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Objekttyp: **Article**

Zeitschrift: **Zeitschrift für schweizerische Archäologie und Kunstgeschichte = Revue suisse d'art et d'archéologie = Rivista svizzera d'arte e d'archeologia = Journal of Swiss archeology and art history**

Band (Jahr): **54 (1997)**

Heft 1: **Unser Umgang mit dem Kulturgut : Gegenwart und Zukunft ; Conservation of metal objects in low-pressure hydrogen plasma = Die Niederdruck-Wasserstoffplasma-Methode zur Konservierung von Metallobjekten : Möglichkeiten ihrer Anwendung und Verbesserung**

PDF erstellt am: **28.04.2024**

Persistenter Link: https://doi.org/10.5169/seals-169512

# Assessment of the plasma treatment for archaeological iron objects in the collections of the British Museum

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## *Introduction*

The British Museum collections contain a large number of archaeological iron artifacts, many of which have been in the museum since the early 19th century and have been extensively conserved. Others have been added more recently from sites excavated by museum staff. In the first half of this century, and earlier, it was a common practice to remove all corrosion from objects, and then impregnate them with hot wax. Most objects treated in this manner are stable, but the practice has lost favour today. Chemical stripping processes are no longer used because they effectively destroy all information which remains in the corrosion layers such as organic and mineralised organic remains. It has also been found that chemical methods for stabilising iron such as alkaline sulphite, are only suitable for use on iron from certain periods, and sites[1, 2].

When newly excavated iron objects are received in the Department of Conservation they are first radiographed. The X-radiographs can be used by the conservator in discussions with the archaeologist/curator, to help select priority objects for further investigative work. X-radiographs do not indicate the presence of mineralised organic remains, and these can only be revealed by careful manual investigative cleaning. Following manual cleaning objects may be given a coating of *Paraloid B72*, an ethyl acrylate co-polymer, to consolidate and/or provide a protective barrier when the objects are handled. Environmental conditions within stores for iron objects are at levels likely to minimise deterioration. However the stability of objects from different sites varies greatly and, as might be expected, no single approach to stabilising iron artifacts has been found satisfactory for the whole collection.

In 1977–79 British Museum conservation scientists in conjunction with L. Holland at The Unit for Plasma Materials Processing at the University of Sussex, carried out research into the use of a reducing, hydrogen/argon plasma to reduce corrosion and tarnish on metal artifacts back to the metal[3]. The focus of the work was on chambers for low frequency, 50 Hz (Hertz), plasmas which were readily constructed. On iron, hematite was reduced to magnetite, but chloride concentrations in objects were not found to be significantly reduced. The process remained experimental, and was never used for the routine treatment of museum objects.

In 1985 Stanislav Vepřek, Jörg Patscheider and Jörg Elmer published a method for the restoration and conservation of ancient artifacts involving the use of high frequency generated plasma[4]. The process was developed further and in 1989 iron objects whose treatment had included the use of radio frequency generated plasmas were seen by the Director of the British Museum. He was impressed with the physical appearance of the objects and the reported stability, and requested that the process be investigated for potential use in the Museum. Discussions were held in Munich with Stanislav Vepřek and Christian Eckmann, who was then involved with the development of the process, and subsequently Christian Eckmann came to the British Museum for further consultations. In these discussions the importance of retaining archaeological and technical data held within the objects was stressed by museum archaeometallurgists, curators and conservators. The priorities were: to maintain the form and original surface of the object; organic or mineralised organic remains adhering to the original surface and those held within the layers of corrosion; to preserve colour on excavation and the metallurgical information held within the metal core which suggests how an object was made. These requirements were seen to be inconsistent with the temperature of 400°C achieved during the generation of the rf plasma. However the publications at that time[4–6] suggested that the plasma treatment would soften corrosion making it easier to remove, and would remove, or substantially reduce the level of chlorides within the iron resulting in stabilisation. The possibility of improved stability resulting from the treatment was considered to be important and the decision was made to continue the investigation by having some museum iron and silver objects treated using the process. Stanislav Vepřek kindly agreed to allow the use of the plasma apparatus at the Institute für Chemie der Informationsaufzeichnung der technischen Universität, Munich, and Christian Eckmann agreed to carry out the treatments in conjunction with two conservators of metal objects from the British Museum. In this paper only the results of the treatment carried out on archaeological iron using rf generated plasma are reported.

## *Plasma treatment of iron objects from the British Museum*

Following Christian Eckmann's visit to the British Museum, the selection of objects from the collection for the trial was made from the types of objects he considered would be suitable for treatment. Objects were chosen from three periods, Iron Age, Roman and Anglo-Saxon, and from collections where there were many duplicates to allow for sampling for metallurgical investigation. They included objects recently excavated and objects which have been in the collection since the mid-19th century. Some had been previously treated, others were untreated. Some had mineral replaced organic remains and there was one object with a silver inlay. In all, 24 objects were selected and they included knife blades, spearheads, lynch pins, pommels, several tools and a piece of mail armour.

Prior to the treatment in Munich, the condition of the objects was recorded by photography and radiography and using a criteria set out under visual assessment, below. Sampling for metallurgical investigation, and for identification of corrosion products by X-ray diffraction was carried out. An iron pommel was considered unsuitable for treatment because it had been heavily restored with wax. Two other objects were eventually not treated because there was not enough time to carryout the treatments. In all, 19 objects from the original 24 selected were treated. Because of concerns about the effects on the metallurgical information of high temperature, treatment at 400 °C, the decision was made to carry out all the treatments at temperatures below 300 °C. A range of treatment regimes was selected, based on Christian Eckmann's experience of working with the process[7].

The apparatus and the plasma treatment process used in this study has been previously described[5,6]. In summary the apparatus consisted of a pyrex glass chamber with external copper electrodes connected to a 27 MHz, 4k Watt radio frequency generator. The chamber was evacuated by a two stage rotary pump to 0.5 Torr and gas mixtures appropriate to the treatment process added. The plasma was generated by applying the output from the generator across the electrodes. The temperature achieved in the chamber was controlled by adjusting the generator output. The process used to treat the British Museum objects involved a plasma pretreatment in a reducing gas mixture of methane and hydrogen, followed by manual cleaning to remove corrosion to reveal the original surface of the object. A passivation treatment using a gas mixture of hydrogen, methane and nitrogen was followed, in some instances, by the application of a solution of *Paraloid B72*.

For the reducing pre-treatment, gas mixtures of hydrogen/methane of 100–120 Torr/ 60–70 Torr were used at temperatures of 250, 260 and 270°C. The treatment times were 2.5 or 4 hours, with some objects being submitted to two or three treatment regimes. Following the pre-treatment the conservators noted that the surface of the objects had become dark brown or black and the corrosion on most of the objects had become softer and more readily removable. The corrosion was removed by manual processes using scalpels and air abrasive before 17 of the objects were treated in a passivating plasma. The gas mixtures used for this process were hydrogen/ methane/ nitrogen at pressures of 50 Torr / 20 Torr / 110–130 Torr at 270 °C for 12 or 13.75 hours. Three objects were submitted to a second passivation regime of 60 Torr / 20 Torr / 120 Torr at 260 °C for 15 hours. Following the passivation treatment the surfaces of the iron objects were very dark grey or black. At this point the conservators reported that all of the objects appeared stable and no spots of reddish corrosion were present. The objects were returned to the museum for examination following treatment.

## Assessment of the objects before and after treatment

### *Visual assessment*

Visual assessment of the condition of the twenty four iron objects was made by conservators prior to treatment in April 1991, after treatment in May 1991, in June 1991, June 1992 and September 1996. The condition of objects was recorded by: colour and black and white photography, written descriptions and diagrams indicating the location of important features such as inlays, mineralised organic remains and the locations of samples taken for analysis. Condition assessments were made against a series of criteria in general use in the museum.

When making the condition assessment ten factors were considered. These included the colour, number of pieces, the presence of flaking, active corrosion, mineral preserved organic remains, soil deposits, metal core; previous conservation treatment including stabilisation and surface coating and the overall physical condition. The condition was described as: good, fair, poor, or unacceptable. The number of objects in the sample categorised as in the conditions poor and unacceptable throughout the period of this project were before treatment in April 1991, 11 objects, (45.8%); after treatment in May 1991, 2 objects, (8.33%); in June 1991, 5 objects, (20%); in September 1996, 8 objects, (42%).

The colour change of objects which underwent all stages of the treatment in Munich, was visually the most dramatic effect of the plasma treatment. The colour of all objects before treatment, whether previously conserved or not, ranged from orange-brown to dark brown. After the plasma treatment all the objects were a dark charcoal grey or black colour. This is still the colour of treated objects in 1996, apart from orange powdery spots on some objects where recent active corrosion has disrupted the passivated surface.

Mineral preserved organic remains were still present on some of the objects following the treatments, e.g. the wood in a spearhead socket (M&LA 1/70 45 Gr2) and on the inside of a nave band (PRBA GW/KF). The mineral preserved organics on the nave bands were examined to see if the treatment caused any change in structure. Unfortunately the results were inconclusive, but suggested that some detail of the wood structure remained after the plasma treatment. The extent to which structure is affected by mineralisation can vary considerably, and it is probably reasonable to say that the treatment with the plasma did not itself destroy the mineralised organic remains. On some objects, however, where extensive mineral preserved organics had been noted before treatment, much, if not all, had been removed during the treatment, probably at the mechanical cleaning stage between the pre-treatment and the passivation treatment. Normally conservators would remove unwanted corrosion leaving the organic or mineralised organic remains attached to the object. Because the plasma process softened the corrosion so effectively it was not possible to do this, and even very careful removal of corrosion resulted in the remains being dislodged.

Several objects were physically more fragile after treatment, with cracks and fissures being more visible and with new breaks having occurred, than they were before. A lump of iron (1982 sf308) appeared to be more fractured and cracked after treatment, increasing physical weakness. However this must in part be due to the removal of concretions which would have helped to strengthen the object. In general conservators decided that these plasma treated objects were more fragile than similar objects treated only by mechanical cleaning at the British Museum.

### *Analytical assessment*

In order to monitor changes in corrosion products due to plasma treatment, 30 samples were removed from 18 objects, prior to treatment. Choice of sample site was influenced by visual examination of different types of corrosion, mainly based on colour considerations. Samples, approxi-

| ***Specimen no.*** | ***Details*** | ***Inclusions*** | ***Etched Structure*** | ***Changes after plasma*** |
|---|---|---|---|---|
| 935 Iron Strip | 1882,2–6,27 | many inclusions, some 2-phased all over the specimen, wide variety of size and shapes. Small and elongated near surface. | Mainly ferritic with one area of ferrite and pearlite near the surface. Traces of cold work near surface. Disturbed grain boundaries due to impurities. Precipitated carbides in grains and boundaries near C-richer surface. | Traces of working at the surface removed. Increase in disturbance at grain boundaries in metal. |
| 938 Knife | OA5691 | Few small elongated inclusions, mainly found parallel to the surface. | Banded structure of irresolvable pearlite and ferrite with some proeutectoid ferrite. | Pearlite now resolvable. Appearance of some disturbance in the grain boundaries. |
| 939 Lynch pin | GW/JK/JN | No metal remains in the before treatment section. The after section has a moderate number of medium to large 2-phased inclusions generally distributed, some elongated, otherwise irregularly shaped. | Large grained ferrite with fine precipitate of carbides at the grain boundaries; disturbed grain boundaries. | No indication of the original structure. |
| 940 Coulter | ML5640 | A few small elongated inclusions. | Probably 3 layers, parallel to surface; ferrite with carbide at grain boundaries; ferrite and pearlite; same, with some distortion and possibly decarburisation near the surface. | Not much change visible. |
| 945 Lynch pin | 1892,11–4,4 | Moderate number of irregular 2-phased inclusions. | Mainly ferritic structure with some ferrite and pearlite at one surface. Carbides in grain boundaries. | Banding more noticeable, grain growth and carbides. Disturbed grain boundaries appear. |
| 946 Sickle | 1882,1–3,269 | Moderate number of small inclusions in bands parallel to the surface. | Variable carbon content with Widmanstatten structure at one surface, grain size small, some grain boundary distortion. | The grain size is increased, with more carbide precipitated. |

Table 1 Results of Metallographic Examination

mately 5 μg, were taken from the objects directly onto gelatine strips, which were subsequently mounted in Debye-Scherrer cameras and their powder *x-ray-diffraction* (XRD) patterns were recorded. The crystalline components of the samples were identified by comparing the unknown XRD patterns with reference standards. Akageneite, ß-FeOOH, was present on 13 objects, and goethite, α-FeOOH, on 16 objects. The corrosion products on two objects were found to be amorphous. Akageneite can form only in the presence of chlorides, and its presence is a sign of potential instability in an iron object.

The objects were resampled within two weeks of completion of the plasma treatment to determine whether akageneite had been removed by the plasma treatment. The corrosion products identified as present were magnetite, $Fe_3O_4$, and hematite, $Fe_2O_3$. Akageneite was identified on two objects sampled.

Although all of the objects in this trial were stored in a dehumidified area when returned to the British Museum, at an inspection on the 7th June 1991, several objects were found to be recorroding. The fresh orange corrosion on the objects was identified by XRD as akageneite, ß-FeOOH. The presence of chlorides in a fragment of iron removed from one object was confirmed using a chemical spot test with silver nitrate and nitric acid.

The structure of low carbon steels and wrought iron can also be significantly modified by the treatment, and thus must also be potentially at risk. On the specimens the following changes were noted (Table 1):

1 Traces of original surface distortion in the surface layers of sample 935 had disappeared.
2 Grain growth could be observed after treatment on specimens 938, 945 and 946.
3 Impurities, mainly phosphorus or oxygen dissolved in the body metal of 939, 945 and 946 had formed poorly defined but real sub-structures within the grains and around their boundaries during the treatment.

| *Number* | *Before* | *After* |
|---|---|---|
| Knife 938 | 220 | 182 |
| Lynch pin 939 | | 228 (carbide)<br>156 (ferrite) |
| Sickle 946 C-rich | 199 | 172 |
| low C impurities | 189 | 165 |
| ferrite impurities | 200 | 206 |

Table 2 Hardness values (Vickers diamond pyramid, 100g wt)

### *Metallurgical Assessment*

The metallurgical examination had a two-fold purpose: to study the effect of the plasma treatment on the microstructure of the surviving metal and to record any changes in the corrosion products which had survived the treatment. Sections were cut before and after plasma treatment from six of the objects, including a knife blade, coulter and sickle blade, where some heat treatment during making would be expected. The sections were mounted in a cold setting resin, polished and carbon coated for examination in the *s*canning *e*lectron *m*icroscope (SEM) with *e*nergy *d*ispersive *x*-ray analysis (EDX). The composition of the body metal, inclusions, and corrosion products were determined. The elemental distribution in the corrosion layers and at the corrosion/metal interface was recorded by digital x-ray mapping using an ISIS mapping programme in the SEM. The results of these studies are reported in more detail elsewhere[8]. The sections were then repolished and etched using *Nital*, a standard metallographic etch, for examination by optical microscopy to allow examination of the structure (Table 1). The hardness of the samples was measured using a Vickers micro-hardness tester (Table 2).

Examination and hardness tests on the knife blade showed it had been heat treated and quenched during manufacture, although martensite had not formed. The tests on the post treatment sample showed that the hardness was significantly reduced, demonstrating that the plasma treatment had a pronounced "tempering" effect, thereby changing the properties that the metal originally possessed.

Our studies here and other published work[9] have shown clear evidence that heat treatments were carried out on some objects of wrought iron and low carbon steel. These would not normally be considered as candidates for such treatment in modern practice. Clearly this could be an important component of early metal working practice, and one which is potentially at risk from treatments that involve heat.

The mapping showed that the chloride concentrations in the corrosion layers are very heterogeneous. Chloride was determined as present in five of the six iron samples before treatment. After treatment chlorine levels in three samples were similar to thoses determined before treatment; in two samples the level was reduced; in one sample chlorine could not be detected after treatment.

### *Discussion*

The stability of the objects treated in this investigation when considered as a group would appear to be no better in 1996 than in 1991. Before plasma treatment, 45.8% were in condition categories "poor" and "unacceptable". In 1996 five years after treatment, 42% were in these categories despite the apparent considerable improvement in their condition immediately after plasma treatment. Full plasma treatment, and passivation, had caused the objects to become dark charcoal grey or black in appearance, due to the formation of a layer of magnetite. However, this was only a surface phenomenon; when sampling, the grey layer was found to be easily removed, to reveal an orange brown subsurface. The majority of objects which did not appear to have akageneite in their corrosion prior to treatment, have remained stable since treatment. However, akageneite was identified in the corrosion on ten of the objects prior to treatment and nine of these have subsequently shown signs of active corrosion. This evidence, coupled with the detection of chlorides in two of the treated objects shows that the chlorides had not been removed during the plasma treatment, and the objects have not been stabilised. This is not suprising given that it is difficult to understand how the plasma, which is made up of very active ions, can react with the material below the actual surface. Internal diffusion among the mineralised corrosion layers should be minimal and the highly active plasma should react at the first contact point on the surface.

The metallurgical structure of the objects investigated showed alteration caused by the treatment. The increased fragility of the corrosion layers following the treatment would reduce the long term physical integrity of the objects. The colour change on treatment was also considered aesthetically undesirable. The process did make the corrosion more readily removable from many objects. For the test group, the extent of removal of corrosion, and the associated loss of mineralised organic remains was considered undesirable. However it is accepted that the extent to which the corrosion is removed is dependent on the conservator carrying out the work in conjunction with the archaeologist.

The British Museum study collections are primarily regarded as a research resource. As such we take the view that we should not destroy evidence which scientists in the future may be able to access in order to gain a greater understanding of the processes used to manufacture objects in the past, and the mechanisms by which objects deteriorate and can be conserved in the present. Since 1991, many modifications have been made to the method used in this study, and many different approaches are being used throughout Europe. The long term effects of these treatments are of considerable interest to the British Museum team, especially those of the low temperature plasma methods. However, so far no evidence is available to make us alter the decision made at the end of the study reported here. That decision was to not implement the plasma treatment method for iron in the British Museum.

### *Acknowledgements*

The authors would like to thank the Keepers of the Departments of Prehistoric and Romano-British Antiquities, and Medieval and Later Antiquities for making objects available for experimentation, and the involvement of their staff in discussions; Ruth Goldstraw for her work on the plasma treatment of the objects; Stan Vepřek for allowing us to use the plasma apparatus in Munich, and for helpful discussions; Christian Eckmann for helpful discussion and carrying out the plasma treatment of the Museum's objects; Caroline Cartwright for examination of the mineralized organic remains before and after treatment.

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