Plasma-Reduction: Its Potential for Use in the Conservation of Metals

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Abstract

The use of optical emission spectroscopy has lead to an optimization of the plasma parameters for the handling of iron artefacts. The effects of plasma reduction have also been investigated through metallographic sampling of iron nails.
It is shown that a pure hydrogen plasma is more effective in reducing corrosion layers than a mixture of hydrogen and argon. As a consequence the temperature of iron artefacts during plasma reduction can be reduced to around 80 °C. Plasma is further applied in the reduction of silver sulphide layers from art historical silver artefacts without altering the surface structures or interfering with the information contained within the historical metalwork.

Keywords: plasma reduction, iron artefacts, silver objects, optical emission spectroscopy, metallographic sampling, scanning electron microscope

1. Introduction

Gas plasmas have been the subject of various investigations since their initial application to metals conservation in 1979 (Daniels, Holland, and Pascoe 1979, Patscheider and Vepřek 1986). Since 1994, plasma reduction has become an integral part of treatment procedures for archaeological iron conservation at the Swiss National Museum. It has also been successfully applied to the conservation of historical silver artifacts.

There are two major advantages to using plasma treatment for iron artefacts. These are firstly the reduction of oxides in the conglomerate layer and the subsequent facilitating of mechanical removal of disfiguring corrosion layers. And secondly, there is the advantage of speeding up the desalination process with alkaline sulphite (Schmidt-Ott 1997).

As applies to silver corrosion, hydrogen plasma can remove the sulphide or chloride layers without removing any metallic silver.

Modern optical emission spectroscopy (OES) was used to monitor the plasma process (Keppner, Kroll, Torres, Goetz and Meier 1997). By measuring gas excitation the plasma operation was optimized. A better understanding of the process has given way to changes in the plasma parameters applied. The effects observed have been cross-checked by the investigation of metallographic samples of archaeological iron artefacts prior to and after plasma reduction.

2. Materials and Methods

2.1 Plasma reduction

Atomic hydrogen is considered to be the key radical produced in hydrogen plasma that leads to a chemical reduction of corrosion products.

The applied plasma is produced by a powerful 27 MHz generator in a 0,7 m^3 quartz vessel at a gas pressure of about 15 to 50 Pa (0.1-0.4 Torr). This reactor is equipped with gas inlets and mass flow meters for hydrogen and argon and a pumping system. Power supplies, matching network, thermocouples for direct temperature measurement and a digital recording of all treatment parameters are parts of this system (Voûte 1997, Schmidt-Ott and Boissonnas 2002).

For conservation purposes, a low ionization plasma is used formed by a mixture of ions, electrons and neutral gas. Placed in the plasma the object becomes negatively charged. This effect is related to higher electron mobility, than ion mobility in the gas. As a consequence, positive ions bombard the object`s surface and as they

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become neutralised act as a strong reducing agent in the case of nascent atomic hydrogen. Thereby iron corrosion products can be chemically reduced to a lower oxidation state and silver corrosion products to metallic silver.

Gas mixtures using methane and/or nitrogen in addition to hydrogen and argon which were proposed at an earlier stage to be useful for surface protection (Vepřek, Eckmann and Elmer 1988), are regarded today as being less than ideal. This is because they can introduce carbon and nitrogen to the artefact and therefore change the contained metallurgical information.

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

It is of importance to avoid changes in metallographic information due to the effect of increased temperature and local heat production. For example, iron artefacts originally subjected to quenching will have a metallurgical structure that is susceptible to higher temperatures (Tylecote and Black 1980, Archer and Barker 1987). Silver artefacts may also be affected if the temperature during treatment reaches the recrystallization temperature (Scott 1991) or age hardening occurs (Thompson and Chatterjee 1954, Schweizer and Meyers 1978). Temperature is therefore the foremost measure that is continuously determined on the objects themselves during plasma reduction. The use of thermocouples enables an online temperature measurement of the artefacts with respect to the plasma parameters applied as well as the surface condition and composition of each artefact.

2.2 Optical emission spectroscopy

Within the plasma reactor measurements were initially performed without specimens. An optical emission spectrometer (OES, Avantes AVS SD2000) sensitive to the radiation of atomic and molecular species was used to monitor the process. It was focused in the middle of the reactor from outside through a quartz glass window in the door.

The formation of atomic hydrogen was measurable by the Balmer H□ line at 656.30 nm (nanometre). The presence of argon in the gas was indicated by a strong line at 706.22 nm. For line identification the software Plasus SpecLine was applied to the measured spectra giving, in many cases, precise and facilitated interpretation. It is assumed that by optimization of gas excitation the plasma operation is also optimized.

During incipient experiments with pure hydrogen and hydrogen-argon mixtures, parameters of gas mixture, gas flow, pressure and power of the generator were varied. Optimal settings were then assumed to also be valid for the treatment of metal artefacts. A group of archaeological iron artefacts was processed with these “ideal” parameters. Another group of artefacts was treated using the “standard” parameters current for the time and compared with the “ideal” group.

2.3 Metallographic sampling of iron artefacts

A group of twenty roman nails (site of Wetzikon-Kempten Hinwilerstr. 1, No. 99) was chosen with typical, visible corrosion damage. These objects underwent radiography before further handling. The artefacts were then cleaned by air abrasion to remove only superficial soil. Metallurgical sampling prior to and after the reduction was performed to help estimate the effect of treatment.

Sample profiles before and after plasma application were then observed under a scanning electron microscope and polarized light microscope. Polished micro sections from the nails were prepared for this purpose (Scott 1991).

The radiographs were used to define similar situations of corrosion states where sampling before and after plasma treatment was planned. The metallographic samples were taken by a precision diamond wire saw (Well 3242), with dimensions of 1 mm thickness and 1-2 mm in depth of the nail. Attention was paid to the fact that the nails were not cut into too deeply so as not to change significantly the electric conductivity of the artefact for the following plasma reduction.

All nails were stored in controlled silicagel for ten months prior to treatment.

The nails were then divided into 3 groups. A reference group of nails was submitted to drying in a vacuum oven at a temperature of ca. 80 °C for 6 hours, as is usual for archaeological iron objects before plasma reduction.

A second group was simply pre-dried in silicagel before undergoing plasma reduction at the parameters currently applied to iron artefacts. Values applied were of hydrogen-argon plasma with 6 litre normal per hour (ln/h) hydrogen and 0.6 ln/h argon, 1100 Watt, at an average pressure of 34 Pa.

A third group was also pre-dried in silicagel only and then treated in a pure hydrogen plasma with 2 ln/h and 1100 Watt. Due to the lower gas inlet, the pressure was lower (about 15 Pa).

From each of the nails in the three groups at least two samples were taken, one before and one after drying and/or plasma treatment. All samples were mounted in a liquid photo curing resin based on mono and difunctional methacrylates (Technovit 2000LC by Kulzer) and then ground, and subsequently polished using a Struers Dap-V polishing device.

Observations of sample surfaces before and after plasma application were made under a polarized light microscope and under a scanning electron microscope (SEM, Amray 3200 ECO-SEM).

2.4 Treatment of silver artefacts

As could be shown previously hydrogen plasma can remove sulphide and chloride from silver samples with artificially produced silver sulphide and silver chloride layers, without any damage to the sample surface (Schmidt-Ott 2004).

In the meantime a number of art historical silver artefacts have been treated in a pure hydrogen plasma. The examinations of a silver spoon (LM 17672) with an apostle figurine on the handle, engraving and mercury gilding are of special interest since the object shows the combination of silver with gold. The spoon dates from 1650-1700, and is 16 cm long and 4.7 cm wide.

Prior to plasma reduction the spoon was examined under the SEM at a magnification of 500x and analysis of the surface composition was performed by means of energy dispersive X-ray fluorescence analysis (EDS). The object was treated for 90 minutes in a pure hydrogen plasma (hydrogen 4 ln/h, 20 Pa, 770 Watt and maximum temperature of artefact being 82 °C) and then was investigated again with SEM and EDS.

Another example shows a dark and uneven tarnished chalice from 1938 (LM 79223) which was also treated in hydrogen plasma for 2.5 hours. The treatment parameters being: hydrogen 6 ln/h, about 29 Pa, 1030 Watt and temperature of object maximum 85° C. This artefact was chosen due to its three dimensional shape to see if plasma reduction, as applied to smaller silver artefacts, could remove the disfiguring sulphide layer from all sides of such an object at one time or if it would be necessary to turn it between treatments.

3. Results

3.1 Measurements with optical emission spectroscopy (OES)

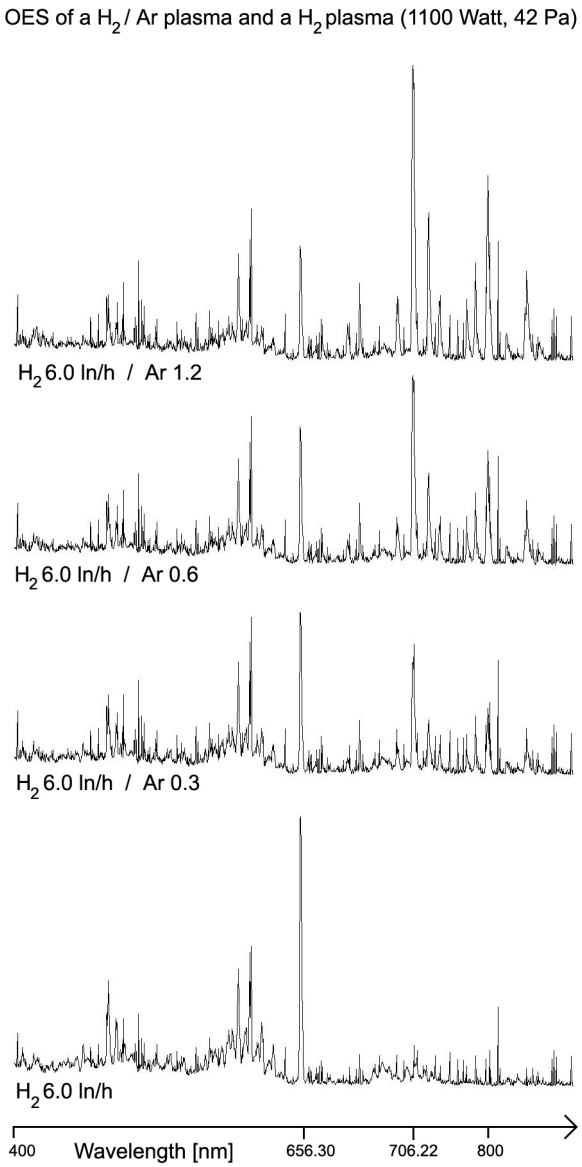

Figure 1. Typical OES from a hydrogen-argon and pure hydrogen plasma at a pressure of 42 Pa and at 1100 Watt. As a parameter the gas-flow ratio was varied. The line at 656.30 nm refers to the hydrogen emission; the line at 706.22 nm refers to argon.

Figure 1 shows OES spectra from hydrogen argon as well as from a pure hydrogen plasma. Only the most significant lines of the emission spectrum are labelled. Since atomic hydrogen plays the key role in the reduction of corrosion products its measurement is of special interest.

Atomic hydrogen has a strong red emission line at 656.30 nm. It is assumed that the intensity of this line is proportional to the steady-state concentration of atomic hydrogen produced from molecular hydrogen gas. Argon has a strong emission at 706.22 nm. If argon is added the intensity of the hydrogen line is reduced. Qualitatively the higher the argon concentration the smaller the hydrogen line becomes. In comparison a pure hydrogen plasma clearly shows a hydrogen line of higher intensity. All measurements were performed at the same level of generator power, and at the same pressure, which was adjusted by regulating the valve of the pump. It can be concluded that in the former standard reduction with 6-8 ln/h hydrogen and 0.6-0.8 ln/h argon, less atomic hydrogen is available in the vessel than in a pure hydrogen plasma.

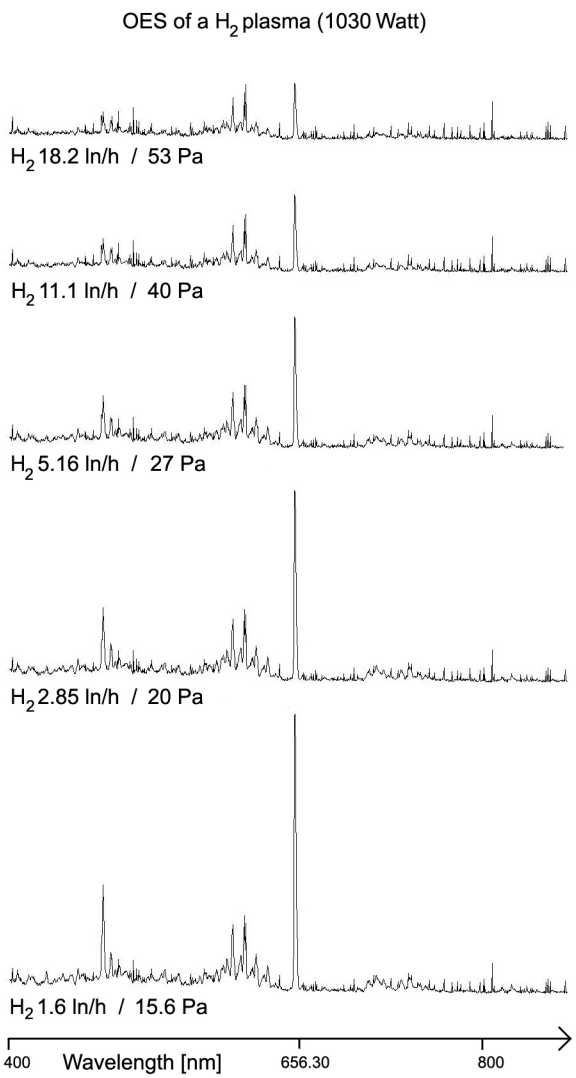

Figure 2. OES spectra observed in pure hydrogen plasma at different pressures in the vessel at 1030 Watt, fully open pump valve and increasing increments of hydrogen. The intensity of the line at 656.30 nm is assumed to be proportional to the steady-state concentration of atomic hydrogen produced.

Thus there might be an optimal amount of hydrogen for a most effective plasma reduction treatment. Figure 2 shows typical OES spectra observed in a pure hydrogen plasma at different pressures in the vessel. This was arranged with a fully open pump valve and by increasing increments of hydrogen. The capacity of the generator was kept to 1030 Watt in this series. It can be seen that there is a clear relationship between pressure and the intensity of the hydrogen line. At 15.6 Pa and 1.6 ln/h hydrogen flow the highest intensity of the hydrogen line is measured. Then the main free path for excitation and ionization corresponds approximately to the sheath layer. Below a flow of 1.4 ln/h hydrogen the plasma becomes unstable and the discharge may even collapse. It can be concluded that it is useful to reduce the amount of hydrogen to about 2 ln/h for the treatment of artefacts.

Similar characteristics can be expected during the treatment of pre-dried iron artefacts. In addition, when placed in the plasma the chemical elements emitted from the artefacts can be traced by their characteristic lines when the released elements and/or formed compounds are present in high-enough concentrations.

The pure hydrogen plasma which because of its gentle treatment nature, was applied only to sensitive materials such as silver, is now also applied to archaeological iron artefacts. The same reduction effect can now be achieved at lower temperatures. For pre-dried iron artefacts the surface temperatures lie around 80 °C as compared to ~120 °C in a typical hydrogen-argon plasma.

3.2 Metallographic sampling of iron nails

All samples showed a clear stratigraphy between outer disfiguring corrosion layers, original surface, and metal cores if still existent.

The SEM images were of special interest since back scattered electron imaging (BSI) shows different states of corrosion. When a sample is being scanned with the electron beam, backscattered electrons are also formed. Their intensity is dependent on the atomic number of the excited element. Light areas in the backscattered electron images correspond to high average atomic numbers. Areas with a metal core are therefore light, heavily corroded areas appear darker (the atomic number of iron is 26, of oxygen 8, of hydrogen 1).

Results between the two groups that had undergone hydrogen and hydrogen-argon plasma reduction showed no significant differences. In many cases, after plasma reduction for the pure hydrogen as well as for the hydrogen-argon, a clear separation of the outer corrosion layer from the original surface was observed. It can be assumed that this separation contributes to the facilitation of the mechanical cleaning.

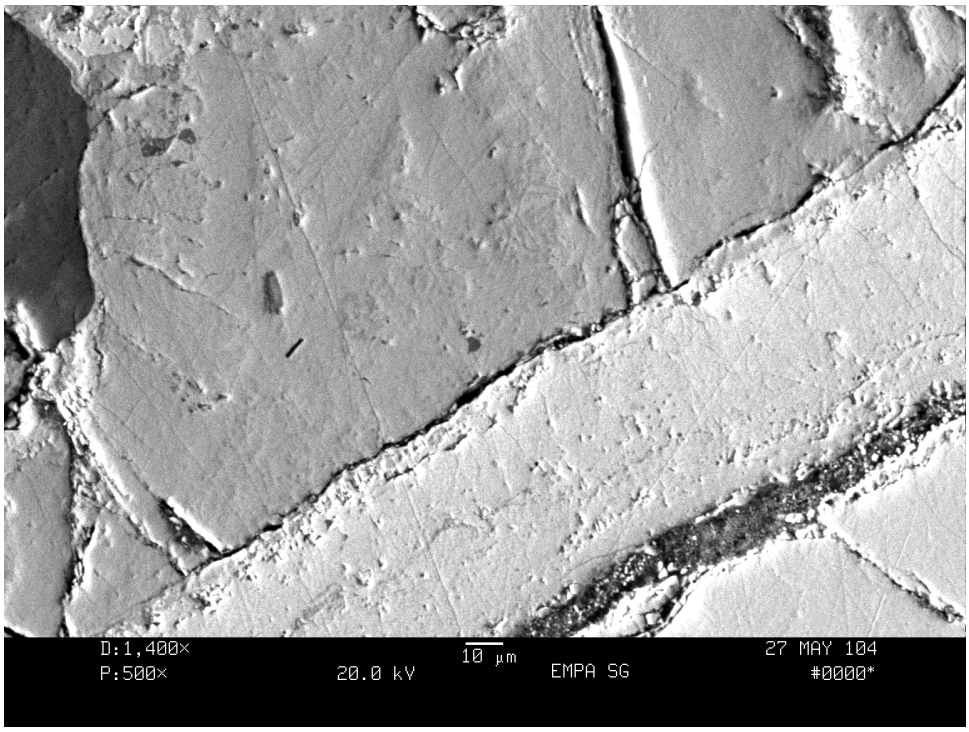

Figure 3. SEM of a polished sample of a nail (No 99.15) after hydrogen-argon plasma reduction, at a magnification of 500x the artefacts temperature being maximum 116 °C.

Figure 3 shows a nail of the group selected for the hydrogen-argon plasma after plasma reduction. The artefact`s temperature measured with thermocouples had reached maximum 116°C.

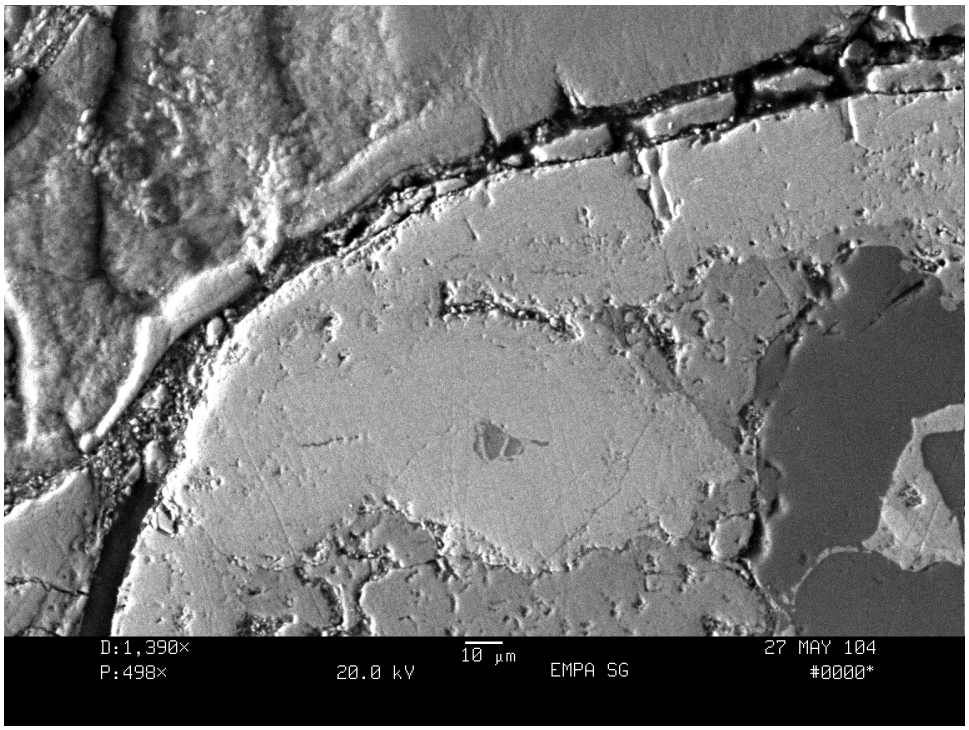

Figure 4. SEM of sample of a nail (No 99.2) selected for the pure hydrogen reduction after treatment, at a magnification of 498x, the artefacts` temperature during reduction was around 70 °C.

Figure 4 shows a representative of the group treated in a hydrogen plasma and at lower pressure after reduction. On account of a connection between pressure and sample temperature, the temperatures measured during plasma were ca. 70 °C.

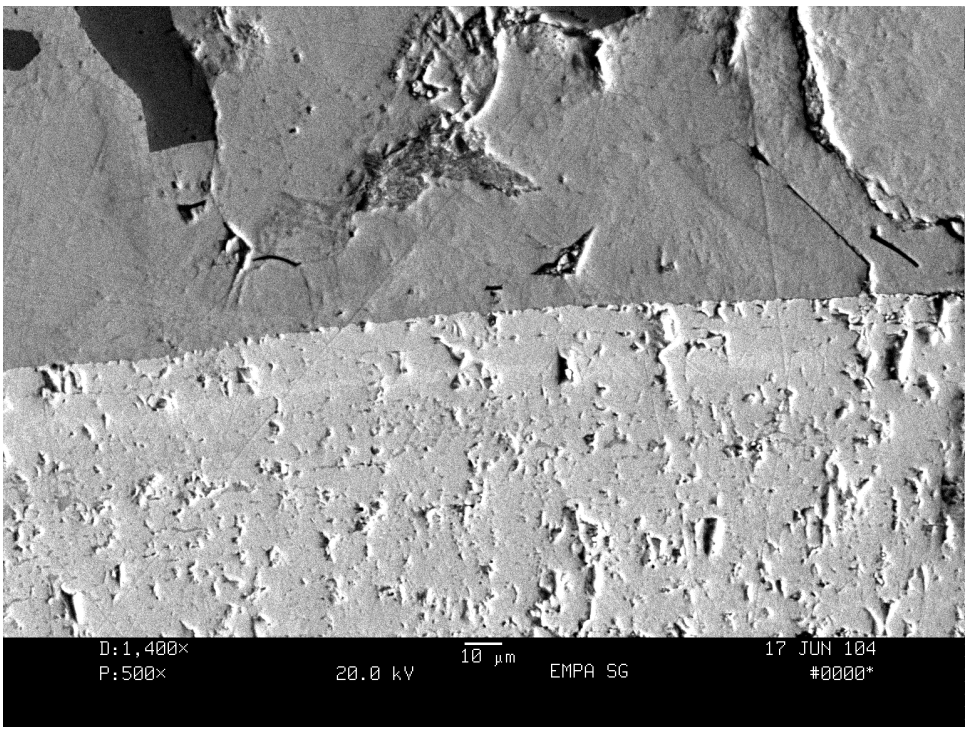

Figure 5. SEM image of metallographic sample of a nail (No 99.16) after pre-drying in a vacuum oven at 85 °C. At a magnification of 500x no separation between disfiguring corrosion layers and original surface can be seen.

The metallographic samples of the nails that had only undergone pre-drying showed no relatable changes in their structure or stratigraphy. Figure 5 shows the sample of a nail after the treatment in the vacuum oven at ca. 85 °C.

From this it can be concluded that the pre-drying at ca. 80 °C as is usually applied to archaeological iron artefacts prior to plasma reduction, will not lead to an improved facilitation of the removal of corrosion layers.

3.3 Silver artefacts

The spoon (LM 17672) was examined prior to and after the plasma reduction. It was of special interest whether the plasma treatment would change any details important to the manufacturing of the artefact.

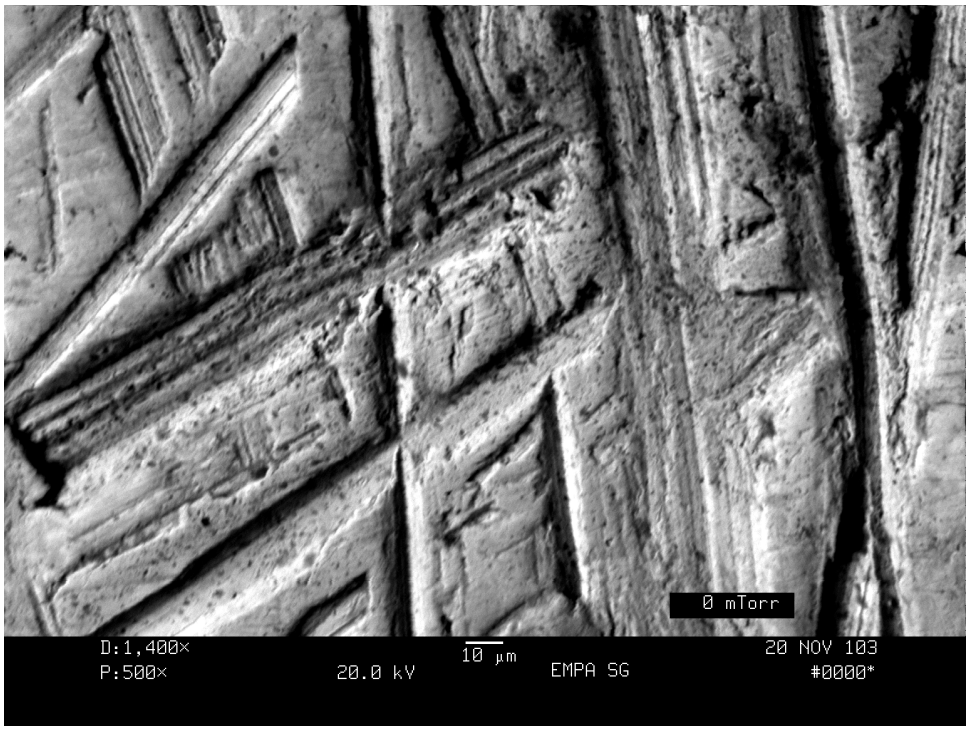

Figure 6. Detail of silver spoon prior to plasma reduction at 500x magnification under the SEM, scratches being visible.

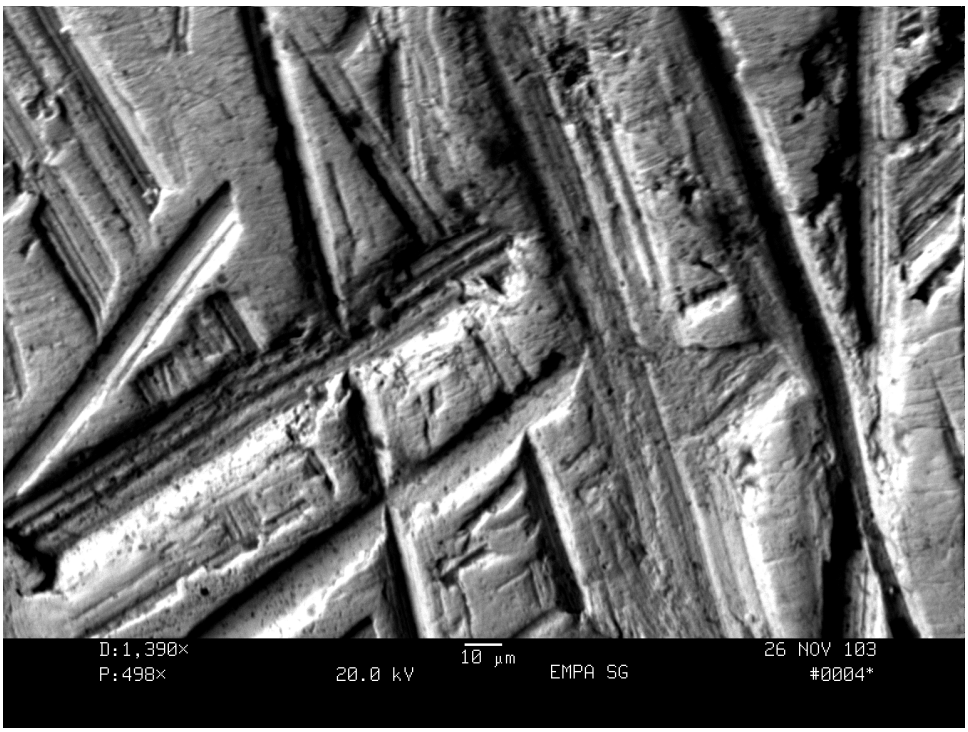

Figure 7. Detail of spoon after hydrogen reduction at 500x magnification, no change of surface structure or additional damage to the surface is visible.

Prior to the reduction treatment, the surface of the artefact showed heavy scratches due to prior handling and possibly also cleaning as can be seen in Figure 6. Figure 7 shows the same detail after plasma reduction. At a magnification of 500x no change of surface structure or additional damage to the surface is visible. As expected the EDS spectrum prior to the plasma reduction showed lines of silver and gold but also of sulphur, mercury and copper, see Figure 8.

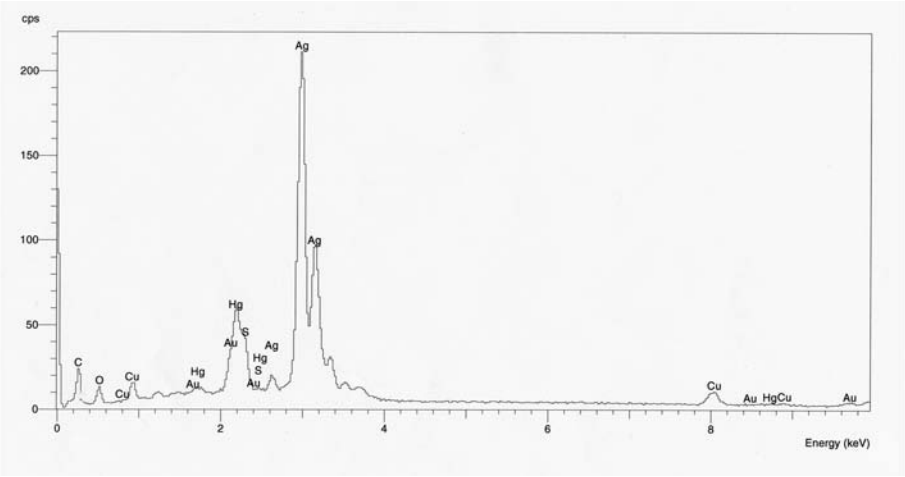

Figure 8. EDS spectra of silver spoon prior to plasma reduction showing lines of silver and gold but also of sulphur, mercury and copper.

After the plasma treatment the EDS spectrum (Figure 9) shows that sulphur has been removed whereas silver, gold, mercury and copper are still present. Here the presence of mercury indicates the gilding method used. It is important that this finding can still be detected after plasma reduction.

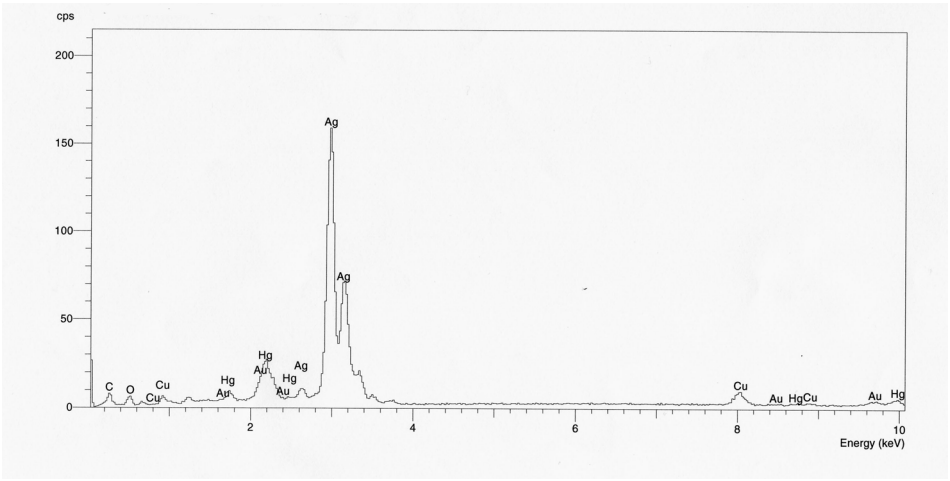

Figure 9. EDS spectra of silver spoon after plasma reduction, showing that sulphur has been removed whereas silver, gold, mercury and copper are still present.

The example also shows that it is possible to remove the tarnish layers with hydrogen plasma reduction without noticeably effecting other chemical elements.
The object looks nicely cleaned after the plasma treatment and is still showing darker areas in the depths and therefore a lively appearance. This is considered to be a major advantage of the method in opposite to electro-chemical and chemical silver cleaning methods. In this case no other surface treatment has been applied.

For the tarnished silver chalice (LM 79223), the tarnish layer was gradually removed within half an hour of the hydrogen plasma reduction, with a few dark areas remaining. After another hour of treatment the dark areas were almost completely lightened.
The object was placed in the reactor lying on glass grids and had not been turned during treatment.

Figure 10. Silver chalice (LM 79223) prior to hydrogen plasma reduction with disfiguring tarnish layer.

Figure 11. Silver chalice after 2.5 hours of hydrogen plasma reduction, no other surface treatment has been applied.

Figure 10 and 11 show the object before and after the plasma treatment and no other surface treatment has been applied in this case.

If very thick tarnish layers were present the surface could appear slightly matt after the plasma treatment. A combination of plasma reduction and gentle polishing with pure cotton wool has been shown to slow down the rate of retarnishing without leading to new scratches (Schmidt-Ott 2004).

4. Discussion

Until recently treatment with pure hydrogen plasma and the application of low pressure during reduction had been applied to silver artefacts only. It has been considered a "softer" process in which the object temperatures remain fairly low (av. 50-80 °C).

The optical spectroscopy of hydrogen plasmas at smaller operation pressure showed that not only lower treatment temperatures can be reached, but also an increase of radical density is present as compared to the hydrogen-argon treatment. It can therefore be assumed that pure hydrogen plasmas with less hydrogen and at lower pressure also supply a high amount of ionized hydrogen and are therefore more effective for reduction of corrosion products than are mixtures of hydrogen and argon which have been applied as a standard treatment for iron artefacts so far.

To cross-check this optical result, the effects of the different plasma applications on iron artefacts were investigated. Pure hydrogen plasma and the hydrogen argon plasma show similar effects on metallographic samples examined so far. In both cases a clear line of separation between outer corrosion layers and original surfaces can be seen and the facilitation of the mechanical cleaning after plasma reduction is ascribed to this fact. Since such a separation also seems to work after application of a pure hydrogen plasma at even lower temperatures it is intended to use such a plasma not only for silver but also for iron artefacts.

5. Conclusions

The introduction of optical spectrometry into the conservation process has delivered a means by which to monitor the plasma reduction. This allows one to visualize the effectiveness of operation parameters applied; the aim being to provide the highest rate possible of ionized hydrogen considered necessary for an effective reduction process.

After such systematic investigation of the plasma it seems that the pure hydrogen plasma originally considered to be less effective than a mixture of hydrogen and argon proved to be at least as efficient. This is of special interest since a pure hydrogen plasma at low pressure causes a reduction of the iron artefact's temperature to about 80 °C during plasma treatment. A change of the metallographic information contained in the artefact during treatment is, therefore, improbable. The positive effect of the facilitation of mechanical cleaning and the speeding-up of the subsequent desalination in alkaline sulphite for archaeological iron artefacts, continues to be a major advantage of plasma reduction for pure hydrogen plasmas as well.

The potential of hydrogen plasma for the reduction of silver sulphide layers remains extraordinary. Sulphides and also chlorides are removed without any damage to the artefact's surface. Compared to other established silver cleaning methods, plasma reduction exhibits many advantages: there is no change to surface structures, no residues from the treatment remain in or on the artefact, and no loss of silver occurs.

Plasma reduction is, therefore, a suitable method for silver artefacts, which are too fragile to be cleaned mechanically or chemically.

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