Case study: **Enclosed Gardens of Mechelen**

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Introduction

Upon visual observation, one of the predominant features in the Enclosed Gardens is the presence of hundreds of round and leaf-shaped sequins with an extremely reflective appearance. 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).

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 showed that both sequins and wires are made of a brass alloy similar in composition.

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 (1, 2). 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 (3,4). 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 (5,6) Furthermore, different types of surface coatings (e.g. tinning, gilding, silvering) (7) were also used since antiquity to improve and preserve the aesthetic 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 archaeological findings. Despite their popularity throughout human history, little is known about composition, metallography and stability of these objects.

Objectives

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).

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.

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. The level of accuracy observed allows a meaningful comparison between the two groups of brass objects in exam.
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 to 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 seconds each one. The spectra showed have not been corrected in order to avoid any kind of distortion.

Results and discussion

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 (Fig. 1).
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(8). 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(9). 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 (1, 9). 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 or inorganic surface finishing is present on the sequins (Fig. 2 and 3)
Metallographic structure and surface morphology. Metallographic features, such as grain size, homogeneity and orientation, and surface properties, such as average roughness and the presence of deep scratches(5,6), 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 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 (Fig. 4). 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).

The microscopy analysis of the sequins showed that, on a microscopic level, the surface is not always as pristine as it appears macroscopically, although a clear difference remains when compared with the heavily tarnished surface of the brass wires (Fig. 5).
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. 6). These two factors together, in fact, substantiate a clear connection between the different surface morphology (Fig. 6a,b,c) and roughness (Fig. 6d) 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 Fig. 6a). Such a smooth surface is different from the one the wires would have shown after being drawn, even before any oxidation process took place.

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.
The material evidence collected on the sequins described in this work confirms that several cold working/annealing steps were alternated in the process. The first phase was the battering of the metal to form thin sheets, followed by the pickling with an acidic solution, 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.

Conclusion

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. The key role played by the final steps of the manufacturing process on the long-term stability of the brass alloy is revealed.
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.

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Tables, figures and graphics

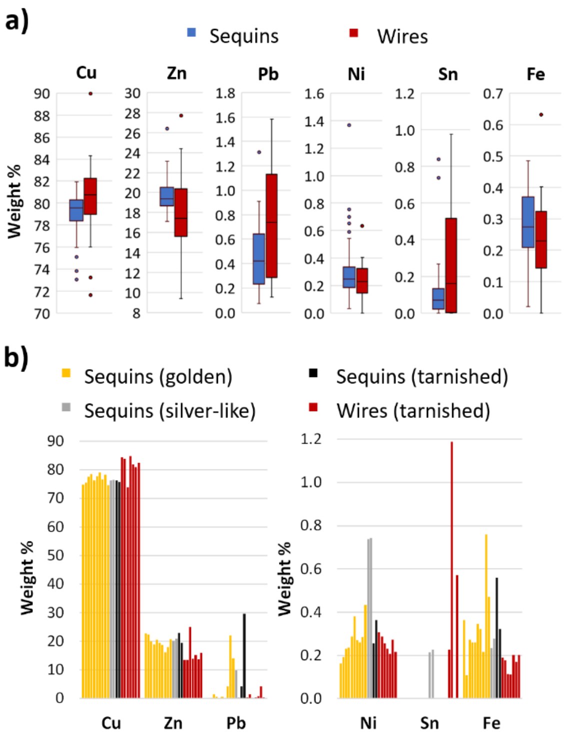

Fig. 1. Elemental composition of the brass samples: a) p-XRF results (78 objects), box-plots; b) SEM-EDX results in cross section, average of 20 points (10 µm long line) in the bulk of the object.

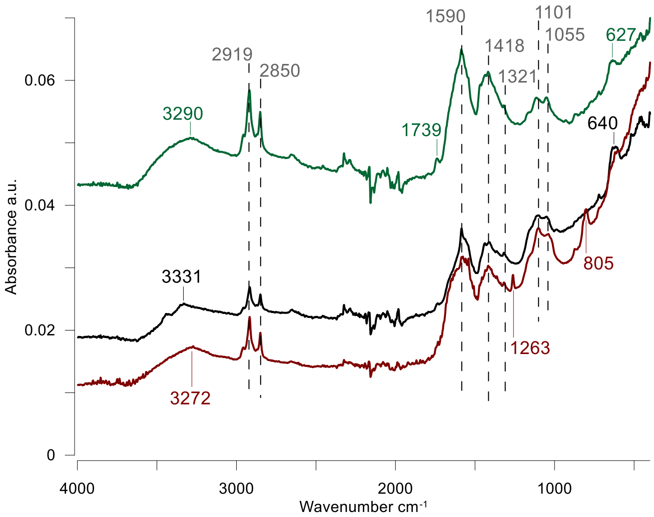

Fig. 2. ATR-FTIR analysis: typical spectrum for the pristinely preserved sequins. The spectra of three sequins are displayed, the dashed lines indicate the bands present in all spectra.

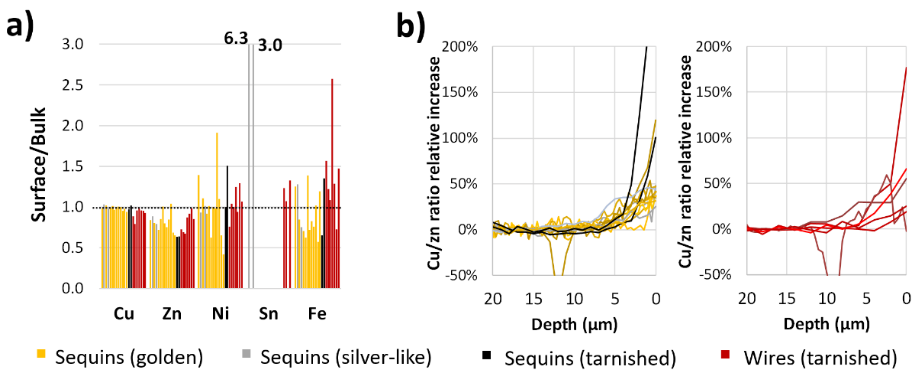

Fig. 3. SEM-EDX elemental analysis in cross section: a) ratio between surface and bulk concentration (average of 20 points, 10 µm long line across the outer surface of the object and in the bulk); b) Relative increase in the Cu/Zn ratio from the bulk to the surface of the samples.

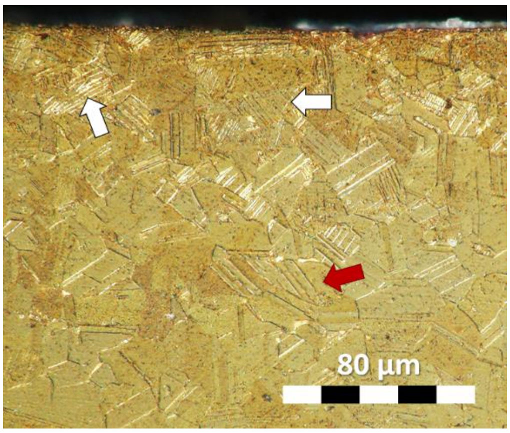

Fig. 4. Photomicrographs in polarized light of the transversal cross-section of one wire after metallographic etching. The main metallographic features are highlighted (red=twin lines; white=strain lines).

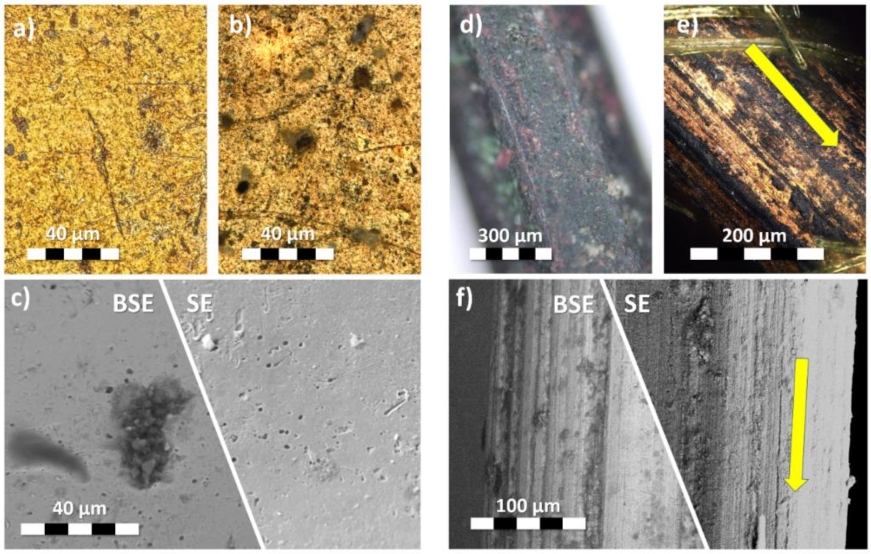

Fig. 5. Photomicrographs of the surface of some of the metallic samples in analysis. OM (a, b) and SEM (c) of macroscopically non-degraded sequins; OM (d, e) and SEM (f) of heavily tarnished

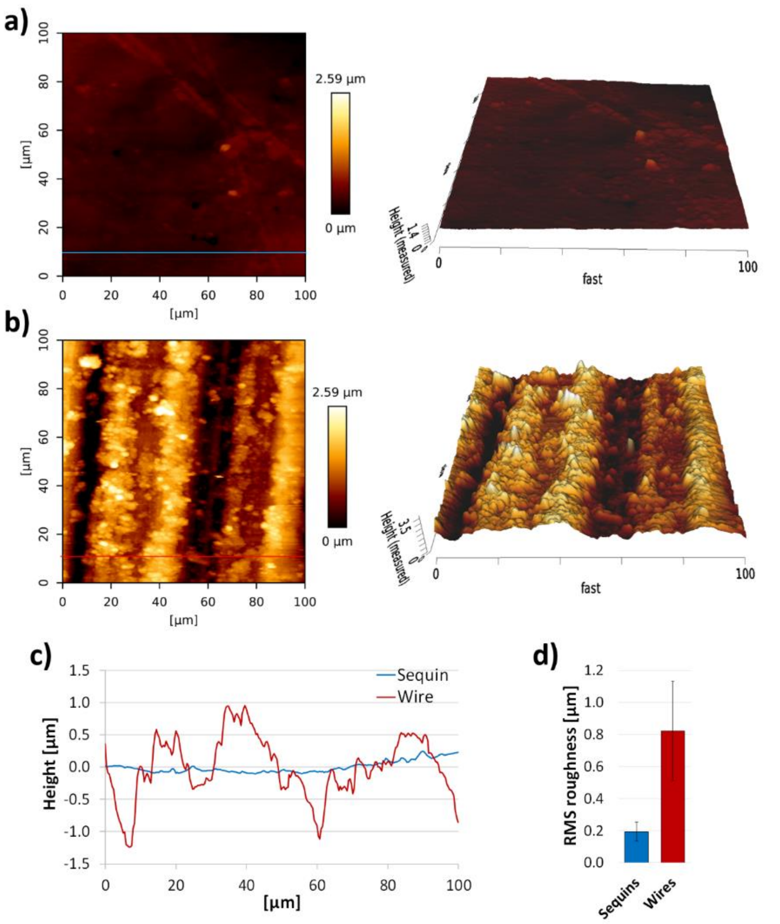

Fig.6. AFM analysis. Representative height and 3D images for a) sequins and b) wires (the drawing direction is vertical); c) height profile along two lines (highlighted in a and b); d) average surface roughness (RMS) for all the areas considered (six for sequins and three for wires).