Portable electrochemical pencil instrumentation in metal conservation science

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INTRODUCTION

Ag-Cu alloys are used in a variety of applications, from jewelry, silverware, medals, coins, to other craft or industrial products. Ag is also frequently used as a plating material for Cu alloys. Therefore, copper compounds occur together with Ag corrosion conversion layers.

Chemical dissolution, mechanical removal, as well as electrolytic or plasma reduction of corrosion products are generally referred to as 'cleaning'. Since the corrosion products are definitely not external contaminants such as dirt or dust, but converted substrate materials, it is misleading to speak of 'cleaning' in this context.

Rather, electrochemical reduction can be considered as a technique of transformation back to the original surface state of the metal. In the present work, the electrolytic reduction of Ag_2S and CuS tarnish layers is described with a portable electrochemical pencil (Figure 1).

Fig.4: Electrolytic pencil application at a silver spoon.
The object is contacted as working electrode.

EXPERIMENTAL

A custom-made three-electrode pencil controlled by a potentiostat system is presented for the electrochemical reduction of sulphide and chloride tarnish layers on Ag-Cu alloys (Figure 1 and 4). The pencil has been applied on naturally aged Ag- artefacts of the 19th and 20th century.
Electrolyte: 0.1 M $NaNO_3$, buffer CH_3COONa/CH_3COOH.
The influence of the potential vs. the reference electrode (carbon rod) of the artefact as well as of the tip diaphragm material (clean room sponge and a felt tip) on the conversion results was evaluated.
A minimized material loss and a good controllability of conser-vation interventions on silver alloys were demonstrated.

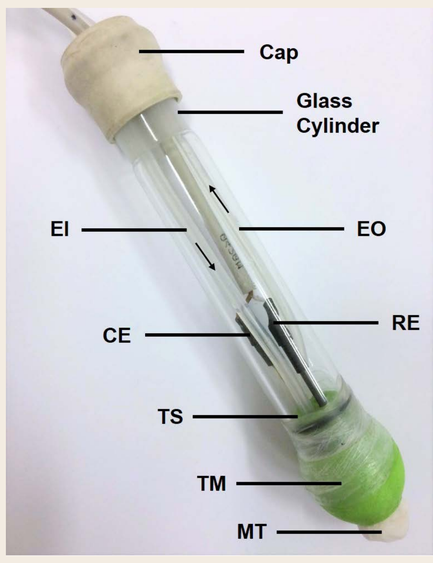

Fig.1: Electrolytic pencil. Glass cylinder fitted with a rubber cap. EI: electrolyte inlet. EO: electrolyte outlet. CE: counter electrode. RE: reference electrode. TS: tube sheet. TM: tip mounting. MT: membrane tip.

CONCLUSIONS

The electrochemical pen is particularly suitable for treating localized corrosion and is a advantageous alternative to electrochemical treatment of artefacts merely by immersion in an electrolyte.

However, the nature of the tip material has a decisive influence on the conversion result of the electrochemical pencil treatment. Localized spot tests were carried out on the unstructured minted reverse of a naturally tarnished commemorative coin. Figure 5 shows optical micrographs of two separate spots treated at −4.5 V. Historical scratches appear dark. The felt tip diaphragm material caused significant scratch marks only after a low treatment time of 60 s (Figure 5B). In contrast, no additional scratches were introduced by the treatment with the clean room sponge material (Figure 5A).

RESULTS AND DISCUSSION

The application of the electrolytic pencil equipped with a clean room sponge tip, at −2.5 V for 20 min, and consecutively at −3.0 V for 5 min, on the pair of Ag sugar tongs (Figure 2b) resulted in a partial reduction of the tarnish and contamination layers (Figure 2b) with a remaining dull appearance. Additional treatment, however, with the electrolytic pencil equipped with a felt tip at −4.0 V for 10 min improved the conversion result with an increase of metal luster (Figure 2c).

Fig.2: Naturally aged silver tongs. (a) untreated. (b) treated with the electrolytic pencil (pH4.5) equipped with a clean room sponge tip, at -2.5 V for 20 min, and consecutively at -3.0 V for 5 min.
(c) Additional treatment with the electrolytic pencil equipped with a felt tip at -4.0 V for 10 min.

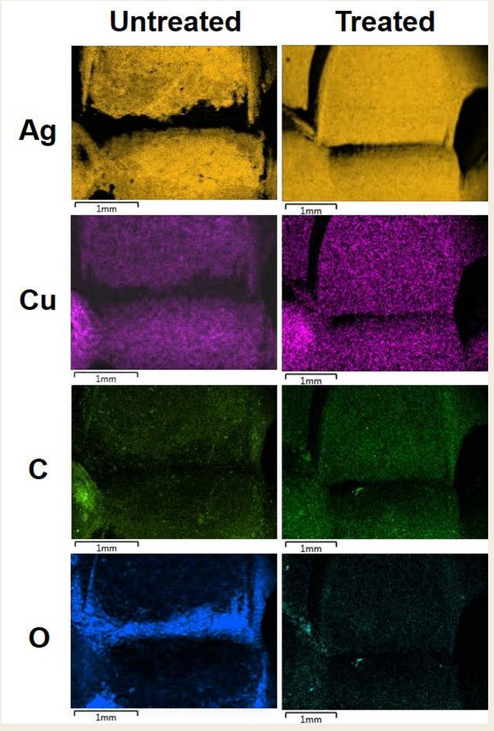

Fig.3: EDX analysis (Ag, Cu, C, O) of a surface detail on the naturally aged silver tongs before and after two steps of treatment with the electrolytic pencil (pH4.5) equipped with the clean room sponge tip, at -2.5 V for 20 min, at -3.0 V for 5 min, and consecutively with a felt tip at -4.0 V for 10 min.

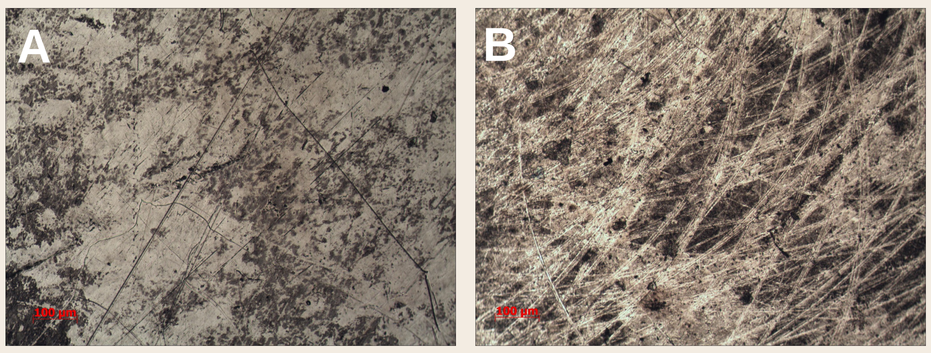

Fig.5: Surface quality in dependence of the tip material (optical micrographs), after electrolytic pencil treatments (electrolyte with pH4.5) at -4.5 V. (A) clean room sponge tip. (B) polyester felt tip. As substrate served the unstructured minted reverse side of a naturally aged commemorative silver coin.

REFERENCES

[1] V. Ljubić Tobisch, A. Selimovic, W. Kautek, Selective Electrochemical Treatment of Naturally Aged Silver Alloy Artefacts, Stud. Conserv. (2022). doi:https://doi.org/10.1080/00393630.2022.2099185.
[2] V. Ljubić Tobisch, A. Selimović, W. Kautek, Portable electrochemical pencil instrumentation in metal conservation science, Heritage. 5 (2022) In publication.

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