LOW-PRESSURE HYDROGEN PLASMA: AN ASSESSMENT OF ITS APPLICATION ON ARCHAEOLOGICAL IRON

Katharina Schmidt-Ott and Valentin Boissonnas

Summary—*Low-pressure hydrogen gas plasma reduction has been used at the Swiss National Museum in metals conservation since 1990. After a critical re-evaluation of the method in 1994, major changes were introduced. Today, it has become an integral part of the conservation procedures for archaeological iron. Its major advantages are improved mechanical cleaning and speeding up of the subsequent desalination process with alkaline sulphite. This study focuses on the changes that have been introduced to the plasma apparatus as well as on the treatment parameters, such as temperature, time, and gas mixture. All of these improvements aim at preserving the integrity of the artifact.*

Introduction

Ever since their first application on metal artifacts in 1979, gas plasmas have been the subject of research in conservation [1]. The Swiss National Museum has been involved in the development of this treatment for iron artifacts since 1984 and has run its own apparatus since 1990. The physical properties of plasmas have been described extensively in the literature [2–5] and will not be described in this paper.

The hydrogen plasma used at the Swiss National Museum is produced by an electrical discharge in a radio frequency (RF) field. The highly reactive plasma, with its partially ionized hydrogen molecules and atoms, will readily react with iron corrosion products. As a result, oxides—and at higher temperatures also chlorides—are reduced.

A partial reduction is preferable to a complete reduction as it yields better results and does not make the object too brittle. With a partial reduction, the overlying reduced corrosion layers will have a decreased density and be more brittle. For example, Fe_2O_3 (the density of natural haematite is $5{\cdot}24 gcm^{-3}$) is reduced to Fe_3O_4 (the density of natural magnetite is $5{\cdot}18 gcm^{-3}$), which facilitates the mechanical cleaning that follows. The micro-fissures that are created improve the subsequent removal of corrosive chlorides.

Changing aims of plasma treatment

In the late 1980s, gas plasma treatments of iron objects, such as those proposed by Patscheider and Vepřek, aimed at facilitating mechanical cleaning and the removal of trapped chlorides. With gas mixtures of hydrogen, methane, nitrogen and argon, standard treatments took about 20 hours and involved temperatures up to 400ºC [6, 7]. To passivate the object against post-treatment corrosion the surface was enriched with carbon and nitrogen and a wax coating was applied to act as an additional surface protection [8].

Objects treated as described were assessed eight years later when it became apparent that such treatments did not lead to the expected long-term stability. Objects were showing corrosion ranging in degree from spots of active corrosion to total disintegration of the object (Figure 1), and a total removal of chlorides had not been achieved [9]. According to Arnoult-Pernot much longer treatment times, of up to 190 hours, and temperatures between 300 and 400ºC would be required to remove most of the chlorides, including insoluble chlorides trapped in akaganeite (β-FeOOH) structures [10].

The attempt to passivate the surface with carbon and/or nitrogen did not yield satisfactory results

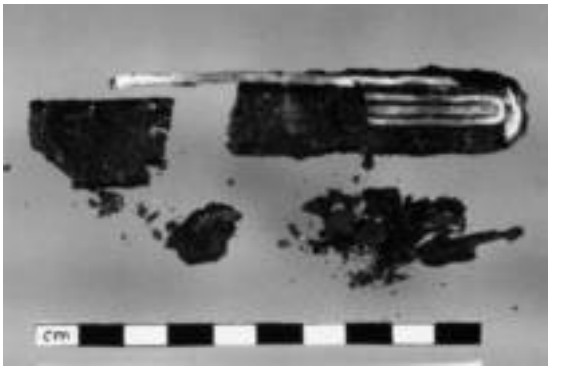

Figure 1 Artifact from Schleitheim, Hebsack, Kanton Schaffhausen, treated in 1988; showing the condition in 1996.

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and also had the disadvantage of causing colour and compositional changes to the surface [2, 9]. It is now known that plasma temperatures around 400°C will affect the metallurgical structure of quenched steel and introduce an irreversible loss of potential information. A better understanding of plasma treatments has led to major modifications in the use of hydrogen plasma at our museum. Instead of being the 'ideal' treatment for iron artifacts, it has become one step in a series of treatments which aim at stabilizing archaeological iron while respecting the integrity of the object.

Current equipment and treatment parameters

Plasma apparatus

The central component is a Pyrex glass tube (diameter 40cm, length 150cm) with two external water-cooled cylindrical copper electrodes located above and below the vessel. A 27·12MHz, 4kW generator (Sairem) is coupled to these electrodes, generating a high-frequency alternating field (radio frequency field) in the glass tube (Figure 2).

Outside the Pyrex cylinder a pick-up loop measures the local field strength. Its reading is proportional to the central field and to the discharge current. For treatment, objects are placed on glass grids in the centre of the reaction tube. As a safety measure, the reaction tube and electrodes are contained within a Faraday cage, which shields the environment from radio frequency radiation (not indicated in Figure 2).

The discharge tube is evacuated with a two stage-pump (Alcatel). A membrane pressure gauge (Baratron, MKS) measures the absolute pressure inside the treatment chamber. After evacuating the tube to <30Pa, the gas inlets are opened. Gas flow and pressure are controlled with thermal mass flow meters (Brooks Instruments BV) and a mixture of hydrogen and argon is used; the ratio of partial pressures is 10 to one. The pressure amounts to 20–90Pa during treatment and, as a safety measure, the pump exhausts are mixed with air and burnt in a combustion chamber at 600°C before being released into the atmosphere.

Temperature measurements

To gain a better understanding and control of the reactions during treatment, the apparatus is equipped with three temperature measuring devices:

1 A mercury, or alcohol, thermometer is placed in a glass tube that protrudes into the treatment chamber. It is only in contact with the Pyrex wall, and not with the plasma or iron artifact. This temperature reading may, therefore, differ from the temperature of the artifact during treatment (Table 1). In all publications prior to 1997 the treatment temperature referred only to this measurement [9]. Experiments have shown this reading to be roughly proportional to the temperature of the artifact, so it can, therefore, be used as a reference to control the operation under constant conditions.

2 An infrared pyrometer is focused on the object from outside the chamber. It measures the

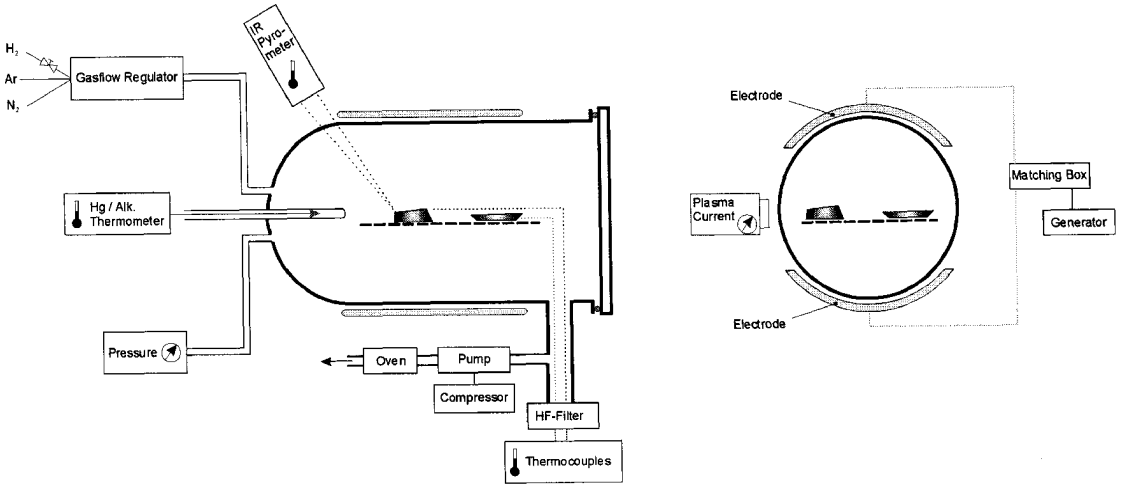

Figure 2 The plasma apparatus at the Swiss National Museum.

Table 1 Illustrative examples of temperature measurements

Compostion of treated sample	*Run number/gas pressure/gas flow/RF power*	*Temperature (°C) liquid thermometer*	*Temperature (°C) infrared-pyrometer*	*Temperature (°C) thermocouple*
Iron, lightly corroded	Run 1388 53Pa 8l.h^{-1} (H_2) 0·8l.h^{-1} (Ar) 1·1kW	147	124	133
Iron, heavily corroded	Run 1415 45Pa 8l.h^{-1} (H_2) 0·8l.h^{-1} (Ar) 1·25kW	148	106	116
Iron, lightly corroded	Run 1405 25Pa 4l.h^{-1} (H_2) 0·4l.h^{-1} (Ar) 1·2kW	107	too low to measure	103
Iron, lightly corroded	Run 1407 21Pa 3l.h^{-1} (H_2) 0·3l.h^{-1} (Ar) 1·1kW	82	too low to measure	79

absolute surface temperature of the artifact. However, surface emission and radiation wavelength are strongly dependent on temperature. The measurement is not possible for temperatures below 110ºC, but at higher temperatures this method performs well on iron artifacts. Since infrared pyrometers are colour sensitive, it is essential to calibrate them on the surface to be measured. Iron has not shown any significant colour change during plasma treatment that could lead to misreadings.

3 At temperatures around 100ºC both the above methods are inadequate to measure the artifact temperature precisely. A thermocouple was therefore introduced into the plasma chamber where it is in physical contact with the artifact. Assuming that the temperature of the specimen is the same over its entire surface, this device will give the precise artifact temperature. In the presence of radio frequency fields, however, the DC-voltage reading of the thermocouple can be disturbed by the pick-up of AC signals. This is avoided by using electric filters comprising suitable capacitors and resistors [11]. The performance of such radio frequency suppression can be easily checked by observing the thermocouple readings with the radio frequency power on and while the power is switched off for a short time [9].

Comparison of the three temperature measurement devices

The temperature readings from the three measuring devices were found to depend on the sample treated and on its surface condition. Contact between thermocouple and metal is clearly improved if the thermocouple is introduced into a crevice, rather than placed on the surface of a corroded artifact. The more corroded a surface, the lower the measured temperature, as the corrosion layer acts as a thermal insulator (Table 1).

The tests showed that, for corroded iron artifacts, the temperature readings from the infrared pyrometer and the thermocouple are comparable, whereas the liquid thermometer will give higher temperature readings. For the time being, the most reliable temperature measurement for corroded iron is provided by the thermocouple. The other two methods are used to cross-check these measurements.

The importance of such reliable temperature measurements becomes crucial when treating arti-

facts that were originally subjected to quenching, making their metallurgical structure susceptible to higher temperatures. In the sections that follow, all references to artifact temperature relate to readings from the thermocouple.

Treatment temperature

When it was introduced into metals conservation, hydrogen plasma reduction was criticized because of its relatively high treatment temperatures (300–400ºC). At such temperatures quenched steel structures will be greatly affected. Martensite will be altered to form ferrite and cementite. Such annealing can result in considerable loss of potential information regarding the original manufacturing of the object. Tylecote and Black suggested that martensic structures will start to be affected around 100ºC [12], but Ehrenreich and Strahan reported that boiling of quenched steel artifacts will not substantially bias archaeometallurgical studies, since both grain structure and hardness should remain characteristic of martensite [13]. Archer and Barker, however, mention temperatures up to 250ºC as still being suitable for treatment of corroded iron artifacts [14]. These results were confirmed by Perlik who considers a plasma treatment temperature of 200ºC (liquid thermometer in the glass tube in the RF field) as safe [15]. He observed the first changes in the martensic structures around 250ºC.

To avoid any metallurgical changes, our plasma treatment temperatures were reduced to 120ºC in 1994. Since a long exposure to higher temperatures increases the risk of annealing martensic structures, the treatment times have also been reduced to an average of six hours. With such parameters, a plasma treatment is still successful in decreasing the density of the corrosion products and therefore facilitates subsequent mechanical cleaning. However, a complete removal of chlorides through plasma reduction becomes impossible. Further studies of temperature measurement during plasma treatment and the different reactions taking place with various metal compositions are the object of current research.

Subsequent treatment

Following plasma treatment, the iron artifacts are mechanically cleaned with a micro sandblasting unit using aluminium oxide (Biloxit F 280, average diameter 37μm) or glass beads (<50μm). Since low temperature plasma treatment will not decrease chloride concentrations within the artifacts, a subsequent desalination procedure becomes necessary. We are using the alkaline sulphite treatment described by Rinuy and Schweizer [16], or more recently by Greiff and Bach [17]. The microfissures, which result from the density changes in the corrosion layer during plasma treatment, facilitate the release of chlorides. Tests with and without use of the plasma showed that a prior plasma treatment will shorten the desalination time up to fourfold.

Protective coatings are still necessary, since treated objects cannot always be stored under ideal conditions, for example during exhibitions, handling or transportation. The microcristalline wax coatings formerly applied have been discontinued as they did not provide the desired long-term protection against post-treatment corrosion, and are not easily reversible. Instead, a more reversible protective coating of Paraloid B44 (ethyl acrylate/methyl methacrylate, identical to Acryloid B-44S) is being used. According to Down *et al.*, B44 retains a stable pH over time, whereas Paraloid B72 tends to become more acid [18]. Furthermore, Paraloid B44 has been successfully used as a protective coating for mineralized organic remains during desalination treatments with alkaline sulphite solutions. Because of its lower glass transition temperature, B72 failed to provide the necessary protection in baths heated to a temperature of 50ºC. The glossy appearance of Paraloid B44 can be reduced by using methylbenzene (toluene) as a solvent. The slower evaporation rate allows a better distribution of the coating while using a puffer. This will also result in a matt surface appearance.

Treated objects are stored at low relative humidity using silica gel and sometimes oxygen absorbers (RP System, Mitsubishi Gas Chemical Company) [19]. Their condition is being regularly monitored.

Objects not to be treated with hydrogen plasma

Corroded iron artifacts carrying mineralized organic remains should not undergo plasma treatment at all. Like the corrosion products, they will also be partially reduced and therefore become more brittle. Whenever non-mineralized organic structures survive, the plasma treatment will lead to drying, shrinking and cracking. Dussère also observed colour changes after treatment [2]. When iron artifacts are associated with copper alloys, the reduction of the copper oxides and carbonates will result in an unacceptable colour change (Figure 3) [20].

Conclusions

Over the last eight years, increased research in the conservation of iron by plasma reduction has

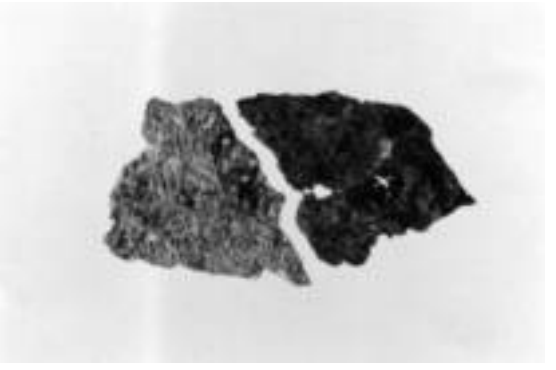

Figure 3 Copper alloy before (left) and after (right) plasma treatment.

Figure 4 Artifacts from Uster-Nänikon, Bühl, Kanton Zürich, treated in 1994; showing their condition in 2000.

yielded new results which have greatly affected its present use at the Swiss National Museum. In order to avoid alterations in the metallurgical structures of quenched iron artifacts, treatment temperatures have been reduced from 400ºC to around 120ºC. By introducing a thermocouple into the discharge tube, precise temperature measurement of the object surface can now be performed during the treatment.

Low treatment temperatures (around 120ºC) do not remove substantial amounts of chlorides, but the reduction process introduces micro-fissures into the corrosion products of the treated artifacts that facilitate subsequent mechanical cleaning and the removal of chlorides during an alkaline sulphite treatment. The desalination process has proved to be up to four times faster after a standard plasma treatment. An easily reversible acrylic polymer coating (Paraloid B44) is applied to all treated artifacts.

Passivation of the objects by introducing nitrogen and/or carbon into the surface has proved to be ineffective in preventing post-treatment corrosion and has, therefore, been discontinued.

Over the last eight years we have had excellent results with the treatment procedures described. Constant monitoring of condition is being undertaken and the objects have continued to be very stable (Figure 4). Hydrogen plasma reduction has proved to be effective and successful in conjunction with other stabilization methods. It has become an integral part of a series of treatment steps in the cleaning and stabilization of corroded iron artifacts.

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Suppliers of materials

Paraloid B44: Kremer-Pigmente, Farbmühle, 88317 Aichstetten, Germany.

Biloxit F 280 (aluminium oxide, average 37μm) and glass beads AQ (<50μm): Wülsag AG, Mühletalstrasse 67, 4800 Zofingen, Switzerland.

Silica gel: CU Chemie Uetikon AG, 8707 Uetikon, Switzerland.

RP-System: Mitsubishi Corporation, 6–3 Marunouchi 2-Chome, Chiyoda-ku, Tokyo 100–86, Japan.

Sodium sulphite: Fluka Chemie AG, Industriestrasse 25, 9471 Buchs, Switzerland.

Sodium hydroxide: Merck AG, Ruchligstrasse 20, 8953 Dietikon, Switzerland.

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Résumé—*La réduction en plasma d'hydrogène à basse pression est utilisée au Musée national suisse pour la conservation des métaux depuis 1990. Après une réévaluation critique de la méthode en 1994, des changements important furent apportés. Aujourd'hui, cette méthode fait partie intégrante des procédures de conservation pour les fers archéologiques. On obtient un meilleur nettoyage mécanique et une accélération du processus subséquent de dessalement par le sulfate alcalin. Cette étude met l'accent sur les modifications apportées à l'appareil à plasma ainsi qu'aux paramètres du traitement, comme la température, le temps et le mélange gazeux. Toutes ces améliorations visent à préserver l'intégrité de l'objet traité.*

Zusammenfassung—*Seit 1990 wird am Schweizer Nationalmuseum die Reduktion durch Wasserstoffgasplasma bei niedrigem Druck in der Metallkonservierung genutzt. Nach einer kritischen Überprüfung der Methode wurden 1994 bedeutende Veränderungen eingeführt: Heute ist sie ein integraler Bestandteil der Konservierung von archäologischem Eisen. Die Hauptvorteile liegen in der Verbesserung der mechanischen Reinigung und der Beschleunigung der nachfolgenden Entsalzung mit alkalischen Sulfiden. Die vorliegende Studie konzentriert sich auf die Veränderungen des Plasma-Generators und der Behandlungsparameter wie beispielsweise der Temperatur, der Zeit und der Gasmischung. All diese Verbesserungen dienen dazu, die Unversehrtheit der Artefakte zu gewährleisten.*

Resumen—*Reducción de plasma por hidrógeno gaseoso de baja presión ha sido usado en el Museo Nacional Suizo en la conservación de metales desde 1990. Tras una reevaluación crítica del método en 1994, se introdujeron cambios importantes en esta técnica. Hoy se ha llegado a convertir en una parte fundamental de los procesos de conservación de hierro arqueológico. Sus mayores ventajas son una limpieza mecánica mejorada y una aceleración del subsecuente proceso de desalinización con sulfitos alcalinos. Este artículo se centra en los cambios introducidos en el aparato de plasma así como en los parámetros de los tratamientos como la temperatura, el tiempo y la mezcla de gases. Todas estas mejoras tienen la intención final de preservar la integridad del artefacto.*