5 IRON AND SILVER OBJECTS – LONGEVITY THROUGH PLASMA?

APPLICATION OF PLASMA REDUCTION ON IRON AND SILVER ARTEFACTS

Katharina Schmidt-Ott

ABSTRACT

Low pressure plasma reduction has been applied for the conservation of metal for a number of years. The use of pure hydrogen plasma and its effects on iron and silver surfaces are described in this study. For iron artefacts the chemical reduction facilitates the mechanical removal of disfiguring corrosion layers as well as helps to accelerate the alkaline sulphite desalination process.

Plasma also offers an interesting alternative to common silver cleaning methods causing less damage to the surface. To avoid changes in metallographic information the actual temperature of the artefacts during treatment is kept to a minimum. In all cases it was below 100° C.

KEYWORDS *Hydrogen plasma reduction, archaeological iron, historical silver artefacts.*

INTRODUCTION

The use of gas plasmas in metal conservation was first reported in 1979 and it continues to be a major subject in conservation research. (Daniels V., Holland, L. and Pascoe, C., 1979, Vepřek S., Eckmann C. and Elmer J., 1988, Patscheider J. and Vepřek S., 1986).

At the Centre for Conservation of the Swiss National Museum, plasma reduction has become an integral part of the conservation treatment procedures for archaeological iron since 1994. It has also been successfully applied to the conservation of historical silver artefacts.

There are two major advantages to using plasma for iron artefacts. Firstly, the reduction of iron oxides in the conglomerate layer causes slight volume changes thus having a loosening effect on that layer. The removal of the disfiguring corrosion products by mechanical cleaning is facilitated. Secondly, and probably also due to volume alteration, the penetration of the agent is made easier and the desalination process with alkaline sulphite is accelerated (Schmidt-Ott K., 1997).

Applied to silver corrosion layers the hydrogen plasma reduces silver sulphide and silver chloride to silver which then stays at the object's surface, at the same time the gaseous products, hydrogen sulphide and chloride, are pumped off.

METHOD AND MATERIALS

For conservation purposes a low ionization plasma is used, formed by a mixture of ions, electrons and neutral gas. Subjected to plasma, the object becomes negatively charged.

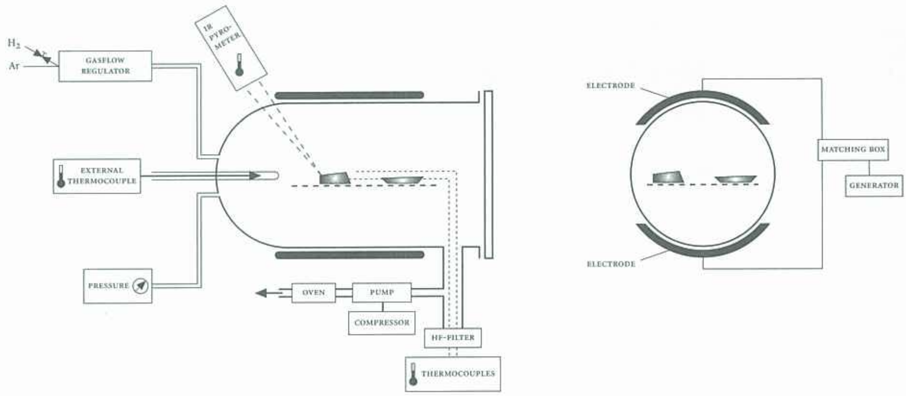

Fig. 1 Plasma apparatus of the Swiss National Museum.

Positive ions accelerated in the potential sheet bombard the object's surface. As atomic hydrogen is a strong reducing agent, iron corrosion products will be chemically reduced to lower oxidation states. Silver corrosion products are reduced to metallic silver.

The applied plasma is produced by a 27 MHz RF-generator in a 0.7 m^3 quartz vessel at a gas pressure of about 15 to 40 Pa (0.1–0.3 Torr). This reactor is equipped with gas inlets, mass flow meters for hydrogen and argon, as well as a pumping system. Power supplies, matching network, thermocouples for direct temperature measurement of objects, and a digital recording of all treatment parameters are parts of this system, see **Figure 1**.

To prevent the loss of metallographic information within the object, temperature during plasma treatment is limited. For example, iron artefacts originally subjected to a quenching process can have a metallurgical structure that is susceptible to temperatures higher than 100° C. (Tylecote and Black 1980, Archer and Barker, 1987). A direct measurement of the artefact during the plasma treatment is necessary. With the use of thermocouples this was achieved (Voûte A., 1997, Schmidt-Ott K. and Boissonnas V., 2002). Silver artefacts may also be affected if the temperature during treatment reaches the recrystallization temperature (Scott D.A., 1991) or age hardening occurs (Thompson F.C. and Chatterjee A.K., 1954, Schweizer F. and Meyers P., 1978). As a valuable measure, therefore, object temperature is determined continuously throughout the plasma reduction process. Specific differences of surface condition, colour and composition are respected.

Investigations have been carried out thus far on a variety of archaeological iron artefacts from Swiss sites, on sterling silver panels with artificially produced layers of silver sulphide and chloride and on various art-historical silver objects. The quality of the conservation is examined by Scanning Electron Microscopy (SEM) and Energy

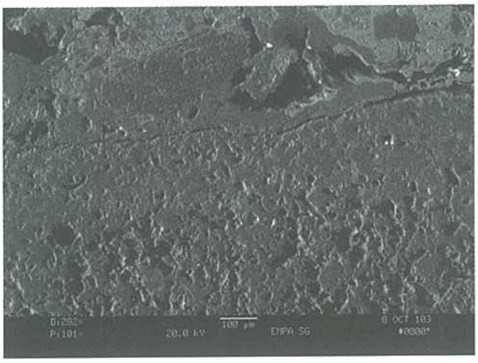

Fig. 2 Scanning electron microscope image of a microsection of a roman nail after hydrogen--argon plasma reduction, treatment time 6 hours, maximum temperature 104° C, (magnification of 100 times).

Dispersive x-ray fluorescence analysis (EDX). If possible the same sector of the surface is examined before and after plasma application.

TREATMENT OF IRON ARTEFACTS

All conservation treatments are aimed to preserve the information contained in each artefact as well as the integrity of the piece. Furthermore, for exhibition purposes or archaeological investigation oftentimes, the original surface of an artefact is uncovered and so it is important that precision be involved in the removal of the outer corrosion layers.

Iron corrosion products constitute generally oxides, oxyhydroxides, chlorides and sometimes carbonates. There may be a preserved metallic core surrounded by a compact inner corrosion layer, the boundry of which compares in shape to the original specimen. Further outside is a layer, a mixture of corrosion products and components of the soil (Neff, D., Reguer S., Bellot-Gurlet L., Dillmann P., Bertholon R., 2004).

Upon excavation, an iron artefact becomes highly unstable. In the presence of atmospheric oxygen and humidity, the chloride which is present from burial plays an active part in the further corrosion of the artefact (Selwyn L., 2004). Akaganéite [ß-FeO(OH)] a chloride containing corrosion product can be formed. This iron oxy chloride is insoluble in water and contains high amounts of chloride. The removal of chlorides is important to the long term stabilisation of iron objects, including those unsolvable in water. This can be done by desalination in alkaline sulphite.

It is supposed that during reduction in hydrogen plasma various iron oxides are transformed to lower oxidation states. Density and structural changes give an indication of this being so. As a consequence and being an asset of the plasma method an easier separation between compact inner layer and disfiguring outer layer becomes the result. **Figure 2** shows a micro section of a roman iron nail after plasma reduction as seen under a scanning electron microscope. A separation between the outer

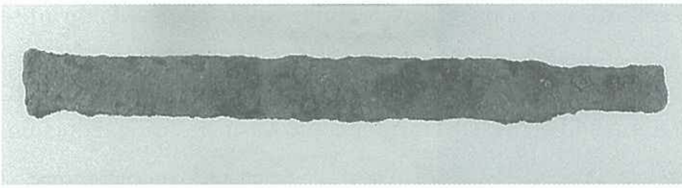

Fig. 3

Iron file status on arrival in conservation laboratory.

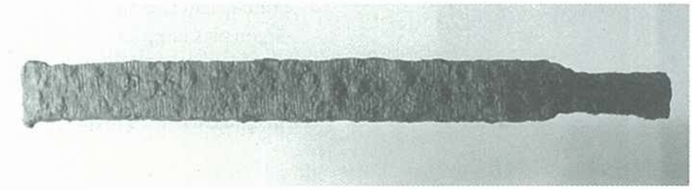

Fig. 4

Conserved iron file, after plasma reduction, mechanical cleaning with air abrasion, desalination in alkaline sulphite and coating with acrylic resin.

voluminous corrosion layer on top and the hard dense corrosion layer below, can be seen, the lower layer approximating the original shape of the object. In the mechanical cleaning that follows, the disfiguring outer corrosion crust can be removed by means of air abrasion.

It is important to note that a partial reduction is often preferable as compared to a complete reduction, causing less brittleness overall.

Figures 3 and 4 show a middle-age iron file before and after its conservation. It comes from the site Rheinau-Austrasse and was excavated by the archaeology service of the Kanton Zurich. It should be emphasised that the file marks to be seen in **Figure** 4 probably would not have been visible and would not have survived mechanical cleaning with a micro motor. This would have been a common cleaning method prior to the use of air abrasive cleaning. The combination of plasma reduction and mechanical cleaning by air abrasion resulted in an exemplary status.

PLASMA PARAMETERS FOR IRON CONSERVATION

Gas mixtures of methane and/or nitrogen in addition to hydrogen and argon have been proposed at an earlier stage of investigation (Veprek S., Eckmann C. and Elmer J., 1988). It was assumed at the time that such mixtures would work to both clean and provide surface protection, without the need for additional desalination.

Today gas mixtures such as these are regarded as being less than ideal (Schmidt-Ott, 1997). Firstly, it has been found that desalination remains essential to the process of slowing deterioration in iron artefacts. Secondly, the introduction of carbon and nitrogen to an artefact`s surface was found to have a negative effect on both appearance and metallurgical information.

Until recently, mixtures of hydrogen and argon were applied in treatment of iron artefacts, the argon being used to stabilize the discharge and to enhance the effect of surface interaction. Argon ions receive larger momentum than hydrogen ions in the sheet at the surface and if argon is added the object will become warmer during reduction treatment.

From 1994 to 2004 at the Swiss National Museum standard treatment of iron artefacts has consisted of a mixture of ten parts of hydrogen to one part of argon. Treatment time was between 6 and 7 hours, the power of the generator around 1 kW, temperature of the artefacts around 100–120° C during the process.

Nowadays the use of pure hydrogen plasmas is shown favourably and as a consequence treatment temperature has been lowered to 80–90° C (Schmidt-Ott K., 2004).

The hydrogen gas pressure ranges from 15 to 40 Pascal. The pressure at constant pumping is regulated by the gas flow. Surface temperature of the object depends on the pressure setting. Normally, a RF power of 1 kW and a plasma treatment time of 6 hours are used. This is sufficient to yield the easier mechanical cleaning operation.

A complete removal of chlorides in the plasma reduction has not been possible and making a subsequent desalination process using alkaline sulphite solution a necessary follow up to the operation (Schweizer F., Rinuy A., 1982; Greif S., Bach D., 2000).

Micro fissures, which might result from density changes in the inner corrosion layer during plasma treatment, facilitate the release of chlorides. Tests with and without plasma use, showed that a plasma treatment will shorten the desalination time (Schmidt-Ott K., Boissonnas V., 2002).

After plasma, desalination and mechanical cleaning, the specimen is in a stabilised state. Further corrosion however, can not be completely prevented by conservation alone. The object would have to be stored continually under ideal conditions (e.g. protective gases) to obtain full stability. Because artefacts are usually kept in everyday conditions during transport, handling and exhibitions, protective coatings are a necessity to the conservation treatment. An acrylic resin, Paraloid B44, has shown good results.

TREATMENT OF SILVER ARTEFACTS

Atomic hydrogen reacts with silver corrosion products. The interaction is more complete than in the case of iron artefacts. Silver sulphide and silver chloride can be reduced to silver with hydrogen. The reduced silver layer remains on the artefact's surface. If a pure hydrogen plasma is used practically no removal of silver takes place. The formed hydrogen sulphide or hydrogen chloride are pumped off.

During earlier experiments gas mixtures from hydrogen and argon were also used. Argon ions with larger momentum however might more easily cause sputtering and

Fig. 5 Daguerreotype from 1850, before treatment showing heavy tarnishing from silver sulphide. Details of the picture are therefore not visible.

Fig. 6 The same daguerreotype after 54 minutes hydrogen plasma treatment, at a maximum temperature of 85° C.

therefore a loss of silver. For silver objects pure hydrogen plasma has been applied as a standard at the Swiss National Museum since 2001.

Without occurrence of sputtering, hydrogen has been proven to be very effective in silver conservation (Schmidt-Ott K., 2004).

The average treatment time for silver artefacts is 5 to 60 minutes, depending on the thickness of the corrosion layer. The artefact`s temperatures usually range from 40–90° C and the pressure in the vessel is 13–40 Pa. The treatment in the reactor can be interrupted for observation of the artefact and continued a new without problem to the process.

A special realm of the hydrogen plasma is the conservation of daguerreotypes. These consist of a polished copper plate with an extremely thin layer of a light sensitive silver compound. By light exposure and development a photographic picture constituted by the silver distributions is formed (Hopkins M.,1887).

The daguerreotype in **Figure 5** is darkened by exposure to H_2S (hydrogen sulphide) contained in air. Such artefacts can not be cleaned mechanically because the picture itself would be removed during the process. In **Figure 6** the object is shown after a series of treatments in a hydrogen plasma with a total treatment time of 54 minutes. The temperature of the daguerreotype had been at a maximum of 85° C.

Fig. 7 Silver box before plasma reduction showing tarnished areas including fingerprints.

Fig. 8 Silver box after treatment in pure hydrogen plasma for 55 minutes, the maximum temperature being 93° C. The tarnish is removed.

While invisible before details of picture, like the floral elements on the tablecloth, can be recognised. Following plasma reduction sensitive artefacts such as daguerreotypes should not undergo any subsequent treatment, storage in a controlled and pollutant free environment being enough to protect the object from new corrosion.

Figures 7 and 8 show a silver box before and after plasma reduction. It was treated in a hydrogen plasma for 55 minutes, the object's temperature at a maximum of 93° C. For artefacts with a 3-dimensional decoration, plasma proved to be ideal since the reduction is more effective in the higher areas than in the pits, leaving a lively silver surface.

For the treatment of such objects, it has proven effective to gently burnish the freshly reduced surface with pure cotton wool. The surface of a heavily tarnished silver generally is slightly enlarged through the corrosion process; subjected to plasma reduction the reduced silver will remain on the surface. A gentle burnishing can give the surface a higher density without introducing new scratches and will therefore make it less susceptible to further corrosion.

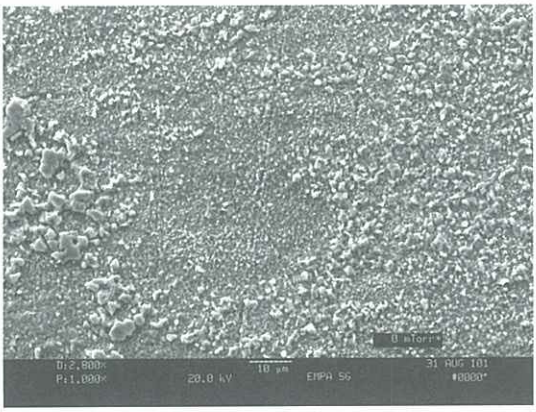

Fig. 9 Sterling silver plate with an artificially produced layer of silver sulphide at a magnification of a 1000 times.

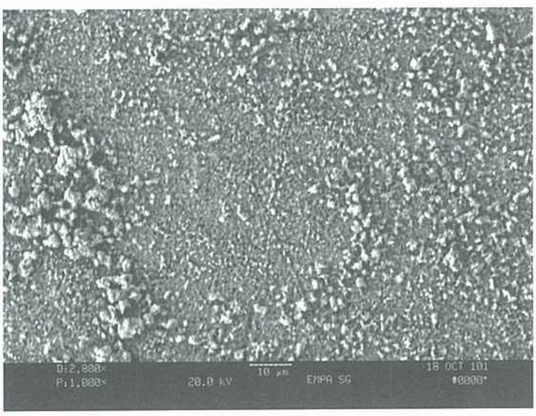

Fig. 10 The same plate as in Figure 9 after 5 minutes of hydrogen plasma reduction (magnification 1000 times).

Scanning Electron Microscope (SEM) and Energy Dispersive x-ray fluorescence analysis (EDX) were applied on artificially produced silver sulphide surfaces on sterling silver plates to show the quality of corrosion product removal by plasma reduction. **Figures 9** and **10** show the same area of a silver sample with such an artificially produced layer of silver sulphide before and after 5 minutes of hydrogen plasma reduction. The removal of the sulphur causes the surface to become slightly enlarged, yet it can be seen that no surface damage occurs, as will happen in mechanical cleaning.

Figure 11a shows EDX analysis of the sample with silver sulphide layer prior to plasma reduction, the sulphur can be clearly measured. **Figure 11b** shows the EDX result of the same surface after hydrogen plasma reduction, the sulphur having been removed and only the metallic silver remaining.

Similar results have been shown for silver chloride surfaces before and after plasma treatment.

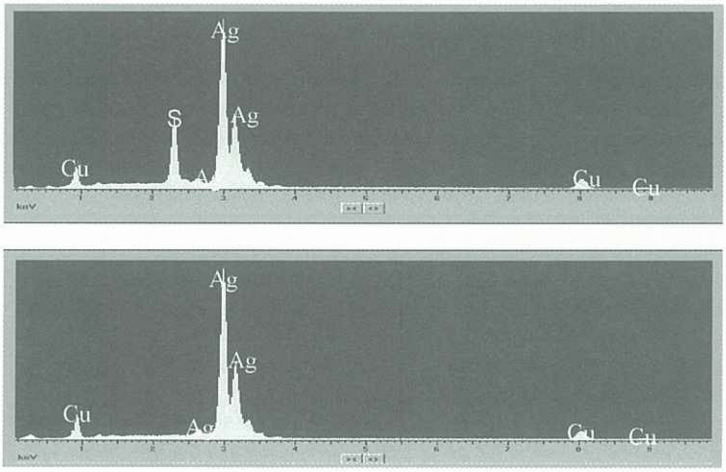

Fig. 11 EDX results obtained for the plates as shown in Figures 9 and 10.
a) Sulphur is seen from the untreated surface.
b) No sulphur can be detected after hydrogen reduction.

RESULTS

Our present investigations have shown that hydrogen plasma reduction is effective and successful when applied as an integral part of a series of treatment steps in the cleaning and stabilization of archaeological iron. Furthermore, plasma reduction can be successfully employed for the conservation of silver artefacts. It is especially useful for objects that cannot be cleaned mechanically or in solutions because of their sensitivity. A particular advantage of hydrogen plasma reduction using the right parameters is that there is no loss of metal and that no damage occurs to the surface.

ACKNOWLEDGEMENTS

This work was performed at the Swiss National Museum Zurich in collaboration with the Ph.D. programme in object conservation at the State Academy of Art and Design Stuttgart. The Swiss National Museum is thanked for the conducive working conditions that contribute towards the realisation and Prof. Dr. G. Eggert, State Academy of Art and Design Stuttgart, for his ongoing interest in this project.

The author would also like to thank Alexander Voûte whose help was crucial for the realisation of the measurement devices as well as Wolf-Dieter Schmidt-Ott and Kim Travis for their support and the colleagues at the Swiss National Museum.

Further the author would like to thank the archaeological service of the Kanton Zurich for the supply of iron artefacts used for metallurgical sampling and study purposes. Special thanks are also due to the Swiss Federal Laboratories for Materials' Testing and Research (EMPA) in St. Gallen, especially for making possible the use of the SEM and EDX equipment.

REFERENCES

Archer P.J. and Barker B.D. (1987), "Phase changes associated with the hydrogen reduction conservation process for ferrous artefacts", *Journal of the Historical Metallurgy Society* 21, pp. 86–91.

Daniels V., Holland, L. and Pascoe, C. (1979), "Gas plasma reactions for the conservation of antiquities", *Studies in Conservation* 24, pp. 85–92.

Greif S., Bach D. (2000), "Eisenkorrosion und Natriumsulfitentsalzung: Theorie und Praxis", *Arbeitsblätter für Restauratoren*, 2000 (2), group 1, pp. 319–339.

Hopkins M. (1887), "The Daguerreian Process", *Scientific American*, 56, No. 4, pp. 47–52.

Neff, D., Reguer S., Bellot-Gurlet L., Dillmann P., Bertholon R. (2004), "Structural characterization of corrosion products on archaeological iron: an integrated analytical approach to establish corrosion forms", *Journal of Raman Spectroscopy*, 35, pp. 739–745.

Patscheider J. and Veprek S. (1986), "Application of low-pressure hydrogen plasma to the conservation of ancient iron artefacts", *Studies in Conservation*, 31, pp. 29–37.

Schmidt-Ott K. (1997), "Application of low pressure plasma treatment at the Swiss National Museum and assessment of the results", *Zeitschrift für Schweizerische Archäologie und Kunstgeschichte*, 54, pp. 45–50.

Schmidt-Ott K. und Boissonnas V. (2002), "Low-pressure hydrogen plasma: an assessment of its application on archaeological iron", *Studies in Conservation*, 47, pp. 81–87.

Schmidt-Ott K. "Plasmareduktion von Silberoberflächen", Exposure 2001 Institute of Conservation, Hildesheim 7th–10th November 2001, publication forthcoming.

Schmidt-Ott K. (2004), "Plasma-reduction: its potential for use in the conservation of metals, In J. Ashton J. & D. Hallam (eds) ICOM *Metal 04*, pp. 235–246 .

Scott D.A. (1991), *Metallography and Microstructure of Ancient and Historic Metals*, Getty Conservation Institute, (Singapore: Tien Wah Press. Ltd.).

Schweizer F. and Meyers P. (1978), "Structural changes in ancient silver alloys: the discontinuous precipitation of copper", ICOM *5th Triennial Meeting*, Zagreb Rapport 78, 23, 5.

Schweizer F. and Rinuy A. (1982), "Entsalzung von Eisenfunden mit alkalischer Sulfitlösung", *Arbeitsblätter für Restauratoren*, 1, group 1, pp. 160–174.

Selwyn L. (2004), "Overview of archaeological iron: the corrosion problem, key factors affecting treatment, and gaps in current knowledge", in J. Ashton J. & D. Hallam (eds) ICOM *Metal 04*, pp. 294–306.

Thompson F.C. and Chatterjee A.K. (1954), "The age-embrittlement of silver coins", *Studies in Conservation*, 1, pp. 115–125.

Tylecote R.F. and Black J.W.B. (1980), "The effect of hydrogen reduction on the properties of ferrous materials", *Studies in Conservation*, 25, pp. 87–96.

Veprek S., Eckmann C. and Elmer J. (1988), "Recent progress in the restoration of archaeological metallic artefacts by means of low-pressure plasma treatment", *Plasma Chemistry and Plasma Processing*, 8 (4), pp. 225–241.

Voûte A. (1997), "The plasma equipment at the Swiss National Museum – observations and improvements", *Zeitschrift für Schweizerische Archäologie und Kunstgeschichte*, 54, pp. 41–44.

BIOGRAPHIC NOTE

Katharina Schmidt-Ott is a conservator for archaeological artefacts at the Swiss National Museum. Since 1994 she has been responsible for the development and the use of the hydrogen plasma method and for the conservation of archaeological artefacts. She received her diploma in objects conservation from the Staatliche Akademie der Bildenden Künste, Stuttgart, Germany, in 1993 and lectured objects conservation at the Staatliche Akademie der Bildenden Künste, Stuttgart from 1993 to 1994.
The present work is part of her Ph.D. thesis. She is enrolled at the Ph.D. programme in object conservation at the Academy of Art and Design Stuttgart.