BROMEC 33

Bulletin of Research on Metal Conservation

January 2012

Editorial

This issue contains a diverse range of metals conservation research themes from Europe and the Middle East. Such evidence of continuing research activity appears despite a continuing ailing global economy and regional political turbulence: recent news from National Contact Persons has highlighted severe funding cuts and closures of conservation schools and conservation research institutes in Hungary, the United Kingdom and Romania (notably the National Research Laboratory for Conservation and Restoration of Movable National Cultural Heritage). It would be of great interest to gauge how much research has been, or will be affected in time, by these recent changes.

Of the *new research projects* featured in this issue, an international call for samples of copper corrosion associated with glass is made from a German conservation school, a new Italian project is evaluating protection given by open-faced active microclimate systems and non-toxic materials for corrosion prevention of gilded bronzes, and from Egypt findings from laboratory tests on bronze treated with corrosion inhibitors and barrier coatings are made. Researchers in Wales are developing a predictive management model for controlling corrosion rates of archaeological iron, while in Iran a PhD student has commenced with a similar objective for archaeological bronzes, as summarised in *ongoing research projects*. Further *ongoing research* is reported from Egypt, where a virtual reconstruction methodology for fragmented archaeological metals is underway and also from Switzerland, where the development of fungi to produce protective patinas on copper/bronze will be evaluated. Another Swiss work, this time a *finalised research project* in the form of a master's thesis, evaluated the potential use of lasers to remove copper corrosion products from archaeological gilded copper. Another master's student, from Egypt, tested laser and local ultrasonication to remove tarnish from metallic threads.

Newly listed *future conferences and seminars* are a multidisciplinary meeting in France on French bronzes and a bronze conservation colloquium to be held in Germany, and lastly the next ICOM-CC Metal Working Group's meeting, *Metal 2013*. *Announcements* include the availability of the proceedings for the last ICOM-CC Metal Working Group's meeting, *Metal 2010*, and the online availability of a PhD thesis on the corrosion of archaeological metals and the alteration of their original surfaces.

Wishing you informative and enjoyable reading!

James Crawford

Contents

Cover image: Uplifting of gilding on copper during preparation by electrochemical replacement plating of an artefact analogue test sample: a temperature greater than 80°C and/or a gilding duration greater than 25-30 minutes could have induced this blistering. Copyright Valentine Brodard/Haute école de Conservation-restauration (HE-Arc). Refer to abstract by Brodard, “Laser removal of corrosion products from archaeological artefacts: gilded copper alloys”.

BROMEC website: http://www2.warwick.ac.uk/fac/sci/physics/research/condensedmatt/sims/bromec/

BROMEC subscription: http://listserv.csv.warwick.ac.uk/mailman/listinfo/bromec-bulletin-of-research-on-metal-conservation

Glass-Induced Metal corrosion on Metal Exhibits (GIMME): samples needed! (SABKS) [1]

New research project

Contact: Gerhard Eggert (gerhard.eggert @ abk-stuttgart.de) (SABKS), Andrea Fischer (SABKS)

Funding: Friede Springer Stiftung

Many historic glasses are unstable because of their high content of alkaline fluxing agents. Alkaline surface films formed in humid atmospheres might attack neighbouring copper alloys (including historic silver) as was determined in the last years [2-5]. Lead (e.g. leading for stained glass, leaded glass mirrors or balls) might be affected as well. So far in Stuttgart, two different copper formates have been identified as corrosion products: sodium copper formate acetate (socoformacite; sodium is present here from glass corrosion) and dicopper-trihydroxy-formate (the necessary alkaline pH>8 is due to glass corrosion). Potentially affected composite glass/metal objects include enamel on copper and silver (e.g. Limoges), glass beads and balls on wire, daguerreotypes with brass frames and cover glass, and silver in contact with glass (mounted glass gems [e.g. on mediaeval book covers or shrines], a glass flute, baroque period ruby glass box and cup).

Successful preventive conservation requires the identification of sources of pollutants. Except for formic acid from wood, formaldehyde (via oxidation or the Cannizzarro reaction on alkaline surface films) can play a role. Other possible sources to be investigated are the hypothetical formation from carbon monoxide or the use of silver cleaning baths containing formic acid. Prevention should remove the source of pollutants or – if not possible – use absorbents, establish dry storage (but not below 35% RH), and apply coatings, if appropriate.

The GIMME research project will investigate the frequency of this phenomenon via systematic surveys of selected collections. Other compounds (containing potassium, carbonate or sulphate...) occur, but they are as yet unidentified; therefore XRD, SEM-EDX, and Raman microscopy will be applied. Laboratory experiments will aim to elucidate the formation and nature of the compounds.

The project asks all conservators for any metal corrosion samples and observations which occur on composite metal objects close to corroding glass only.

1. Original language version; submitted by author in English.

2. Eggert, G., 2010. Corroding glass, corroding metals: survey of joint metal/glass corrosion products on historic objects. Corrosion Engineering, Science and Technology, 45 (5), 414-419.

3. Eggert, G., Wollmann, A., Schwahn, B., Hustedt-Martens, E., Barbier, B., Euler, H., 2008. When glass and metal corrode together. In: J. Bridgland (Ed.), 15th ICOM-CC Triennial Conference New Delhi, Preprints Vol. 1, 211-216. New Delhi: Allied Publishers.

4. Eggert, G., Bührer, A., Barbier, B., Euler, H. 2010. When glass and metal corrode together II: A Black Forest Schäppel and further occurrences of socoformacite. In: H. Roemich (Ed.), Glass and Ceramics Conservation 2010, 174-180. Corning (NY): Corning Museum of Glass.

5. Eggert, G., Haseloff, S., Euler, H., Barbier, B. 2011 When glass and metal corrode together III: The formation of dicoppertrihydroxyformate. In: J. Bridgland (Ed.), 16th ICOM-CC Triennial Conference Lisbon. Preprints CD.

Innovative conservation strategies for gilded bronzes (UNIFE, IFAC-CNR, POLIMI, UNIBO) [1]

New research project

Contact: Cecilia Monticelli (mtc@unife.it) (UNIFE), Andrea Mencaglia (IFAC-CNR), Sara Goidanich (POLIMI), Carla Martini (UNIBO)

Funding: Italian government (PRIN 2009)

A 2-year 4-partner national research project will focus on the conservation of gilded bronzes. Preservation against indoor or outdoor corrosion is a very difficult problem, which in the case of precious masterpieces is not solved by current maintenance and protection procedures. In particular, strong cleaning and protection limitations are encountered whenever the artwork has gilding. Today, the preferred way to counter deterioration phenomena is to implement preventive measures, including controlled microclimate conditions, which are applicable to confined environments. For example, in order to effectively control relative humidity and temperature, as well as to prevent accumulation of deposits, conservation in sealed showcases is usually proposed. These methods are widely adopted, but their use is often very questionable for important art objects since they potentially hinder the enjoyment of the artwork by the visitors of the museum. In recent years, intensive research activity in the cultural heritage field has been dedicated to synthesize and test novel corrosion inhibitors, associated with or without protective coatings. They must be suitably formulated in order to avoid any perceptible change to the treated surfaces. In this project innovative conservation methodologies for outdoor and indoor gilded copper alloy artworks will be developed. These are based on both controlled environmental conditions and non-toxic surface treatments with silanes, thiadiazoles and tetrazoles; the effectiveness of which will be assessed using non-invasive diagnostic techniques. Microclimate controlled open-faced showcases with theoretically modelled distributed dry air fluxes and non-toxic surface treatments will be designed and systematically tested on sets of samples including patinated and gilded copper alloys. The partners will rely on a collaboration with OPD.

1. Original language version; submitted by author in English.

Evidence-based condition monitoring of heritage iron (CU, UoM) [1]

New research project

Contact: David Watkinson (watkinson@cardiff.ac.uk) (CU), Melanie Rimmer (CU), Stuart Lyon (UoM), James Dracott (UoM)

Funding: AHRC/EPSRC Science and Heritage Programme

A 3-year project will provide quantitative evidence for the conservation and management of heritage iron. Archaeological iron objects often suffer from chloride-induced post-excavation corrosion, which severely disrupts the information-bearing corrosion product layers and renders the object useless for study or display. Although low-humidity storage below 15% RH is known to prevent chloride-induced corrosion, many heritage organisations do not have the resources to maintain such tight environmental parameters indefinitely. It is therefore essential to develop the concept of managed corrosion control, which requires a quantitative understanding of the relationships between environmental conditions, corrosion rate, chloride content and the physical integrity of the objects. Using this data, the development of a predictive management model for controlling corrosion rates and extending the lifespan of iron objects is planned.

The study will quantitatively record the corrosion rate of ~300 archaeological wrought iron nails at room temperature in controlled RH by measuring the oxygen consumption of the corrosion reaction. During this process, the physical integrity of the corrosion layers will be monitored via high-resolution photographic documentation that will be used for qualitative assessment of heritage value loss by the extent of cracking/flaking that occurs. Afterwards, each nail will be digested to measure the total chloride ion content. Tests using incremental RH changes will evaluate how changing environmental parameters affect the corrosion rate of individual objects. Relationships between RH, chloride content and corrosion rate will be assessed in relation to the physical integrity and therefore useful lifespan of the objects.

Initial results show that it is possible to measure room temperature corrosion of real iron objects in a range of 20% to 80% RH. Corrosion rates at 20% are typically two orders of magnitude slower than at 80%. Physical change in the form of opening and widening of cracks, ‘weeping’ and loss of corrosion products has been documented at 80% RH. The project is currently expanding the RH range and completing initial tests examining the effect of removing chloride ions through alkaline desalination.

A related PhD project at University of Manchester School of Materials is continuing work carried out there on ERCM sensors that measure corrosion rate in a given environment using an iron sensor pre-corroded with chloride ions. By relating data from ERCM monitoring to the corrosion rates of real objects, the sensors will aim to monitor environments for their corrosivity and predict the behaviour of archaeological material.

For more information on the project, visit http://www.cardiff.ac.uk/share/research/projectreports/conservationiron/index.html

1. Original language version; submitted by author in English.

Laboratory evaluation of corrosion inhibitors and protective coatings used on bronze artefacts (SVU, CU) [1]

New research project

Contact: Yussri Salem Mahrouse Ali (Yussri_25@yahoo.com) (SVU), Mai Mohammed Rifai (CU)

Funding: No external funding

The main objective of this accelerated study was to evaluate, by electrochemical measurements and gravimetry, the performance of some common corrosion inhibitors and barrier coatings used on bronze artefacts. The corrosion inhibitors used were benzotriazole (BTA: $C_6H_5N_3$) and 2-mercaptobenzothiazole (MBT: $C_7H_5NS_2$), while the protective coatings used were Paraloid ™ B-72 and Paraloid ™ B-66. Barriers and inhibitors alike were applied by simple immersion using 3% w/v in ethanol solutions for 24 hours. Their resulting thicknesses were not determined. An uncorroded polished bronze with a binary copper alloy composition of Cu 93: Sn 6 was used for all tests.

Potentiodynamic polarization measurements (scan rate: $5 mV.s^{-1}$) were carried out using two corrosive aqueous media:

- a mixed salt solution (Na_2SO_4 [0.2 $g.L^{-1}$] + $NaHCO_3$ [0.2 $g.L^{-1}$] + NaCl [0.2 $g.L^{-1}$]; in tap water acidified to pH 5 by addition of dilute [0.5 M] HCl; and
- HCl [0.5 M] in tap water solution

In the mixed salt solution, the current decreased in the presence of all the different inhibitors: the decrease of the cathodic current was the same for all the inhibitors, while the decrease of the anodic current varied slightly: it was greater for BTA, and the same for B-66, MBT and B-72. So all these inhibitors were effective, but BTA was the best performing for the mixed salt solution. In HCl, the current (mainly cathodic currents) increased in the presence of BTA, B-66 or B-72. The current decreased only with MBT. A precise quantification of corrosion rates in both solutions has not yet been established.

Weight loss tests were performed on rectangular coupons (30 x 20 x 1 mm). Coupons treated with B-72, B-68, BTA and MBT were immersed in extreme conditions: cupric chloride ($CuCl_2$: 20% w/v). Weight loss attributable to metal corrosion was calculated after chemically stripping the corrosion products from their metal substrates. Corrosion protection efficiencies of the selected inhibitor compounds and polymer coatings after two and four weeks were rated relatively: BTA > MBT and B-66 > B-72.

Further tests in real atmospheres would be required to confirm if the relative corrosion protection indicated by the tested materials, in these extreme and aqueous conditions, are representative of atmospheric conditions.

1. Original language version; submitted by author in English.

Systematic corrosion and burial environment investigations to improve risk assessment for collections of newly excavated archaeological bronzes (AUI, SUT) [1]

Ongoing research project

Contact: Omid Oudbashi (o.oudbashi@ aui.ac.ir) (AUI), Seyed Mohammadamin Emami (AUI), Parviz Davami (SUT)

Funding: No external funding

To better anticipate during- and post-excavation conservation requirements, this PhD project is methodically investigating the material-environment systems of bronzes found on terrestrial archaeological sites. Naturally, the metallurgy of the artefact and the burial environment itself are implicated in the possible corrosion mechanisms, and their subsequent corrosion morphologies. However, it is usually the artefact and its newly formed corrosion products that become the first indication of artefact instability: after corrosion has already occurred. Investigations of some corrosion morphologies (so-called “Type I” and “Type II”) present on excavated bronzes have previously been performed to establish probable corrosion mechanisms [2], and such deductions have been extended to include similarly appearing corrosion morphologies on bronze artefacts from sites elsewhere [3]. However deviations from these two well-known categories exist. So to identify other potentially unstable bronzes, the present study extends such categorization to include bronze corrosion with other aspects. Such a body of systematically collated data aims to practically improve archaeological conservation strategies by collating evidence from current excavations; possibly enabling predictive risk assessments for future excavations. This could assist decision-making for excavation procedures (including preliminary cleaning, packing, transport and storage), conservation treatments and display methods.

It seems that an integrated and complete investigative approach based on three main parameters is required. A material-environment system named *metal-corrosion-soil* has been established to help systematically characterise the corrosion morphologies and stability of a collection of excavated bronze artefacts from two Iranian sites, where excavations are still in progress. The corrosion morphologies of the artefacts vary, and they are being studied during and after excavation to document alterations. In addition to the metallurgy of the artefact (e.g. composition and manufacture), the main parameters studied are its corrosion (e.g. species, quantities, morphology, inferred mechanism) and the description of its burial soil (e.g. type, texture and grain size, pH, redox potential, conductivity/resistivity, contained water, soluble salts, organic materials). Finally, an attempt to determine the presence of any correlations with the various parameters of the metal-corrosion-soil system and the current conservation condition for about 3000 artefacts will be made.

The main anticipated contribution of this research is to establish a practical on-site guide for archaeological conservators during excavations of bronze collections. It is hoped the methodology could be extended to include other archaeological metals. Using such a method, it is thought many problems can be identified before starting, or in the early stages of excavation; especially helpful when an excavation yields artefacts in their thousands.

1. Original language version; submitted by author in English.

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, 2083-2111.

3. Oudbashi, O, Emami, S. M., 2010. A note on the corrosion morphology of some Middle Elamite copper alloy artefacts from Haft Tappeh, southwest Iran. Studies in Conservation, 55 (1), 20-25.

An integrated methodology for the documentation and virtual reconstruction of metal fragments (CU, CULTNAT) [1]

Ongoing research project

Contact: Wafaa A. Mohamed (wafaaanw@yahoo.com) (CU), Ibrahim El-Rifai (CULTNAT)

Funding: No external funding

This research explores the possibility of the virtual reconstruction of archaeological metal objects from fragments. A collection of six hundred and twenty-one heavily corroded Greco-Roman metal fragments found in an archaeological hoard are being examined. The research proposes the integration of traditional and advanced documentation and analysis techniques to derive the physical shape, its features and the chemical composition of the fragments, thereby forming the basis for the classification and matching of fragments and their virtual reconstruction into objects.

The shapes and features were examined by a preliminary manual classification accompanied by hand sketching and labelling. Close range 3D laser scanning was used to capture the geometry, particularly for large objects. Measurements were taken by callipers, as well as by CAD software. Microphotography was used to capture colours and surface details. The microstructure was examined using optical microscopy (OM), polarizing light microscopy (PLM) and scanning electron microscopy (SEM). The alloy composition and corrosion products were respectively analyzed using SEM coupled with energy dispersive spectrometry (EDX) and X-ray diffraction.

It was found that the proposed reconstruction procedure worked only when the size of the fragment is large enough to build up the proposed model and the fragment itself belongs to a symmetrical shape, e.g. a vase. Meanwhile, other objects were identified and their shapes were estimated since their fragments constructed a well known shape of a historical object, e.g. patera and jug. Of course, if only a low number of fragments are available, a reconstruction is not yet possible. Small fragments were only documented photogrammetrically since reconstructed models could not be proposed unless they carry distinguishable marks that relate them to other objects. Another issue hindering the matching is alteration processes, such as the preferential dissolution and re-deposition of alloying components that can more or less affect both chemical composition and the microstructure. Lastly, any chemical and structural differences attributable to differing fabrication processes in multi-component artefacts, need to be considered, e.g. wrought jug body joined to a cast handle or base.

To date, data has been processed for six potential virtual reconstructions; enabling visual presentation of these highly damaged objects, without interventive restoration procedures. A proposed outcome from this specific methodology is a general framework for the documentation, description, grouping and virtual reconstruction of metal objects from fragmentary remains.

1. Original language version; submitted by author in English.

Development and evaluation of an innovative biological treatment for the protection of metal artefacts (SNM, LAMUN, ISMAR, M2ADL) [1]

Ongoing research project

Contact: Edith Joseph (edith.joseph@snm.admin.ch) (SNM), Daniel Job (LAMUN), Paola Letardi (ISMAR), Rocco Mazzeo (M2ADL), Marie Wörle (SNM)

Funding: Marie Curie Intra European fellowship

In the framework of the BAHAMAS project, alternative possibilities offered by a fungal treatment for the protection of metal artworks are being evaluated. This research aims to modify existing corrosion products into more stable and less soluble compounds, while maintaining the surface's physical appearance. In the literature, some species of fungi have been reported for their ability to transform metal-bearing minerals into metal oxalates [2]. This synthesis is part of the natural resistance and tolerance mechanisms developed by some fungi in the presence of heavy metal ions [3]. Metal oxalates are known to be highly insoluble and chemically stable, even in acidic atmospheres (pH 3) [4]. In fact, copper oxalates have been observed on outdoor bronze monuments; favourably however, these are not associated with the phenomenon of cyclic corrosion [5, 6]. Thus the potential for fungi to transform existing corrosion patinas into metallic oxalates patinas is being explored.

The ability of *Beauveria bassiana* to produce copper oxalates was evaluated and its growth performance tested and compared with other fungal strains on various copper-containing media. The formation mechanisms and adhesion properties of the newly formed metal oxalates are being investigated on copper/bronze substrates with either urban or marine patinas [7]. The treatments' performances are now being characterized with complementary analytical techniques: X-ray diffraction (XRD), FTIR microscopy, Raman microscopy, scanning electron microscopy (SEM-EDS), colourimetry and electrochemical impedance spectroscopy (EIS). Their behaviour under ageing is also being evaluated and compared with that of reference materials (e.g. wax: Cosmolloid H80; silane: Dynasylan® F8263…). The stable patinas created are expected to provide a very high protection and allow the inhibition of corrosion processes. It is worth noting that the synthesis of metal oxalates by natural fungi is a process occurring at neutral pH and near ambient temperature and pressure. The use of these biological treatments represents an ecologically friendly strategy with few to no side effects on health and the environment. A substantial progress is expected in terms of durability, effectiveness and toxicity. This work is based on a collaboration between the Swiss National Museum (SNM), the Istituto di Scienze Marine (ISMAR) and the Universities of Neuchâtel (LAMUN) and Bologna (M2ADL) and is supported by the European Union, within the Seventh Framework Programme (FP7).

1. Original language version; submitted by author in English.

2. Sayer, J.A., Kierans M., Gadd G.M., 1997. Solubilisation of some naturally occurring metal-bearing minerals, limescale and lead phosphate by Aspergillus niger. FEMS Microbiology Letters, 154 (1), 29-35.

3. Gadd, G.M., 2007. Geomycology: biogeochemical transformations of rocks, minerals, metals and radiounuclides by fungi, bioweathering and bioremediation. Mycological Research, 111, 3–49.

4. Marabelli, M., Mazzeo, R., 1993. La corrosione dei bronzi esposti all'aperto: problemi di caratterizzazione. La metallurgia italiana, 85 (4), 247-254.

5. Nassau, K., et al., 1987. The characterisation of patina components by X-ray diffraction and evolved gas analysis. Corrosion Science, 27 (7), 669–684.

6. Mazzeo, R., Chiavari, G., Morigi, G., 1989. Identificazione ed origene di patine ad ossalato su monumenti bronzei: il caso del Portale Centrale del Duomo di Loreto (AN) In: Le Pellicole ad ossalati: origine e significato nella conservazione delle opere d'arte. Centro del C.N.R. "Gino Bozza", Milano.

7. Joseph, E., Simon, A., Prati, S., Wörle, M., Job, D., Mazzeo, R., 2011. Development of an analytical procedure for evaluation of the protective behaviour of innovative fungal patinas on archaeological and artistic metal artefacts. Analytical and Bioanalytical Chemistry, 399 (9), 2899-2907.(Paper in Forefront)

Laser removal of corrosion products from archaeological artefacts: gilded copper alloys (HE-Arc) [1]

Finalised research project

Contact: Valentine Brodard (valentine.brodard@gmail.com) (HE-Arc)

Funding: No external funding

Corrosion products on archaeological artefacts made from gilded copper alloy pose problems during their removal. The risk of damaging the object is significant, mechanical removal methods can scratch gilding and chemical methods can damage the underlying metal, and in the long term, accelerate corrosion [2-3].

The purpose of this work, conducted during a master [4], specialising in archaeological and ethnographic artefacts, was to test laser as an alternative method to routine cleaning techniques for pre-Columbian gilded copper alloys. These materials feature a layer of cuprite (Cu_2O), and above there is malachite ($CuCO_3.Cu(OH)_2$). This study was mainly focused on the removal of cuprite covering these objects; malachite was investigated to a lesser extent.

Investigation of pre-Columbian objects, showed that the base material was a low alloy copper and that gilding could have been carried out by electrochemical replacement plating. So some copper coupons were gilded, according to this technique, and were used to simulate the behaviour of such materials being subjected to lasers. Following a literature survey and according to equipment availability a selection of lasers was made:

- Nd: YAG short free running, (1064 nm, 100 µs),
- Nd: YAG long Q-switch, (1064 nm, 100 ns),
- Q-switch (1064 nm, 13 ns).

The selection of the flux (i.e. energy density, J/cm^2) was made starting with tests on the gilding exposed to the various laser beams. The selected values were: maximum 0.48 J/cm^2 for the long Q-switch laser and 3.6 J/cm^2 for the Q-switch laser. It was not possible to avoid deterioration of gilding during the tests carried out using the short free running laser (pulse duration: 100 µs, frequency: 1-5 Hz, flux: 0.3 J/cm^2).

The ablation tests on cuprite at these fluxes did not allow removal. The use of stronger fluxes led to the deterioration of gold in various ways: darkening, to melting, through to complete disappearance, and partial fusion of the copper.

Although focussed on one type of gilding, this research highlights the difficulties of removing corrosion products from a gilded metal. The increase in temperature during the treatment is a problem which cannot be ignored. Currently, it is difficult to advise the use of the laser on archaeological artefacts made from copper alloy gilded by electrochemical replacement plating: the obtained results do not make it possible to ensure the objects are not damaged.

1. Translated by J. Crawford. Original version submitted by author in French; refer to BROMEC 33 French version.

2. Volfovsky, C. 2001. La conservation des métaux. Paris : CNRS éditions.

3. Eichhorn, P., 1985. Bergung, Restaurierung und Konservierung archäologischer Gegenstände aus Bronze. H. Born, Archäologische Bronzen Antike Kunst Moderne Technik. Berlin: SMPK. 153-157.

4. Master obtained in August 2011 from la Haute école de Conservation-restauration Arc

Preliminary testing and empirical application of laser and ultrasonic tarnish removal from metal textile threads (CU) [1]

Finalised research project

Contact: Fatmaa EL-Zahraa Sadat Mohamed (hamees_angel@yahoo.com) (CU)

Funding: No external funding

To clean, or not, metal-textile composite threads of their tarnish layers remains a debated treatment option [2, 3]. If proceeding with cleaning, commonly applied techniques can be unsuitable: mechanical techniques might remove surfacing; e.g. gilding. And due to their intricate construction, most conventional cleaning techniques do not assure an efficient locally controlled removal of tarnish without damaging organic components. Some studies have explored laser techniques on gilded silver and silvered copper threads [4] and tarnished silver threads [5]; reporting unwanted side effects or limited results. Ultrasonic probe descaling is another potential unconventional metallic textile cleaning technique; with few reports [6].

A master's project involved the testing of these unconventional tarnish removal techniques with a view to lessening black tarnish present on an Indian Mogul textile (circa 17th-18th century AD) embroidered with metal threads. The organic and inorganic composition of the textile was first determined by examinations via optical microscopy (OM), polarizing light microscopy (PLM) and scanning electron microscopy (SEM), and by micro-analyses via energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR), atomic absorption spectroscopy (AAS), and X-ray diffraction (XRD). The fabric was woven from a cotton and silk ground. The metallic embroidery was made from a double-sided gilded copper-based strip wrapped around a cotton core. The copper strip contained traces of silver, gold, zinc and lead, and was mechanically gilded on both sides with a "gold layer". The textile featured different signs of physical degradation and metal tarnish (cupric sulphide, as determined by XRD).

Dry application was the preferred condition for each technique and was first performed on test samples taken from fragments that had previously separated. Stereo microscope examination of the test samples after cleaning helped evaluate any:

- chromatic alterations (e.g. due to any exposure of the copper substrate by removal of the gilding layer and patina);
- morphological alterations (e.g. curving or delamination of the metal strip, due to thermal actions); and
- other microscopically observable alterations of the fibre core or the remaining gilding layer.

The preliminary study on the test materials demonstrated the ultrasonic probe (frequency: 30 kHz ±3 kHz) applied at its mid-range power level (~7.2 - 9.3 watts) with a total of 5 x 10 ns pulses from a Q-switched Nd: YAG laser (2nd harmonic 532 nm wavelength; fluence: 4 J/cm^2) to locally lessen accessible tarnish.

Both of these techniques were deemed suitable for application to the artefact. However only the ultrasonic probe was available for a museum-based treatment where a digital microscope (200x) assisted surface inspections during a partial tarnish removal; resulting in an aesthetic improvement.

To form a holistic conclusion to this empirical research, a conservation treatment and preventive conservation strategy was implemented (i.e. a physical reinforcement and a conditioned microclimate for storage).

1. Original language version; submitted by author in English.

2. Howell, D., 1989. Experiments with Chemical Cleaning for Metal Threads. In Scientific Analysis of Ancient and Historic Textiles informing Preservation, Display, and Interpretation: Post prints, AHRC Research Centre for Textile Conservation and Textile Studies, 1st Annual Conference 13-15 July.

3. Landi, S., 1992. The Textile Conservators' Manual, 2nd ed. London: Butterworth-Heinemann.

4. Degrigny, C., Tanguy, E., Le Gal, R., Zafiropulos, V., Marakis, G., 2003. Laser cleaning of tarnished silver and copper threads in museum textiles. Journal of Cultural Heritage, 4. 152s-165s.

5. Sokhan, M., Hartog, F., McPhail, D.S., 2005. Surface Analysis of Laser Cleaned Metal Threads, In LACONA V, Springer proceedings in physics, 100, part V.

6. Balázsy, Á.T., Eastop, D., 1998. Chemical Principles of Textile Conservation. London: Butterworth- Heinemann.

Abbreviations and acronyms

AAS: atomic absorption spectroscopy

AHRC: Arts and Humanities Research Council

AUI: Faculty of Conservation, Art University of Isfahan, Isfahan, Iran

BAHAMAS: Biological patinA for arcHaeological and Artistic Metal ArtefactS (PIEF-GA-2009-252759, 2010-2012)

BTA: benzotriazole

CAD: computer aided design

CU: Cairo University, Cairo, Egypt

CU: Department of Archaeology and Conservation, Cardiff University, United Kingdom

CULTNAT: Center for Documentation of Cultural & Natural Heritage, Giza, Egypt

EDS/EDX: energy dispersive X-ray spectroscopy

EIS: electrochemical impedance spectroscopy

EPSRC: Engineering and Physical Sciences Research Council

ERCM: electrical resistance corrosion monitor

FP7: Seventh Framework Programme

FTIR: Fourier transform infrared spectroscopy

GIMME: Glass-Induced Metal corrosion on Metal Exhibits

HE-Arc: Haute école de Conservation-restauration Arc, La Chaux-de-Fonds, Switzerland

IFAC-CNR: Istituto di Fisica Applicata “Nello Carrara” - Consiglio Nazionale delle Ricerche, Florence, Italy

ISMAR: Istituto di Scienze Marine, Genova, Italy

LAMUN: Laboratoire de Microbiologie, Université de Neuchâtel, Neuchâtel, Switzerland

M2ADL: Microchemistry and Microscopy Art Diagnostic Laboratory, University of Bologna, Ravenna, Italy

MBT: 2-mercaptobenzothiazole

Nd: YAG: neodymium-doped yttrium aluminium garnet (Nd:$Y_3Al_5O_{12}$)

OM: optical microscopy

OPD: Opificio delle Pietre Dure, Florence, Italy

PLM: polarizing light microscopy

POLIMI: Dipartimento di Chimica, dei Materiali e Ingegneria Chimica, Politecnico di Milano, Milan, Italy

RH: relative humidity

SABKS: Staatliche Akademie der Bildenden Kuenste Stuttgart, Germany

SEM: scanning electron microscopy

SNM: Konservierungsforschung, Sammlungszentrum, Swiss National Museum, Affoltern am Albis, Switzerland

SUT: Faculty of Material Science and Engineering, Sharif University of Technology, Tehran, Iran

SVU: Conservation Department, Archaeology Faculty, South Valley University, Qena, Egypt

UNIBO: Scienza dei Metalli, Elettrochimica e Tecniche Chimiche, Università di Bologna, Bologna, Italy

UNIFE: Centro di Studi sulla Corrosione e Metallurgia “Aldo Daccò”, Università di Ferrara, Ferrara, Italy

UoM: School of Materials, University of Manchester, United Kingdom

XRD: X-ray diffraction

General information

Future seminars and conferences

French bronzes: history, materials and techniques of bronze sculpture in France (16^{th}-18^{th} centuries) (9-12 June, 2012, Paris, France). Musée du Louvre and Centre de Recherche et de Restauration des Musées de France (C2RMF), Paris, France. This international symposium held at the Musée du Louvre and at the Centre de Recherche et de Restauration des Musées de France aims to bring together a diverse group of specialists – e.g. historians (of technology, art, trade, ideas), conservation scientists, curators, and conservator-restorers – to engage in an inter-disciplinary exchange on the development and cross fertilization of ideas and technology related to the making of bronzes in France (and by French artists abroad) from the Renaissance to the 19th century. For more information: http://frenchbronze.net/

Bronze conservation colloquium (22-23 June, 2012, Stuttgart, Germany). The State Academy of Art and Design Stuttgart, Germany in cooperation with ICOM-CC Metals WG, will host this conference covering all aspects of the conservation of copper and its alloys including investigation, manufacture, corrosion, conservation methods and case studies.

Metal 2013 (16-20 September, 2013, Edinburgh, Scotland). The International Council of Museums Committee for Conservation Metal Working Group is pleased to announce the next Interim Meeting: http://www.metal2013.org/

Announcements

Metal 2010 proceedings available: The Editors and ICOM-CC Metal Working Group Coordinator announce that the conference proceedings from Metal 2010 are available for sale. Please go to www.lulu.com and search for “METAL 2010” to purchase your full colour or black and white copy. Included in the proceedings are 49 full text papers, 13 poster abstracts, transcripts of the question and answer session for each paper, transcripts of the panel discussion for all 12 sessions, and an author index; totalling 489 pages.

La limite de la surface d’origine des objets métalliques archéologiques (“The original surface limits of metallic archaeological artefacts”): PhD thesis by Régis Bertholon, establishes a detailed methodology for determining and describing the location of the former original surface, as modified by its corrosion mechanisms. In French, the document provides an invaluable archaeological metals conservation resource through its synthesis of archaeology, mineralogy and corrosion science. Useful for the conservator and researcher alike, numerous detailed photographs and schema complement the comprehensive text: http://tel.archives-ouvertes.fr/docs/00/33/11/90/PDF/Limitos.pdf

Websites

ANDRA: Agence Nationale pour la Gestion des Déchets RadioActifs. The following documents can be ordered for free from this website: *Analogues archéologiques et corrosion* (French) and *Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems* (English) (http://www.andra.fr/interne.php3?publi=publication&id_rubrique=82&p=produit&id=5).

Archaeological Iron Conservation Colloquium 2010 (24-26 June 2010, State Academy of Art and Design, Stuttgart) extended abstracts (Gerhard Eggert and Britta Schmutzler (Eds.)) are online:

- http://www.iron-colloquium.abk-stuttgart.de/Documents/Tagungsband_session_1.pdf
- http://www.iron-colloquium.abk-stuttgart.de/Documents/Tagungsband_session_2.pdf
- http://www.iron-colloquium.abk-stuttgart.de/Documents/Tagungsband_session_3.pdf
- http://www.iron-colloquium.abk-stuttgart.de/Documents/Tagungsband_session_4.pdf
- http://www.iron-colloquium.abk-stuttgart.de/Documents/Tagungsband_postersession.pdf

ARTECH network: Network facilitating the access of conservation professionals to different investigation techniques for Cultural Heritage artefacts (http://www.eu-artech.org/).

BigStuff 2004: Care of Large Technology Objects (http://www.awm.gov.au/events/conference/bigstuff/index.asp).

BROMEC ListServ: For direct email notification of BROMEC publication web links and calls for submission of abstracts and announcements, simply subscribe with your preferred email address: http://listserv.csv.warwick.ac.uk/mailman/listinfo/bromec-bulletin-of-research-on-metal-conservation

CAMEO: Chemical, physical, visual, and analytical information on over 10,000 historic and contemporary materials used in the conservation, preservation, and production of artistic, architectural, and archaeological materials (http://cameo.mfa.org/).

Cost Action G7: Artwork conservation by laser: (http://alpha1.infim.ro/cost).

Cost Action G8: Non-destructive analysis and testing of museum objects: Abstracts and booklets from previous workshops can be downloaded as well as announcements of past activities (Short Term Scientific Mission deadlines, training schools…) (http://srs.dl.ac.uk/arch/cost-g8/).

Cost Action D42: ENVIART: Chemical Interactions between Cultural Artefacts and Indoor Environment. Register (free) to access all information (http://www.echn.net/enviart/).

Electrochemistry in Historical and Archaeological Conservation (11-15 January 2010, Leiden, the Netherlands). The majority of presentations from this workshop held at the Lorentz Center (http://www.lorentzcenter.nl/), are available for download: http://tinyurl.com/lorentzpresentations

e-Preservation Science: Online publication of papers in conservation science (http://www.morana-rtd.com/e-preservationscience/).

European Cultural Heritage Network: European network of professionals interested in the conservation of Cultural Heritage (http://www.echn.net/).

European Federation of Corrosion's Working Party 21: dedicated to corrosion of archaeological materials http://www.efcweb.org/Working+Parties/WP+21.html

Ge-Conservacion is a periodical published by GEIIC (Grupo Español de Conservación/Spanish Conservation Group of the International Institute for Conservation of Historic and Artistic Works: www.ge-iic.com/) in association with the Duques de Soria Foundation. Its purpose is to contribute to the scientific development, dissemination and exchange of cultural heritage conservation and restoration knowledge: http://ge-iic.com/revista/index.php?lang=en

ICOMAM: International Committee of Museums and Collections of Arms and Military History: (http://www.klm-mra.be/icomam/).

ICOM-CC Metals Working Group: (http://www.icom-cc.org/31/working-groups/metals/). This site is for all official ICOM-CC Metals WG activities, forums, news, file downloads and information. The co-ordinator can email members from this site once members have registered on-line as a member of the Metals WG. Public access to this site is limited.

Incredible Industry: The proceedings from the Nordic Association of Conservators 18th Conference, "Incredible Industry, Preserving the Evidence of Industrial Society" (25-27 May 2009, Copenhagen, Denmark) are now freely available online (www.nkf-dk.dk/Bulletin/NKF-Incredible-industry09.pdf).

Industrial artifacts review: Industrial design and the role of art and photography in promoting cultural heritage (http://industrialartifactsreview.com/).

Infrared and Raman for cultural heritage: (http://www.irug.org/default.asp).

Laboratoire Pierre Sue: LPS PhD thesis related to the alteration of archaeological artefacts can be downloaded in French. Follow the link to "Archéomateriaux et prévision de l'altération" (http://www-drecam.cea.fr/lps/).

LabS-TECH network: (http://www.chm.unipg.it/chimgen/LabS-TECH.html).

METALCons-info: Metals Conservation Information (http://metalsconservationinfomation.wetpaint.com/) is where the old METALCons-info site is being moved and redeveloped. This is a wiki based site, which means it can be grown by contributions from "writers" - i.e. you. Its power depends on how willing you are to use it. Each week it sends a summary of activity to members – so sign up! It is currently publicly visible, but this may change with any unwanted activity.

M2ADL: Microchemistry and Microscopy Art Diagnostic Laboratory (http://www.tecore.unibo.it/html/Lab_Microscopia/M2ADL/).

New York Conservation Foundation: (http://www.nycf.org/).

PROMET: A 3.5 year European 6th Framework funded project (21 partners from 11 countries around the Mediterranean basin) that developed conservation strategies for outstanding metals collections throughout the Mediterranean (http://www.promet.org.gr).

Restauración Metal Sur América: (http://www.restauraciondemetales.cl/).

TEL: PhDs on line (http://tel.ccsd.cnrs.fr/).

Yahoo Groups Metals Conservation: A discussion group for all who are interested in Metals Conservation. Join in and make this a "Metals Cons-Dist List" (http://groups.yahoo.com/group/Metals-Conservation-Discussion-Group).

National Contacts

Argentina: Blanca Rosales (brosales@fibertel.com.ar), researcher, CIDEPINT, La Plata.

Australia: David Hallam (dhallam@nma.gov.au), senior conservator-restorer of objects, National Museum of Australia, Canberra.

Belgium: François Mathis (francois.mathis@ulg.ac.be), archaeometrist, Centre for Archaeometry, University of Liège (Université de Liège), Liège.

Bulgaria: Petia Penkova (petiapenkova@yahoo.com), conservator-restorer, National Academy of Arts, Department of conservation-restoration, Sofia.

Chile: Johanna Theile (jtheile@udd.cl), conservator-restorer and lecturer, Faculty of Art, University of Chile The Oaks (Facultad de Arte, Universidad de Chile Las Encinas), Santiago de Chile.

Croatia: Zoran Kirchhoffer (zoran.k@tehnicki-muzej.htnet.hr), conservator-restorer, Zagreb Technical Museum (Tehnički muzej Zagreb) and Sanja Martinez (smartin@fkit.hr), electrochemist and lecturer, Faculty of Chemical Engineering and Chemical Technology, University of Zagreb (Sveučilište u Zagrebu), Zagreb.

Denmark: Karen Stemann Petersen (karen.stemann@natmus.dk), conservator-restorer, The National Museum of Denmark (National Museet), Copenhagen.

Egypt: Wafaa Anwar Mohamed (wafaaanw@yahoo.com), conservator-restorer, Giza.

Finland: Pia Klaavu (pia.klaavu@nba.fi), conservator-restorer, National Museum of Finland (Suomen kansallismuseo), Helsinki.

France: Elodie Guilminot (elodie.guilminot@arcantique.org), conservation scientist, Arc'Antique, Nantes.

Germany: Britta Schmutzler (britta.schmutzler@gmx.de), PhD "object conservation" student, State Academy of Art and Design (Staatliche Akademie der Bildenden Künste), Stuttgart.

Greece: Vasilike Argyropoulos (bessie@teiath.gr), assistant professor, Department of Conservation of Works of Art, Technological Educational Institution, Athens.

Hungary: Balazs Lencz (lenczb@gmail.com), senior conservator-restorer, Conservation Department, Hungarian National Museum (Magyar Nemzeti Muzeum), Budapest.

India: Achal Pandya (achalpandya@hotmail.com), head of department, Cultural Archives and Conservation, Indira Ghandi National Centre for the Arts, New Delhi, India.

Italy: Paola Letardi (paola.letardi@ismar.cnr.it), scientist, Institute for Marine Corrosion of Metals (Istituto per la Corrosione Marina dei Metalli), Genova.

The Netherlands: Ineke Joosten (ineke.joosten@icn.nl), conservation scientist, The Netherlands Institute for Cultural Heritage (Instituut Collectie Nederlan), Amsterdam.

Norway: Douwtje Van der Meulen (d.l.v.d.meulen@iakh.uio.no), conservator-restorer, Conservation Department, University of Oslo (Universitetet i Oslo), Oslo.

Portugal: Isabel Tissot (isabel.tissot@archeofactu.pt), conservator-restorer, Portuguese conservation-restoration Institute (Instituto Português de Conservação e Restauro), Lisbon.

Romania: Dorin Barbu (barbu_dorin_laboratory@yahoo.com), conservator-restorer, National Brukenthal Museum (Muzeul Naţional Brukenthal), Sibiu.

South Africa: Bradley Mottie (bmottie@iziko.org.za), conservator, Iziko Museums of Cape Town, South Africa.

Russian Federation: Andrey Chulin (andrey_chulin@yahoo.com), conservator-restorer, the State Hermitage Museum, St Petersburg.

Spain: Emilio Cano (ecano@ cenim.csic.es), scientist, National Centre for Metallurgical Research (Centro Nacional de Investigaciones Metalúrgicas), Spanish Council for Scientific Research (Consejo Superior de Investigaciones Científicas), Madrid.

Sweden: Helena Strandberg (helena.st@ comhem.se), conservator-restorer and conservation scientist, freelancer, Göteborg.

Switzerland: Valentin Boissonnas (valentin.boissonnas@ he-arc.ch), conservator-restorer and lecturer, Technical University (Haute école de conservation-restauration Arc), La Chaux-de-Fonds.

United Kingdom: Maickel van Bellegem (Mbellegem@ thebritishmuseum.ac.uk), conservator-restorer, British Museum, London.

United States of America: John Scott (NYConsnFdn@ aol.com), New York Conservation Foundation, New York.