins and wires is made of brass (78 out of 84 objects). The only exception are six silver sequins, all belonging to the stylistic Group 4 (Fig. 1d), which also appear completely tarnished in contrast with the other sequins. Since the main aim of the study is to explain the conservation state of the well-preserved brass sequins, these few degraded silver objects have been excluded from further analysis.

The remaining brass sequins show a pristine conservation state and a reflective appearance, with only seven presenting localized signs of degradation. These tarnished sequins do not belong to one specific stylistic group, but they rather represent isolated exceptions belonging to different groups (one in Group 1, one in Group 2, two in Group 5, two in Group 7, one in Group 8). The wires, albeit appearing systematically and significantly tarnished, show a similar bulk composition to the sequins (Fig. S1).

The content of Zn (Fig. S1b) appears lower in the bulk of the wires (~15%) than in the sequins (~20%). Such a difference is not clearly visible in the p-XRF results likely due to the contribution of the tarnished layer on the surface of the wires. A higher Zn content is normally associated to a higher tendency to degrade, with the conventional safety “threshold” set at 15%[1]. Since the sequins show a higher Zn concentration, but also a much better conservation state, the Zn content does not seem to play a preeminent role in the long-term stability of these objects.

On the other hand, the concentration of minor elements in all the samples is so low that they most likely represent impurities in the starting ores rather than intentional additions[2–4]. Pb is the impurity in the highest proportion. In small amounts it can improve the machinability of brass but in larger than few percentage points it negatively affects the aesthetical and mechanical properties[3]. Since Pb is not soluble in the brass alloy and therefore is sparsely distributed in the volume[5], the p-XRF bulk results represent a better estimate of the real average concentration (Fig. S1a). The large majority of samples contains less than 1% Pb, low enough to be certainly not voluntarily added[2] and to not affect negatively the properties of the alloy. Such a low-Pb alpha brass alloy, in fact, would have had a golden color and ideal mechanical properties for the drawing of wires as well as for the battering of thin sheets[3,6]. The other minor components observed in the samples are Fe, Sn and Ni. Fe is often present as an impurity in historical brasses[2,5] and it can lead to a decrease in the resistance to corrosion of both alpha and beta phases[7]. In an opposite fashion, Ni and Sn concentrations might increase the resistance to corrosion of brass alloys[7]. Similar amounts of Fe and Ni are observed in the two different groups of objects. Sn is certainly present only in few tarnished wires and non-tarnished silver-colored sequins (Group 6, Fig. 1f). Few wires show Sn concentrations high enough to potentially have a positive effect on the long-term stability of the alloy. Since these wires appear as heavily tarnished as all the others, Sn does not play an active role on the long-term stability of these objects.

S2_Presence of surface coatings on the sequins. The results of the ATR-FTIR analysis allow to discard the presence of a varnish or any other organic protective layer on the outer surface of the sequins (Fig. S2).

The spectra show mainly the presence of silicates, resulting from dust, and carboxylates, resulting from the reaction between the dust and the fatty acids deposited on the surface when the pieces were touched with bare hands. The presence of carboxylates can be seen at 2919 and 2850 cm^{-1} (C-H stretching from CH_2 groups) and 1590 and 1418 cm^{-1} (asymmetric and symmetric stretching of COO^- groups). The bands related to silicates are found at ≈3300 (O-H stretching) and ≈1100 cm^{-1} (Si-O stretching)[8,9]. Additionally, there are smaller amounts of free fatty acids (band at 1739 cm^{-1}, C=O stretching) and oxalates (1321 cm^{-1}, C-O stretching), related to the degradation of organic compounds[10–12].

In any case, the FTIR signal has very low intensity, indicating that these compounds are found in a very low amount. Given the surface nature of the technique, if any varnish (original or subsequently added) was present on the surface of the sequins a much higher signal would be expected (e.g. in the C=O stretching region and in the C-H stretching regions).

The possible presence of a metallic coating was investigated by means of p-XRF and SEM-EDX analysis. In the first place, it is particularly relevant to notice that no gold was detected in any of the sequins. This excludes the possibility of a gilding treatment being responsible for the gold-like appearance.

A protective surface coating, and in particular a tinning treatment, was observed only on three sequins. These are samples that also show a different macroscopic appearance compared to the gold-like majority of the sequins: two silver-looking sequins belonging to the stylistic Group 6 (Fig. 1f), which were already found to have small amounts of Sn also in the bulk of the alloy (Fig. S1b), and one tarnished sequin belonging to the stylistic Group 8 (Fig. 1h). A thin discontinuous Sn layer was observed on the surface of these samples (Fig. S3). The limited thickness of the Sn layer suggests that the finished objects might have been tinned through a galvanic process, such as contact tinning, rather than through hot tinning with molten Sn[13]. Such a process, already well-known in medieval Europe[13], produces extremely reflective but also very thin finishing layers completely covering the surface of the object. Due to the very thin nature of the coating, the Sn layer appears discontinuous and completely abraded in the areas where slight friction took place (Fig. S3d,e).

The results for all the other sequins show some differences between bulk and surface composition, but no clear protective surface layer (Fig. S4). The main systematic difference observed is a decrease of the Zn concentration on the surface, not only for the sequins but also for the wires. The leaching of a portion of Zn from the surface of Cu/Zn alloys due to the interaction with the environment is a widely documented phenomenon[2,14–18]. Zn, in fact, is more readily oxidized than Cu, can form soluble degradation products when interacting with the environment (e.g. Zn chlorides and hydroxides[1]) and can migrate, to a certain extent, through the metallic lattice of the alloy[14,15,17]. The level of dezincification in the samples in analysis, however, is much less pronounced than the one normally described in the literature on both modern and archaeological brasses[16,18,19]. In both sequins and wires, in fact, the average Zn concentration is only 15% lower on the surface than in the bulk, and the dezincification only affects the outermost 5-10 µm (Fig. S4b). This is an extremely important detail when it comes to the macroscopic appearance and aesthetical qualities of the sequins. Even when degradation products are not present on the surface of the samples, in fact, the dezincification of brass alone might negatively affect the aesthetical properties of the alloy. In particular, the leaching out of part of the Zn might shift the color of the alloy from a yellow/gold-like color towards a more reddish/copper-like hue[1]. In this specific case, however, the Zn fraction on the surface remains high enough (16.2 wt% on average) for the alloy to still preserve its gold-like appearance.

The lower level of dezincification observed in the samples might be due to the fact that the Enclosed Gardens' environment (indoor and partially enclosed) is not as aggressive towards the metal as the ones usually considered in the literature (e.g. seawater, soil, acidic solutions)[16,18,19]. The selective solubilization of Zn from the most superficial layers of the alloy is in fact the first phase of brass dealloying, followed only in a later stage by the formation of Cu-rich deposits[14,17].

On one hand, a non-corrosive atmosphere could therefore explain the small scale of the dezincification observed. On the other hand, however, a chemical interaction in a relatively dry environment should have left nonetheless some Zn degradation products and a clearer degradation layer on the surface[14,15,20]. This is the case for the wires, where a thick crust with a layered structure is visible (Fig. S5b and Fig. S6d,e), but not for the sequins, where only small amounts of extremely thin and localized degradation products are visible (Fig. S5a and Fig. S6a,b,c). The dezincification not associated to a clear degradation layer in the sequins might also be a result of their production process. Procedures such as intensive hammering and annealing, necessary to produce thin sheets of metal and often followed by pickling in acidic solutions, can in fact also lead to a loss of Zn from the alloy[1,21].

S3_Metallographic analysis of the wires. The metallographic analysis of the wires showed some differences in grain size but overall similar features in all the samples (Fig. 2a and Fig. S7).

All the wires show recrystallized and twinned grains, with no clear elongation in the direction of drawing. The presence of annealing twins is not surprising, since the wires are normally annealed in between the different drawing stages in order to maintain a certain plasticity[22]. Such a cyclic alternation of thermal treatment and cold working reduced the size of the grains to few tenths of microns on average (from a minimum average diameter of 9.3 µm to a maximum of 43.8 µm). As expected, the thinnest wires present also the smallest grain sizes (Fig. S7), due to the higher number of cycles they were subjected to. The lack of elongation and the absence of visible residual strain suggests that the last step of the production was either the annealing of the wire or a very light cold work. This would have produced extremely ductile wires, with the necessary plasticity to build the complex structure of the fine floral decorative elements in the Enclosed Gardens. Some of the smallest wires show a certain amount of strain lines in the most superficial grains (Fig. S7). This might be the result of a final drawing step but might also be due to the folding of the wire while assembling the decorative elements. Either way, this limited amount of strain would not significantly affect the overall mechanical properties of the wire.

S4_Degradation products on the surface of sequins and wires. Only small amounts of extremely localized corrosion products (Fig. S5a and Fig. S6a) or, in the few macroscopically degraded samples, thin degradation layers (Fig. S6b and c) are observed on the surface of the sequins. These contain mostly Cu, C, S, O and/or Cl. In the wires, on the contrary, a thick crust with a layered structure is visible (Fig. S5b and Fig. S6d,e). In detail, an inner Zn- and Cl-rich layer is present, which is covered by a series of overlapping layers containing mostly Cu and Cl, O and S respectively. In general, S is more systematically present than Cl in both types of objects (Fig. S8). This is possibly a result of the large presence of silk and other proteinaceous textiles (felt, wool) containing sulfur in the Enclosed Gardens.

µ-Raman analyses on the degraded areas of sequins and wires (Fig. S9) confirmed the hypothesis that similar degradation mechanisms take place on the two different types of objects. Since all the samples showed an intense fluorescence band above 1000 cm^{-1}, only lower frequencies are shown. In this region some characteristic bands can be observed, which highlight striking similarities on a molecular level between the degraded areas of sequins and wires. These results complement the elemental similarities previously described.

In detail, the main band appears at 286 cm^{-1} and has been assigned to CuCl[23]. Other minor signals can also be noticed, around 515 cm^{-1} (probably related to $Cu_3Zn(OH)_6Cl_2$)[23], at 458 cm^{-1} (probably related to $Cu_2Cl(OH)_3$, mainly found on the sequins)[24] and around 630 cm^{-1} which, together with the shoulder at 220 cm^{-1} is probably linked to the presence of Cu_2O[24]. Following the SEM-EDX analysis, additional compounds containing S would be expected. The lack of Raman signals related to these compounds is likely due to the fact that these tend to fall at higher wavenumber and thus, in this case, they are likely hidden by the fluorescence band[25].

The analyses show also the presence of Al and Si on the outer surface of most sequins and wires (Fig. S8), mostly in combination with O in what appears as a surface deposit (Fig. S6), in agreement with the FTIR data (Fig. S2). Al, unlike Si, appears to be present not only on the surface, but also in the bulk of both sequins (tarnished and non-degraded) and wires (Fig. S8). Al is an element often added to brass in order to improve its resistance to degradation, due to its tendency to form a passivating Al_2O_3 layer on the surface of the metal[26]. The addition of Al to brass, however, is a modern practice and the amount of Al added in order to obtain a protective effect is much larger (~2 wt%) than the one encountered in all the samples[27].

Based on this evidence there are three possible reasons for the presence of an Al- and O-rich layer on the surface of sequins and wires. The first hypothesis is that the Al observed in cross-section is the result of a contamination during the preparation of the samples. An alumina sub-micron sized powder was in fact used during the mechanical polishing and it might have been partially embedded in the soft metal. This contamination might also account, at least in part, for the higher Al concentration observed on the surface of the objects in cross section. The Al_2O_3 polishing paste might in fact accumulate at the interface between the metal and the resin due to the presence of discontinuities and cracks. However, since Al was observed on the surface of most samples even before embedding them, a certain amount of Al is undoubtedly present on the surface of the objects and is not a product of contamination. A second possibility is that the Al rich layer observed on the surface is the result of the deposition of Al-containing dust. The presence of high levels of Al in the dust of the Enclosed Gardens would not be surprising. The very large amount of textiles in the gardens, in fact, were most likely dyed using alum as a mordant (the most commonly used mordant in antiquity) and are now heavily oxidized, embrittled and pulverized. A third hypothesis is that Al is actually present in the bulk of the metal as yet another minor impurity rather than as a voluntary addition, and that small amounts of Al_2O_3 are formed on the surface during the oxidation of the alloy. Since similar amounts of surface and bulk Al are present both on non-degraded and heavily tarnished objects (Fig. S6 and Fig. S8), however, this process clearly does not play a significant role in the different conservation state of sequins and wires. All things considered, it is not unlikely for the real situation to be a combination of these three possible scenarios. What is certain, however, is that the Al distribution cannot account for the different appearance of sequins and wires.

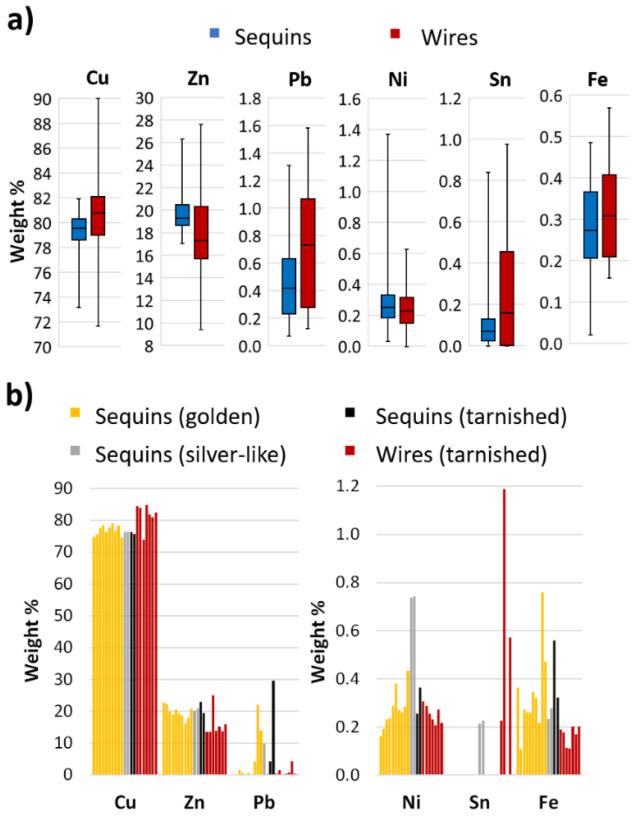

Fig. S1. Elemental composition of the brass samples: a) p-XRF results (78 objects), box-plots; b) SEM-EDX results in cross section, average of 20 points (10 µm long line) in the bulk of the object.

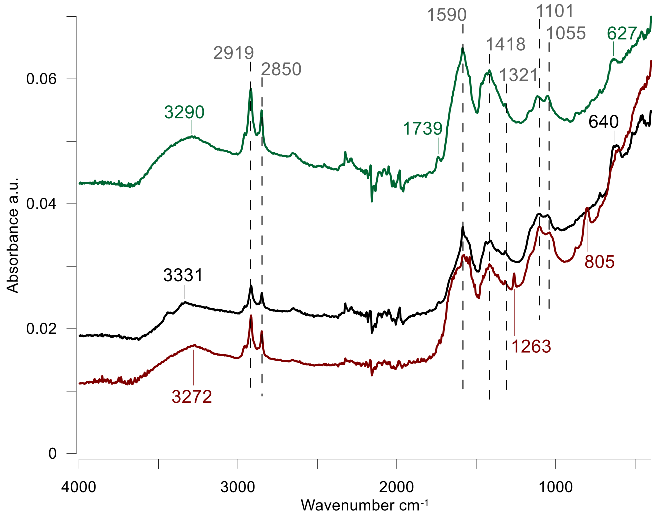

Fig. S2. ATR-FTIR analysis: typical spectrum for the pristinely preserved sequins. The spectra of three sequins are displayed, the dashed lines indicate the bands present in all spectra.

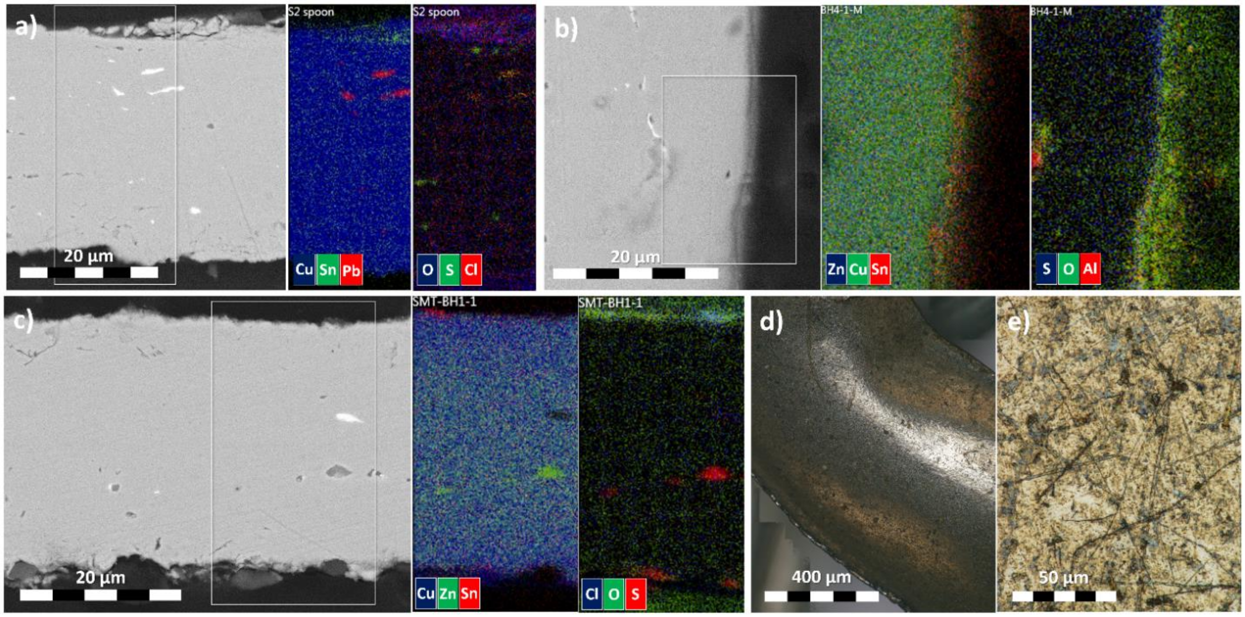

Fig. S3. Partially abraded and oxidized remnants of a tinning treatment on the surface of three sequins: a,b,c) SEM-EDX in cross-section of two non-degraded, silver-like sequins (stylistic group 6) and one tarnished sequin (stylistic group 8); d,e) microphotographs of a macroscopically non-degraded sequin (Stylistic group 6).

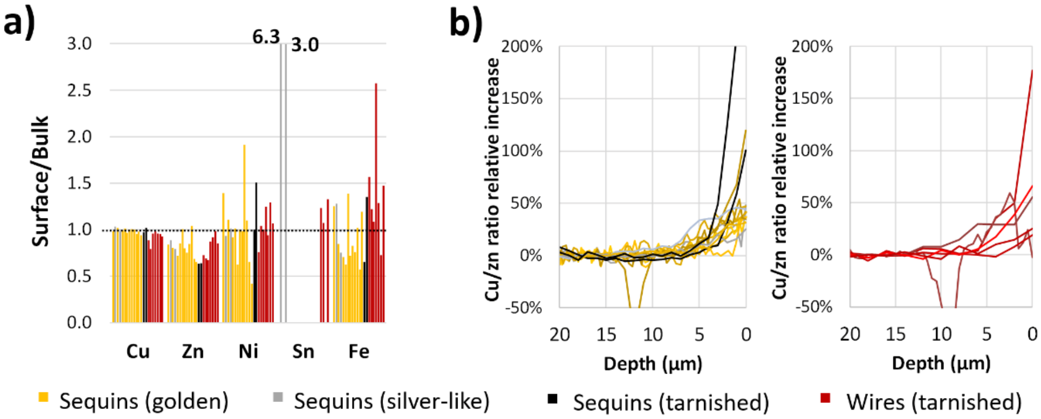

Fig. S4. SEM-EDX elemental analysis in cross section: a) ratio between surface and bulk concentration (average of 20 points, 10 µm long line across the outer surface of the object and in the bulk); b) Relative increase in the Cu/Zn ratio from the bulk to the surface of the samples.

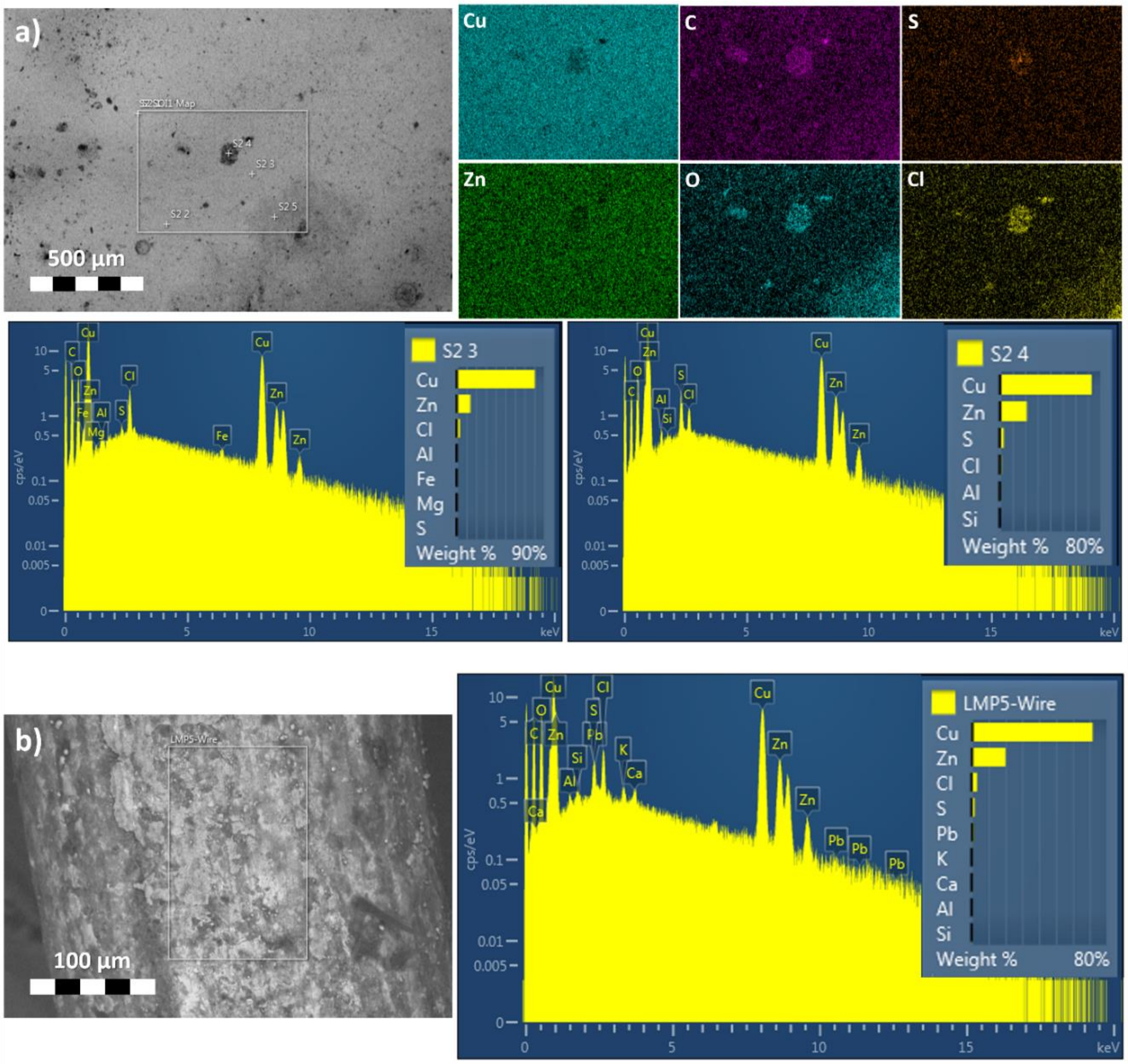

Fig. S5. SEM-EDX elemental surface analysis of a) a macroscopically non-degraded sequin (Group 5) and b) a heavily tarnished wire.

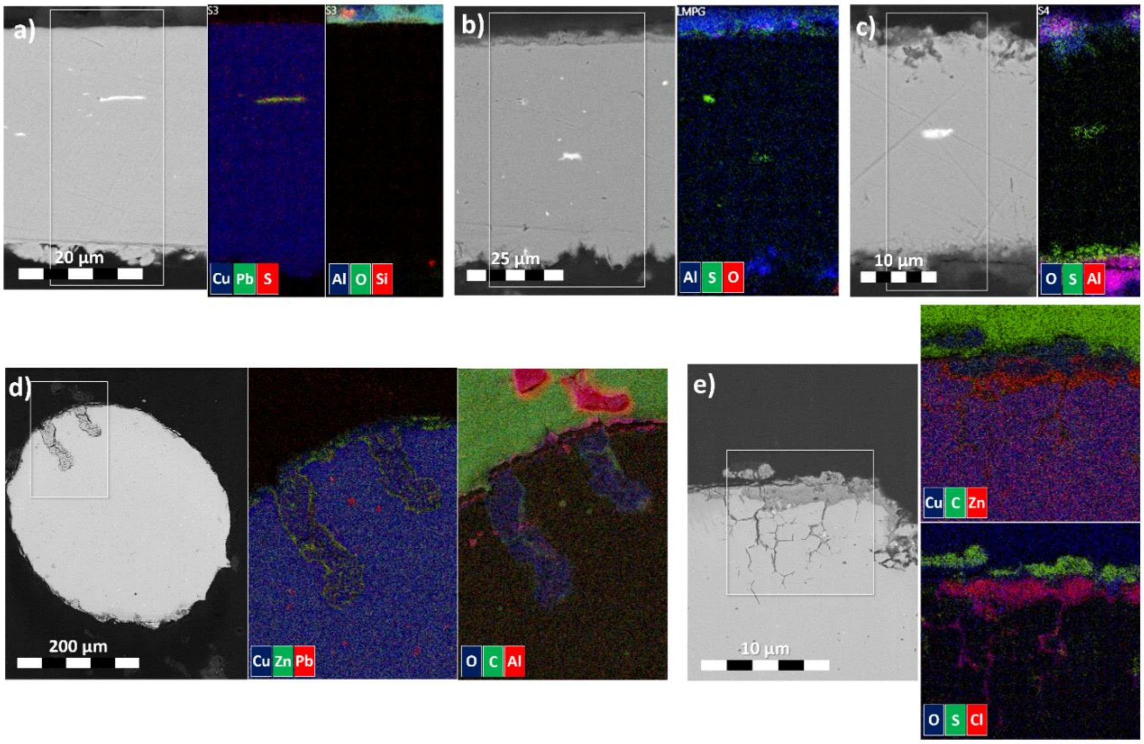

Fig. S6. SEM-EDX elemental surface analysis of a) a macroscopically non-degraded sequin (Group 5) and b) a heavily tarnished wire.

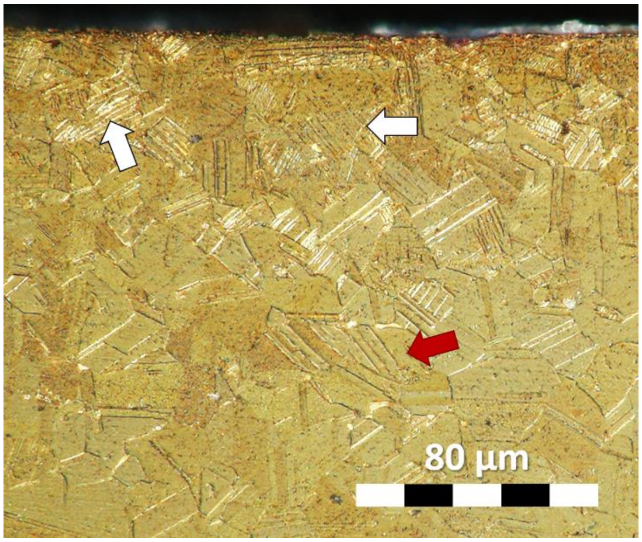

Fig. S7. Photomicrographs in polarized light of the transversal cross-section of one wire after metallographic etching. The main metallographic features are highlighted (red=twin lines; white=strain lines).

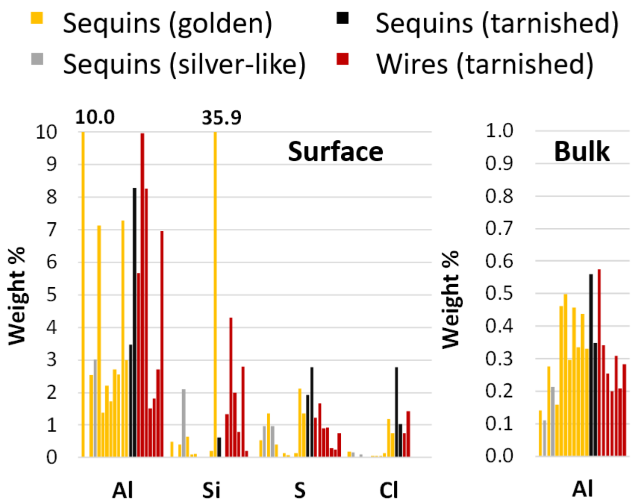

Fig. S8. SEM-EDX results in cross section: average surface and bulk concentration of elements linked to degradation or surface deposition.

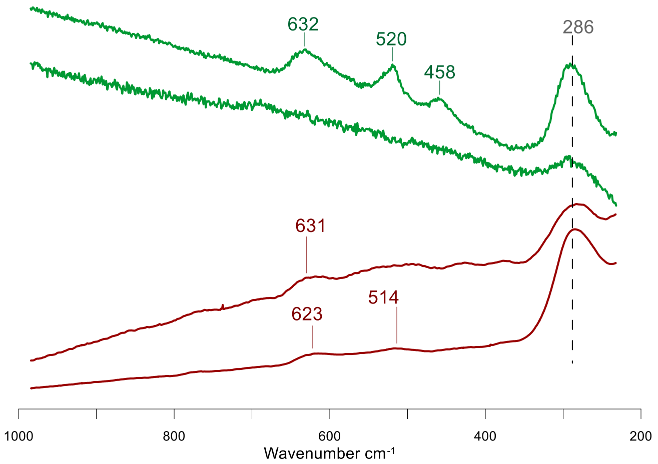

Fig. S9. μ-Raman spectra of the degradation products on the sequins (green) and the wires (red).

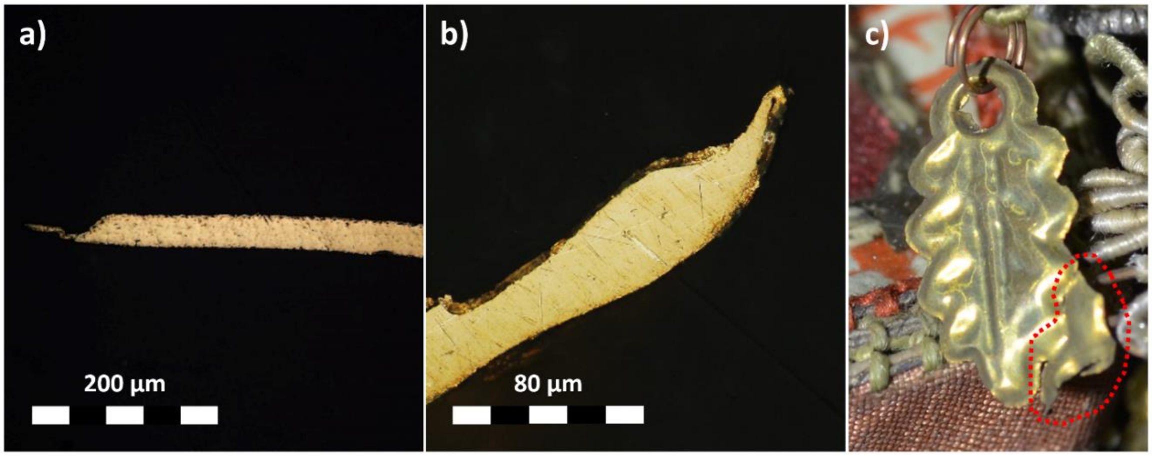

Fig. S10. a), b) Photomicrographs of the thinner outer border of two different sequins in cross section; c) detail of an imprecisely cut sequin, in evidence the presence of a residual fragment of metal sheet still attached to the edge of the object.

Table S1. p-XRF control analysis conducted on the CHARM set of reference copper alloys[28] for the elements of interest in this study. Measured = experimental concentration in weight % (average ± standard deviation of triplicate measurements); Certified = certified concentration in weight %; Error = measured value - certified value.

		Fe	**Ni**	**Cu**	**Zn**	**Sn**	**Pb**
CHARM #1	Measured	0.02±0.00	0.22±0.03	73.46±0.06	21.79±0.03	0.44±0.01	2.91±0.07
	Certified	0.04	0.16	72.70	21.55	0.45	3.22
	Error	**-0.02**	**0.06**	**0.76**	**0.24**	**-0.01**	**-0.31**
CHARM #3	Measured	0.05±0.00	0.17±0.00	61.95±0.02	35.58±0.02	0.11±0.00	0.53±0.00
	Certified	0.09	0.11	61.49	35.62	0.13	0.58
	Error	**-0.04**	**0.06**	**0.46**	**-0.04**	**-0.02**	**-0.05**
CHARM #5	Measured	0.83±0.01	0.22±0.00	81.48±0.08	4.91±0.01	4.18±0.01	5.41±0.09
	Certified	0.69	0.20	78.86	4.96	4.50	7.53
	Error	**0.14**	**0.02**	**2.62**	**-0.05**	**-0.32**	**-2.12**
CHARM #6	Measured	0.43±0.00	0.32±0.00	86.18±0.04	2.07±0.01	6.72±0.01	1.66±0.02
	Certified	0.37	0.30	85.73	2.00	6.78	1.64
	Error	**0.06**	**0.02**	**0.45**	**0.07**	**-0.06**	**0.02**
CHARM #9	Measured	0.04±0.00	0.29±0.00	82.20±0.02	1.24±0.01	12.37±0.03	2.19±0.01
	Certified	0.04	0.28	81.21	1.14	12.45	2.31
	Error	**0.00**	**0.01**	**0.99**	**0.10**	**-0.07**	**-0.12**
CHARM #10	Measured	0.10±0.00	1.56±0.00	84.53±0.10	5.90±0.02	2.84±0.03	4.95±0.06
	Certified	0.09	1.48	84.02	5.90	3.02	5.27
	Error	**0.01**	**0.08**	**0.51**	**0.00**	**-0.18**	**-0.32**

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