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Rapid Low-Temperature Hydrogen Plasma Treatment of Archaeological Iron

by ANKER SJØGREN, TROELS MATHIESEN, JETTIE VAN LANSCHOT, STEVE TURGOOSE and CATHERINE HAWKINS

Introduction

Plasma treatment of archaeological iron is a physical process where gas is split into reactive ions and atomic radicals (plasma) that react with the surface of the object. The plasma can be generated in many ways but for metal conservation the use of either high voltage or radio frequency (RF) waves is most common since this allows a relatively low treatment temperature. These methods are carried out at low pressure in vacuum in a temperature range of 100–400°C depending on the applied power. The main motive for using plasma treatment is the ability to reduce the oxides in the conglomerate layer, thereby opening the structure and facilitating uncovering of the original surface and removal of chloride, which normally is the main cause of the instability of iron artifacts. Chloride removal can either be done by a post-treatment (e.g. washing in alkaline solutions) or by the plasma itself if it contains elements like hydrogen that react with chloride and to some extent removes it.

As summarized in Table 1 several authors have studied the plasma technique for conservation of metals by using a wide range of power sources. It is generally observed that the plasma treatment greatly facilitates removal of the con-

glomerate layers. Regarding stability or chloride removal it seems to be a compromise of either using a low temperature involving a long treatment times or alternatively increasing the temperature to 300–400°C. Considerations of these conditions suggest that microstructural changes to artifacts cannot be ignored. More than 300°C for 1 day or more will cause significant tempering of quenched microstructures and so would often not be considered appropriate in conservation.

Given the advantages reported in literature, the overall aim of this study has been to develop improved and effective gas-plasma conditions that are suitable for both cleaning and stabilisation of archaeological iron. In this respect four important criteria were chosen to be met:

- 1 Treatment of archaeological iron should be carried out without electrical connection to the object itself.
- 2 The original surface of the object should be well preserved.
- 3 The temperature of the object during treatment should not exceed 300°C for long time in order to preserve the original microstructure.
- 4 The plasma equipment should be quite simple in operation and economically feasible to suit a conservation workshop.

Author	Ref.	Year	Power source	Gas	Pres. mBar	Temp. °C	Treatment time
Daniels	1	1979	AC 50 Hz, 2,5 kV, 5 mA	H ₂ , Ar, O ₂	0.1–1.0	50	?
	2	1981	RF 13, 56 MHz, 100 W	H ₂ , O ₂		>100	?
Sjøgren	3–5	1980	DC*, 4,5 kV, 150 mA	H ₂	0.5–1.0	50–120	1–3 weeks
Veprek	6, 7	1986	RF 80 MHz, 2 kW	H ₂ , Ar,	0.5–1.5	300–400	50 hrs
	8	1988	RF 27 MHz, 4 kW	CH ₄ , N ₂			
Aoki	9	1989	DC, 350 V, 17 A	H ₂ , Ar, CH ₄ , N ₂	7	350–400	20 hrs
De Graaf	10, 11	1993	Cascade arc, 40 A	H ₂	1.0	400	20 min
				H ₂ , Ar, N ₂		160–400	
Arnould-Pernot	12	1994	DC*, 400 V	H ₂	10	200–450	2–8 days

* Object connected as cathode

Table 1 Overview of plasma techniques used for metal conservation.

As a combination of the results from the literature and from our own experience in the work of Sjøgren et al.⁵ the direct current (DC) power source was selected rather than alternate current (AC), radio frequency (RF) or the cascade arc gun. The main reasons for this choice were the possibility of controlling the temperature and the simplicity of this technique.

In preliminary experiments, with a hollow artifact functioning as cathode, a very intense plasma was observed inside the object when compared to the surrounding plasma. This effect is due to "trapping" of the electrons in the hole surrounded by the cathodic walls. In contrast to a flat cathode geometry, the electrons are unable to "escape" in the normal way and move directly to the anode. In the "trap" the electron path to the anode is prolonged and thereby creates a plasma with significantly improved intensity, as observed.

Experimental Methods

Plasma treatment

The plasma treatments were carried out with the equipment illustrated schematically in Fig. 1. The samples are placed on a steel grid inside the cathode tube measuring 6 cm in diameter and 11 cm in length. The cathode tube is shielded on the outer side to improve current efficiency. The steel grid is isolated from the cathode tube, but can be switched in as a cathode. During treatment a small flow of hydrogen (or gas mixture) is maintained by the gas supply system and the gas is let out near the samples in the middle of the cathode tube. The vacuum pump ensures a pressure of about 1 mbar in the chamber. The plasma is formed by applying a high DC voltage (about 1000 V) between the anode and the cathode tube (or both cathodes). Throughout the treatment, voltage, pressure and gas flow are adjusted to achieve a stable plasma and a temperature below 300 °C. The temperature is measured by a Pt-100 (Platin-100) probe placed inside the cathode tube.

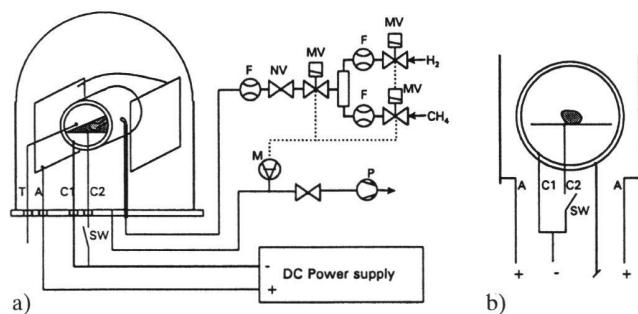


Fig. 1 Schematic of a) the plasma apparatus and b) the electrical connections. Abbreviations: A anode, C1 cathode 1, "electron trap", C2 cathode 2, sample holder, SW switch, T Pt-100 temperature sensor, P vacuum pump, M manometer, MV magnetic valve, NV needle valve, F flowmeter.

Samples

Most of the archaeological artifacts treated in this study are of minor archaeological value, in fact primarily nails. They were chosen at random, since previous work has shown that there appears to be more variation between samples from a given site than between sites when stability is evaluated in solution¹³. The objects are plasma treated as received, i.e. covered by the conglomerate layers of soil and corrosion products. After treatment in plasma the conglomerate layers of the samples are manually removed by means of a scalpel.

Assessment

For assessment of stability the treated samples are exposed to high humidity (95% relative humidity) created by a saturated sodium carbonate solution in the test chamber. Stability is also assessed for some of the samples by means of electrochemical techniques that have been described previously^{13, 14}. Measurements of the corrosion potential are carried out either by immersion in 0.05M sesquicarbonate solution (pH 10) for 6 weeks or by mapping the potential variation along the sample surface at atmospheric conditions. Both techniques are performed at ambient temperature using a saturated calomel electrode (SCE) as reference electrode.

Stage	I (start)	II	III	IV (end)
Emission light color	Purple	Deep purple	Blue	Purple
Probable process	None (water evaporation)	Degassing of organic compounds	Reduction of corrosion products (chloride removal)	Slow reduction of corrosion products (chloride removal)

Table 2 Sequential stages and emission light colors observed during a typical plasma treatment and their interpretation.

Results and discussion

Controlling the plasma

The first series of experiments carried out with the new electrode arrangement focused on controlling the intense plasma created in the trap. In this regard the temperature should be kept below 300°C while still ensuring an intense plasma. Care should also be taken to prevent arc-discharges which might cause spot damage of the object. Use of different gases such as hydrogen, helium and nitrogen did not show any differences as regards ignition or control of the plasma, since the electron trap in all cases ensured an intensive plasma. Furthermore, the concentrated plasma in the “trap”-tube elucidated the emission light which showed a sequence of characteristic changes in colour during a typical treatment. Although these colours have not been studied by optical emission spectroscopy (OES), it is suggested that the sequential changes in the visible colour observed during treatment reflect the reactions taking place, see Table 2. This interpretation is also supported by the rise in pressure observed in stage II and to less extent in stage III.

From the observations of the preliminary experiments a basic procedure was defined involving the following two steps:

- 1 Plasma treatment with electrical connection to cathode 1 (electron trap) but no connection to cathode 2 (the sample holder). The intense plasma created in this way will mainly react by diffusion and scattering, but appeared to be able to open the structure of the conglomerate by reduction of the outer corrosion products layers, i.e. Hematite and Goethite. *X-ray diffraction (XRD)* analysis of removed corrosion products indicates transformation to magnetite with increasing treatment time.
- 2 Plasma treatment with electrical connection to both cathodes. At this stage it is assumed that there is electrical connection between the sample and sample holder making the object a cathode itself.

The stage where the second cathode (the objects) can be connected without the risk of arc-discharges is determined from the characteristic changes in colour of the plasma, i.e. normally the second cathode is connected after stage II.

Preservation of the original surface and microstructure

Based on the basic treatment procedure a series of experiments were performed to study the preservation of the original surface after removal of the conglomerate layer. This study included hydrogen as well as hydrogen with about 25% methane. Table 3 summarises the results of these treatments, which were stopped after different times resulting in different end-stages identified by the emission colour.

From the results in Table 3 there is no clear effect of either the gas composition nor the treatment time. This is probably due to the natural spread of the objects and in particular the thickness of the corrosion product layer. Earlier treatments have also indicated that the time from excavation could be an important parameter as 4 year old samples were much more difficult to treat than newly excavated samples. Although the samples could be sorted to more homogeneous groups before treatment it seems difficult to give exact parameters for an optimum pre-treatment procedure as some variation between objects may still be expected. However, it appears that the largest number of well preserved objects in all cases are obtained in treatments that ended just before or during stage III. It is therefore believed that the treatment time should be adjusted from observation of changes in the emission light to achieve optimum conditions.

No.	Number of samples	Gas	Treatment time, min	Observed stage at stop ^{a)}	Preservation of original surface ^{b)}			
					Excellent	Good	Poor	Unacceptable
A	3	H ₂	120	III		2		1
B	4	H ₂ /CH ₄	105	III		3	1	
C	3	H ₂	60	IV	2		1	
D	3	H ₂	120	IV		1		2
E	3	H ₂	180	IV		2	1	
F	3	H ₂ /CH ₄	60	IV				3
G	5	H ₂ /CH ₄	120	III	1	2	2	2
H	4	H ₂ /CH ₄	180	IV		1		1
I	4	H ₂ /CH ₄	35	II-III		1	2	1
J	4	H ₂	30	II-III	3	1		
Total	36				6	13	7	10

a) Defined from the emission light, see Table 2.

b) Criteria are used to rank the preservation of the original surface:

Unacceptable: Significant loss of original surface. No details preserved.

Poor: Some damage to the original surface. No details preserved.

Good: Most of the original surface is maintained. Some details preserved.

Excellent: The whole original surface is maintained and details are preserved.

Table 3 Effect of time and gas composition on the preservation of the original surface of iron nails treated in a D.C. plasma at about 300°C.



Fig. 2 Hinge after plasma treatment (left) and a similar artifact covered by its conglomerate layer (right).

An example of a plasma treated iron artifact from Iron Age is shown in Fig. 2. After plasma treatment and uncovering (which only took a few hours) it turned out that the artifact was much more interesting than initially suggested. Fine details and shape were well preserved, and the artifact was identified as a hinge, involving a rather sophisticated mechanism with a stop pin. For comparison a similar artifact covered by conglomerate is shown in Fig. 2. This example may illustrate the aspects and advantages of the rapid plasma procedure.

The question of microstructural changes has been addressed by comparing the annealing of martensitic structures treated in plasma and in furnace at 300°C for 1–3 hours. These experiments show only minor changes in hardness as expected from available tempering diagrams. The results also indicate that the temperature measured in the plasma apparatus reflects the artifact temperature, with slightly less softening in the plasma for the same time, since temperature slowly rises to the maximum.

Stability

Efficiency of the trap-system as concerns the degree of desalination (chloride removal) and thereby stability of the objects was mainly estimated by visual examination. Out of the total number of 133 treated objects, 56 have been exposed in a humidity chamber for 6 weeks (95% R.H. at ambient temperature). Of these objects 49 turned out to be stable, which here means that no sign of the characteristic sweating droplets was observed when using a stereo microscope with 12 times magnification. This result gives some confidence as similar samples treated in conventional alkali

solutions showed a higher degree of instability in previous work¹⁴. From the few unstable objects no significant difference between plasma treatments using different gases could be defined.

The correlation between chloride removal and stability has also been examined by electrochemical measurements, since it has previously been shown that a combination of potential, R_p , and visual assessment can define the stability of the artifact¹⁴. For these investigations five unstable artifacts were treated in plasma using different gas mixtures and different treatment times, see Table 4. After 6 weeks exposure to humidity chamber only one showed instability.

A potential mapping performed on 20 points per object showed that the plasma treated artifacts have a rather uniform potential across the surface. This is expressed by the low standard deviation which is comparable to that obtained for objects treated for 6 weeks in alkaline solutions¹⁴. The exception was number five, which also appeared unstable in the humidity chamber. Additional treatment for 15 min lowered the standard deviation indicating even more stable objects.

Fig. 3 shows the potential versus time behaviour for the plasma treated artifacts in a 0.05 M (molar) sodium sesquicarbonate solution. In contrast to non-treated archaeological artifacts 0.05 M sodium sesquicarbonate is able to passivate the plasma treated artifacts within 200 hours. This is seen as a rise of the measured potential. Again the exception is number five which needs longer time to passivate. In our former work non-treated archaeological artifacts were treated in 0.5M sodium sesquicarbonate for 120 days without any remarkable change in potential.

Conditions gas/time (min)	Mapped potentials after first treatment and 6 weeks in 95% R.H. (mV SCE)			Mapped potentials after retreatment for 15 minutes (mV SCE)		
	Min.	Max.	St.Dev.	Min.	Max.	St.Dev.
1. H ₂ /80	– 302	– 85	55	–542	–358	54
2. H ₂ /210	– 699	–360	88	–563	–261	71
3. H ₂ /1200	– 353	–157	54	–523	–275	64
4. H ₂ /CH ₄ /90	– 525	–168	73	–543	–350	55
5. H ₂ /CH ₄ /90	–1030	–400	154	–556	–325	61

Table 4 Results of potential mapping of plasma treated artifacts after exposure in humidity chamber and after retreatment in plasma. All values are obtained by 20 potential measurements on each object.

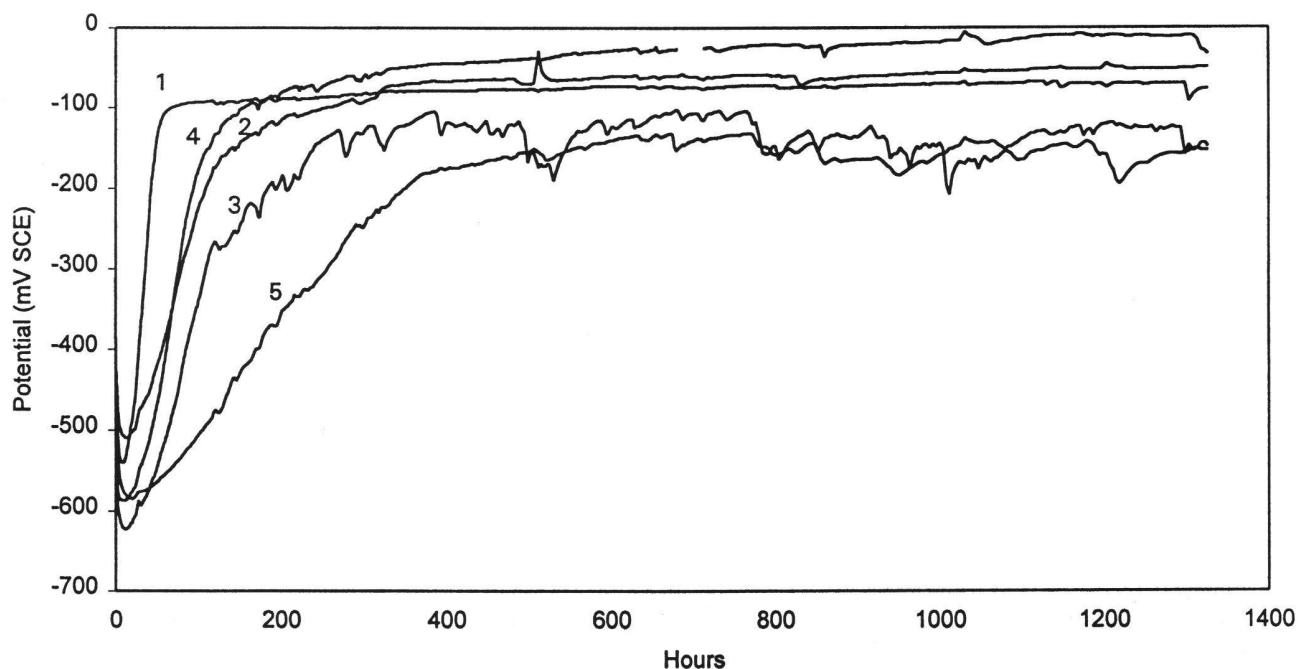


Fig. 3 Potential-time behaviour in 0.05 M sesquicarbonate of plasma treated nails compared with the typical behaviour of non-treated nails.

Conclusion

By use of a DC power supply and a tubular cathode design intense plasma conditions were obtained with no needs for electrical connections to the artifacts, still enabling relative low treatment temperatures ($<300^{\circ}\text{C}$). The intense emission light colours observed in the “electron-trap” offered better control during treatment. Treatment of iron artifacts for short time (1–3 hours) enables easy uncovering of the original surface. Use of longer treatment times may damage the details of the original surface. Further treatment for 2–3 hours with electrical connection to the sample holder can be applied to remove chloride without loss of surface details. High humidity tests and electrochemical measurements show significant improved stability of plasma treated iron artifacts when compared to untreated samples and alkaline treatment.

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Summary

Archaeological iron artifacts were treated in plasma generated by a high direct current (DC) voltage in a hydrogen containing atmosphere at low pressure. Compared to other plasma procedures described in the literature a new electrode arrangement was used with no need of electrical connection to the artifact thereby eliminating physical damage of the surface. The artifacts were placed in the centre of a tubular cathode acting as an “electron trap”. By this a very intense plasma was created around the artifacts still ensuring a quite low working temperature (less than 300°C) in order to minimise the risk of microstructural changes. During treatment the emission colour of the plasma is observed to enable control of the process and distinguish between the different stages involved (e.g. degassing of organic compounds and reduction of oxides). The method was tested on iron artifacts which afterwards were assessed to study effects on preservation of the original surface and stability. The plasma treatment proved to make the removal of the conglomerate layer very easy even at short treatment times (about 1 hour). However, too long treatment times caused to some extent degradation of the inner magnetite layer that outlines the original surface. Stability of the artifacts was evaluated by exposure to high humidity and by electrochemical techniques. In most cases the stability was significantly improved when compared to the stability of untreated objects.

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