



SHINGLE OF A ROOF - CU ALLOY - MODERN TIMES - SWITZERLAND

Artefact name Shingle of a roof

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Url /artefacts/220/

▼ The object

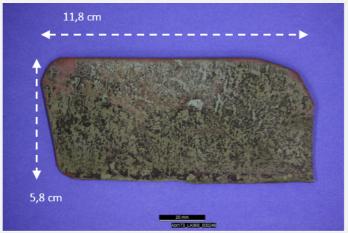


Fig. 1: Copper alloy shingle, internal side,

Credit HE-Arc CR.

▼ Description and visual observation

Description of the artefact Shingle, slightly curved, the internal side is covered with green and black corrosion products distributed

heterogeneously (Fig. 1). The external side shows a regular dark green corrosion crust. Dimensions: L =

11.8cm; W = 5.8cm.

Type of artefact Architectural element

Origin Roof of the abbey of St. Gallen, Sankt Gallen, Saint Gallen, Switzerland

Recovering date None

Chronology category Modern Times

chronology tpq 1780 A.D. 🗸

chronology taq

Chronology comment 1780

Burial conditions / environment Outdoor atmosphere

Artefact location Conservation Department of the Musées d'art et d'histoire, Genève, Geneva

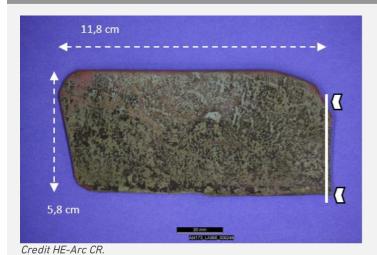
Owner Abbey of St Gallen, Sankt Gallen, Saint Gallen





Inv. number

Recorded conservation data Not conserved



None

Fig. 2: showing the location of sampling area,

Stratigraphic representation: none

★ MiCorr stratigraphy(ies) - Bi

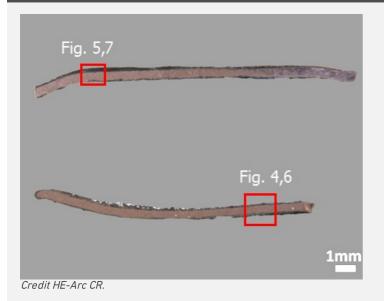


Fig. 3: Micrograph of the cross-sections showing the locations of Figures 4 to 7,

Description of sample

The polished samples show a well-preserved metal surface with a thin corrosion crust (Fig. 3). T = 0.5 mm.



Alloy Cu Alloy

Technology Rolled (probably hot rolling) and annealed

Lab number of sample MAH-98-257

Sample location Empa (Marianne Senn)

Responsible institution Conservation Department of the Musées d'art et d'histoire, Genève, Geneva

Date and aim of sampling 2009, integration of sample to the MIFAC-Métal project

Analyses performed:

Metallography (etched with ferric chloride reagent), Vickers hardness testing, LA-ICP-MS, SEM/EDX, XRD, Raman spectroscopy.

The remaining metal is a copper alloy (Table 1). The evenly distributed inclusions observed under SEM, SE-mode, are either lightgrey or white (Fig. 4). The oval shape of the light-grey inclusions is due to deformation, probably hot rolling (common in the 18th century). Under polarised light they look red (Fig. 6) and their analysis reveals a composition similar to cuprite/Cu20 (Table 2). The white inclusions are rich in Pb and are remnants of the refining process (Table 2). The etched copper shows a structure of polygonal and twinned grains (Fig. 5). The grain size is variable. The average hardness of the metal is about HV1 70.

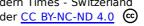
Elements	Cu	Pb	As	Sb	Ag	Bi	Sn	Zn	Ni	Fe	Со
mass%	99	0.7	0.1	0.1	0.05	<	<	<	<	<	<
RSD %	0.3	25	20	7	4						

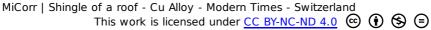
Table 1: Chemical composition of the metal. Method of analysis: LA-ICP-MS, Laboratory of Basic Aspects of Analytical Chemistry at the Faculty of Chemistry, University of Warsaw, PL.

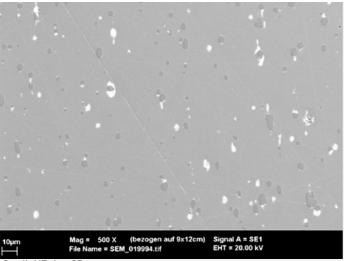
Elements	0	Cu	Pb	As	Sb	Total
Light-grey inclusion	9.8	86	<	<	<	96
White inclusion	9	9.1	68	5.1	2.6	94

Table 2: Chemical composition (mass %) of the inclusions in the metal (from Fig. 4). Method of analysis: SEM/EDX, Laboratory of Analytical Chemistry, Empa.

Fig. 4: SEM image, SE-mode, of the metal sample from Fig. 3 (detail). Light-grey and white inclusions are distributed evenly,







redit HE-Arc CR

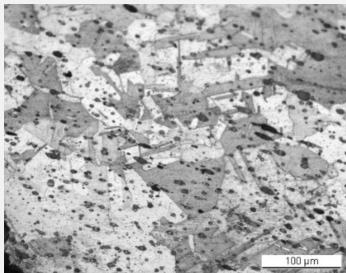


Fig. 5: Micrograph of the metal sample from Fig. 3 (detail), etched, bright field. The metal shows a structure of polygonal and twinned grains. Cuprite inclusions appear as dark spots,

Credit HE-Arc CR.

Microstructure Polygonal and twinned grains, elongated inclusions

First metal element

Other metal elements

The corrosion crusts of the external and internal sides are distinctively different (Fig. 6). On the internal side an irregular red-orange corrosion layer has developed and pitting corrosion has occurred. The more uniform corrosion layers on the external side are composed of a red-orange layer, followed by a thicker green outer layer. In some areas, dark-red corrosion products can be observed between the green and red-orange sub-layers. The same dark-red sub-layer can be seen in areas on the internal side covering the red-orange corrosion products. The red-orange corrosion layer has a chemical composition similar to cuprite/Cu₂O, while the green layer contains Cu, S and O and is enriched on its upper surface with Si (Table 3 and Fig. 7). XRD analysis of the $corrosion\ products\ on\ the\ external\ side\ of\ another\ shingle\ fragment\ from\ the\ same\ roof\ identified\ brochantite/Cu_4SO_4(OH)_6\ and$ cuprite as corrosion products (Rapport d'analyse no MAH 98-257). These results are confirmed by Raman spectroscopy of the external side of this sample where the same compounds were clearly identified (Figs. 8 and 9).

Elements	0	Cu		Total
CP1e	20	59	6.2	85
CP2i	11	86	<	97

Table 3: Chemical composition (mass %) of the corrosion layers of the external side. Method of analysis: SEM/EDX, Laboratory of Analytical Chemistry, Empa.





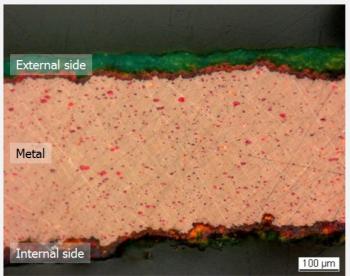


Fig. 6: Micrograph of the metal sample from Fig. 3, polarised light. External side: the regular corrosion crust with outer green, inner redorange corrosion products and intermediate dark-red corrosion products. Internal side: the irregular corrosion crust with inner redorange and outer dark-red corrosion products,

Credit HE-Arc CR.

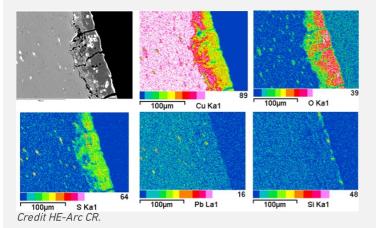


Fig. 7: SEM image, SE-mode, and elemental chemical distribution of the selected area of Fig. 3 (rotated image, detail). Method of examination: SEM/EDX, Laboratory of Analytical Chemistry, Empa,

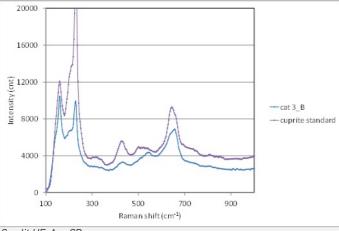
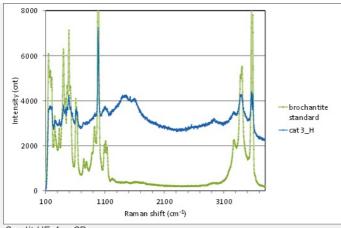


Fig. 8: Raman spectrum of the red-orange inner corrosion layer of the external side (cat3_B) compared to a cuprite standard spectrum. Settings: laser wavelength 532nm, acquisition time 100s, one accumulation, filter D2 (0.75-0.8 mW), hole 500, slit 80, grating 600. Method of analysis: Raman spectroscopy, Lab Swiss National Museum, Affoltern a. Albis ZH,

Credit HE-Arc CR.

Fig. 9: Raman spectrum of the green outer corrosion layer of the external side (cat3_H) compared to a brochantite standard spectrum. Settings: laser wavelength 532nm, acquisition time 100s, one accumulation, filter D2 (0.75-0.8 mW), hole 500, slit 80, grating 600. The peak indicated with an arrow on the cat3_H spectrum is due to fluorescence. Method of analysis: Raman spectroscopy, Lab Swiss National Museum, Affoltern a. Albis ZH,



Credit HE-Arc CR.

Corrosion form Uniform - pitting

Corrosion type Type I (Robbiola)

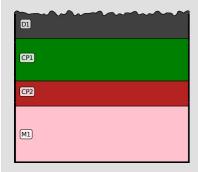


Fig. 4: Stratigraphic representation of the object in cross-section using the MiCorr application. This representation can be compared to Fig. 7.

➤ Synthesis of the binocular / cross-section examination of the corrosion structure

Corrected stratigraphic representation: none

♥ Conclusion

The copper shingle was rolled (probably hot rolling) and annealed to recover the ductility of the original material. The metal is covered on its external side by a typical "urban outdoor" patina consisting of copper sulphate (brochantite/Cu4(OH)6SO4) formed on top of a cuprite/Cu20 layer. The surface of the internal side, protected from the diluted sulphuric acid present in urban rain water, has developed only a cuprite layer. The silica present in the brochantite on the external side is due to airborne particle pollution. The corrosion is probably of type 1 after Robbiola et al. 1998.

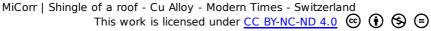
▼ References

References on object and sample

1. Rapport d'analysen° MAH 98-257. Laboratoire Musées d'art et d'histoire, Genève. The report describes a sample from another shingle. References on analytic methods and interpretation

2. Robbiola, L., Blengino, J-M., Fiaud, C. (1998) Morphology and mechanisms of formation of natural patinas on archaeological Cu-Sn alloys,





Corrosion Science, 40, 12, 2083-2111.

3. Selwyn, L. (2004) Metals and Corrosion: A Handbook for the Conservation Professional, Ottawa, ON: Canadian Conservation Institute, 68–70. 4. Stöckle, B., Mach, M. and Krätschmer, A. (1997) La durabilité des couvertures en cuivre selon les conditions environnementales. Résultat de l'UN/ECE-Programme d'exposition climatique, Les couvertures métalliques, matériaux et techniques, Les cahiers de la section française de l'ICOMOS, Paris, 129-135.

5. Welter, J-M. (2007) La couverture en cuivre en France: une promenade à travers les siècles, Le métal dans l'architecture, Monumental, 104-112.

