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Application of low-temperature low-pressure hydrogen plasma: treatment of artificially prepared corrosion layers

Abstract: The aim of this work is the application of low-temperature low-pressure hydrogen plasma on artificially prepared corrosion layers, so called plasma chemical reduction. It is necessary to use samples with artificially prepared corrosion layers because it is impossible to use the real artifacts for fundamental research. The bronze was chosen as a sample material. Formation of corrosion layers on the bronze samples was carried out in concentrated hydrochloric acid vapors with the addition of sand. The radio-frequency hydrogen plasma was generated in the flowing regime at a pressure of 160 Pa. Different values of supplied power were chosen as well as different discharge modes: continuous or pulsed mode with varied duty cycles. By the combination of supplied power and mode factors, we selected two values of effective power. The process of plasma chemical reduction was monitored by optical emission spectroscopy (OES) and simultaneously, the sample temperature was measured. Rotational temperatures were calculated from OH radicals spectra. Changes in the structure and elemental composition were determined using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX).

Keywords: bronze, corrosion layers, hydrogen plasma, optical emission spectroscopy, microanalysis.

1 Introduction

Historical evolution brought the usage of different materials. For example, copper and its alloys are known since the Bronze Age or iron since the Iron Age. Nowadays, many objects made of these materials are excavated by the archaeologists around the world. With the presence of these objects, so called artifacts, there is a necessity to restore and conserve them to keep their historical information. Classical conservation and restoration processes have several steps (mechanical treatment, desalination or surface cleaning and protection from further degradation) leading to protection of archaeological artifacts. After the optimization of process conditions, the plasma chemical reduction could be one part of that process. Our research is focused on bronze artifacts found in soil.

The method of plasma chemical reduction is based on the reduction of corrosion products by reactive species generated in hydrogen glow discharge plasma at low-pressure and low-temperature [1]. In the glow discharge plasma, electrons accelerated by an external electric field have enough energy – among many other interactions – to dissociate hydrogen molecules, \( \text{H}_2 \), to form atoms H at low pressure and temperature. All these active particles can react with the corrosion layers at the object surface and thus they induce chemical reduction of broad variety of corrosion products [Schmidt-Ott K., Proceedings of Metal, 2004, p. 235-246]. The plasma treated corrosion layer becomes brittle and can be removed easily by conservators without additional mechanical stress. In addition, corrosion compounds containing chlorides can be destabilized, and chlorine can be removed to the gaseous phase of the discharge [1]. It is very important for our research because chlorides play the key role in soil corrosion.

Plasma chemical reduction is a relatively new method. Its history goes back to the 70's during the last century. First remarks were given by the group around V.D. Daniels in London. They successfully used the low
frequency discharge in gas mixtures for the treatment of silver artifacts and Daguerreotypes, but their procedure was not successful for the iron artifacts [2]. The next group which successfully developed and improved this method was gathered around S. Vepřek from Zürich. They constructed an apparatus working on the base of high frequency hydrogen plasma [3-6].

The main advantage of the plasma chemical reduction is that there is no contact with aggressive chemicals during the treatment. It is also possible to treat more artifacts simultaneously. This makes the procedure faster, cheaper and more extensive. In the past, the trend was to remove the whole corrosion layer. However, the original shape and surface of the artifact was destroyed. Nowadays, conservators and restorers are focused on the corrosion process abatement and preservation of the surface patina layer because it holds information about the object’s history. Of course, the plasma chemical reduction, as well as all the other methods used in conservation, has some disadvantages like high price of the apparatus (vacuum system, generator, etc.) and possible unwanted structural changes of material due to elevated temperature of treated samples.

Nowadays, plasma chemical reduction is used at several institutions, for example Swiss National Museum (Centre for Conservation, Zurich, Switzerland) [7], National Technical University of Athens (Laboratory of Physical Chemistry, Greece) [8], Museum of Central Bohemia in Roztoky [http://www.muzeumroztoky.cz/Panely/oddkonzervace.htm (in Czech)] or Technical Museum in Brno (the last two in the Czech Republic).

2 Experimental procedure

The original archaeological artifacts could not be used for the fundamental research due to their invaluable historical value and also due to the fact that each artifact has its own history, in other words there are no two same objects. Thus, we treated artificially prepared corroded model samples for which we used the same material as known in corrosion layer composition and structure according to the original artifact.

The experimental part of this work contains several steps: preparation of samples surfaces, creation of model corrosion layers, plasma chemical reduction monitored by OES including the calculation of rotational temperature, measurement of sample temperature and also the surface microanalysis (SEM, EDX) performed before and after the treatment.

2.1 Sample preparation and corrosion layer creation

The bronze samples were represented by blocks with dimensions of 50×10×10 mm³ with a weight of approximately 80 g. Due to the unification of the surface roughness, samples were grinded by an electric grinder using the sandpaper with roughness of 600 grains per square inch. The exposure to the corrosion environment followed immediately.

Vapors of hydrochloric acid (35%) were used as a corrosive environment (chlorines are the main corrosive agent affecting directly in the soil [9]) in combination with river sand. Thus, the obtained corroded samples were very similar by their face as well as corrosion structure to the real excavated artifacts. A Petri dish with 20 mL of concentrated hydrochloric acid was placed at the bottom of a desiccator. A ceramic holder with samples and added sand was placed above the dish. The closed desiccator was stored in the dark place for 30 days. After that, they were removed, dried under vacuum at 60°C for 24 hours. The dried samples with corrosion layers were placed in the desiccator together with a humidity and oxygen absorber where they remained until the plasma chemical treatment was performed in order to stop consequent corrosion.

Scheme 1: Photography of the reactor in operation (top). Schematic drawing of the apparatus (bottom): mass flow controller (1), thermocouple (2), aeration valve (3), reactor (4), grounding (5), two copper electrodes (6), corroded sample (7), glass holder (8), pressure gauge (9), optical fibre (10), ball valve (11), butterfly valve (12), rotary oil pump (13).
2.2 Plasma chemical reduction

Our experimental equipment was constructed according to the original design of Vepřek [3], and was further improved (see Scheme 1). A quartz cylindrical reactor (length of 90 cm, inner diameter of 9.5 cm) was continuously pumped by rotary oil pump allowing the based pressure under 10 Pa before the start of each experiment. The pressure was measured by a capacitance gauge (Leybold Vakuum, CRT 90). Pressure in the reactor is around 160 Pa during the experiment. The reactor was connected to the rotary oil pump through an electromagnetic butterfly valve and a ball valve for the operating pressure adjustment. Pure hydrogen (99.9%) was fed into the reactor through a mass flow controller at a constant flow rate 50 sccm. The RF generator (Cesar, 13.56 MHz) supplied through automatic matching network two copper electrodes placed out of the cylindrical reactor. The plasma chemical process of corrosion layers removal was continuously monitored by optical emission spectroscopy (Jobin Yvon - SPEX, TRIAX 550 with CCD detector) collecting emitted light at the reactor axis. The sample temperature, that is one of the most critical experimental parameters, was controlled by a K-type thermocouple mounted inside the treated sample. Due to the strong influence of electromagnetic field on the reading values, temperature was measured every minute at the end of the discharge switch-off period for 5 seconds. The whole experimental system was fully PC controlled.

Hydrogen reactive species (as mentioned in Introduction) are created after the discharge is turned on. The OH radical is produced by the reaction of atomic hydrogen from the discharge with oxygen contained in compounds forming the corrosion layer, and thus, its radiation can be used for experiment monitoring [10]. An emission spectrum was collected and evaluated each minute during the first 30 minutes and then every 5 minutes until the end of the experiment (60 minutes).

The aim of this study was to compare the effect of various plasma treatment conditions on the plasma chemical reduction process. The specific values of supplied power and discharge duty cycle were chosen before the plasma chemical treatment of each process (Table 1). Each process was repeated five times and the average values are presented in the Results.

The pulsed mode was operating at 1000 Hz frequency and the effective power was calculated according to the equation

\[ P_{\text{eff}} = P \frac{t_{\text{on}}}{t_{\text{on}} + t_{\text{off}}} \]

where \( P \) is real value of delivery power, \( t_{\text{on}} \) is time of active discharge and \( t_{\text{off}} \) is time of inactive discharge.

However, the mean energy in the pulsed regime was significantly lower. The process kinetics was different in each regime because the reactive particles generated by the discharge can react with the surface during the post-discharge period, too [11].

2.3 Temperature

In contrast to other artifact materials such iron, brass, copper or silver, bronze brings one significant problem because it is the most temperature sensitive material. Tin lines can be recognized in the emission spectrum as well as a thin film of tin (tin “mirrors”) was created inside of the apparatus at sample temperature elevated up to about 160 °C. Although this temperature is much lower than tin melting point, the sample surface can be locally overheated by plasma ions impacting in the vicinity. Moreover, the direct surface sputtering can contribute to this effect. The elevation distorts results, causes the destruction of the sample and causes problems in apparatus cleaning after each experiment. Therefore, monitoring of the sample temperature together with emission spectra is necessary to minimize this negative effect.

2.4 Microanalysis

All samples were analyzed by a scanning electron microscope (SEM) Philips XL 30 in order to obtain high resolution surface morphology and chemical composition by energy dispersive X-ray analysis (EDX) Edax analyzer. The samples were coated by a thin layer of carbon to prevent the charging effect during the EDX microanalysis. The surface details were imaged at 20 keV by the backscattered electron detector from the area of 3.45×4.45 µm². The same
area was used for the EDX analyzes to decrease the local fluctuations in composition.

3 Results and discussion

3.1 Optical emission spectroscopy

The time dependences of OH radical relative intensity for two selected effective powers are shown in Fig. 1. Two maxima of OH radical intensity can be recognized at all conditions. The first maximum corresponds to the reduction of an outer corrosion layer consisting of sandy grains, and it was observed in the first 10 minutes of plasma treatment. The second maximum corresponds to the reduction of an inner corrosion layer which is in touch with the original sample surface and it was determined to occur between 10 and 15 minutes. The decrease of relative intensity of OH radicals followed after that. The changes in relative intensity of OH radicals were negligible after 30 minutes, so we can consider it as a steady state system.

In the case of samples treated at effective power of 100 W (Fig. 1, left), creation of maxima of OH radical intensity was slower and less significant than at higher effective power (Fig. 1, right, effective power of 200 W). This means that higher effective power is more efficient for the corrosion removal.

3.2 Temperature

The time dependences of the sample temperature during the plasma treatment are shown in Fig. 2. The situation is the same for both effective powers applied, and maximal value of sample temperature decreases with a duty cycle parameter. Results from OES (Fig. 1) show that the main reduction process takes place during the first 20 minutes and it corresponds with sample temperature increases. After that, the sample temperature remains nearly constant.

Temperature of the samples treated at 200 W in the continual mode is approaching values at which the tin mirrors are created.

The plasma rotational temperature, which value is close to the neutral gas temperature, was calculated from OH radical spectra. The comparison of rotational and sample temperature is shown in Fig. 3. The results show that rotational temperature is time independent, except the first few minutes, and affected by the whole setup heating. Table 2 shows the average rotational temperature values for all processes. It can be concluded that rotational temperature is more or less independent on the plasma conditions and thus it could not be used for the process monitoring. This temperature is a little bit above tin melting point and thus this result indicates possibility of a local surface overheating by surface bombardment driven by plasma active particles.

3.3 Microanalysis

Results from the EDX analysis of the original bronze sample showed the ternary alloy of Cu-Sn (87% copper and 13% tin) with occasionally presented Pb particles (see Fig. 4).

The SEM images show the significant change in the surface morphology (Fig. 5). It is obvious that the layer
of corrosion products becomes less compact and thus it is easily breakable after the plasma treatment, so the corrosion can be easily removed by further mechanical cleaning.

All bronze samples were corroded under the same conditions (in one desiccator) and for the same time (30 days). Thus it was possible to presume that corrosion products would have the same average composition. Due to this fact, the EDX analysis was performed only on one sample from Process 1 before the plasma chemical reduction (Table 3). Table 3 contains average values obtained from 5 different samples; each of them was measured 10 times at different places.

The EDX analysis revealed the presence of eleven elements: three are elements from bronze (Cu, Sn and Pb); Cl and O are coming from corrosion environment and the remaining elements (Al, Ca, Fe, K, Mg, Si) are typical soil elements (incrustation layer) coming from ambient river sand [12].

Cu, Sn, O and Cl are the most present elements, other elements could be neglected. The mass decrease of O and Cl and the increase of Cu and Sn masses are significant by comparing values before and after plasma chemical reduction (Table 3). This means that the real bronze corrosion products (chlorides and oxides) were partially removed. The full corrosion removal by plasma is not possible because the remaining corrosion layers block the direct interaction between plasma and sample surface. Thus, the process used in practice is carried out in more plasma steps separated by the mechanical removal of

Table 2: Values of average rotational temperature and its uncertainty.

| Process | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---------|---|---|---|---|---|---|---|---|
| Average rotational temperature [K] | 590 | 580 | 570 | 570 | 570 | 600 | 590 | 590 |
| Uncertainty of average rotational temperature[K] | 60 | 60 | 60 | 60 | 70 | 10 | 70 | 70 |

Table 3: The results of EDX analysis from the sample area (3.45×4.45 μm²) after the plasma chemical reduction. All values are in mass %.

| Process | Cu | Sn | Pb | Cl | O | Al | Ca | Fe | K | Mg | Si |
|---------|----|----|----|----|---|----|----|----|---|----|----|
| 1*      | 34.5 | 11.2 | 0.6 | 25.3 | 22.6 | 1.1 | 0.1 | 0.6 | 0.1 | 0.2 | 3.7 |
| 1       | 44.6 | 10.7 | 4.7 | 20.3 | 13.9 | 0.8 | 0.2 | 2.2 | 0.3 | 0.2 | 2.1 |
| 2       | 49.5 | 12.3 | -  | 21.0 | 12.1 | 0.8 | 0.2 | 1.6 | 0.1 | 0.1 | 2.3 |
| 3       | 46.6 | 9.5  | 5.5 | 19.8 | 14.4 | 0.7 | 0.1 | 0.8 | 0.5 | -  | 2.5 |
| 4       | 48.7 | 9.8  | -  | 22.8 | 13.6 | 0.9 | 0.1 | 1.4 | -  | -  | 2.7 |
| 5       | 51.0 | 12.6 | -  | 18.9 | 13.6 | 0.7 | 0.1 | 0.7 | -  | 0.6 | 1.8 |
| 6       | 50.0 | 10.1 | 4.3 | 23.2 | 9.4  | 0.5 | -  | 0.9 | 0.3 | -  | 1.3 |
| 7       | 48.1 | 16.0 | -  | 17.7 | 13.5 | 0.8 | 0.3 | 1.3 | 0.1 | 0.1 | 2.1 |
| 8       | 51.2 | 8.7  | -  | 21.7 | 12.9 | 1.0 | 0.1 | 1.5 | 0.1 | -  | 2.8 |

*The results from EDX analysis of one sample from Process 1 before plasma chemical reduction. Each value is obtained using 5 samples measured 10 times at different places.
corroded layers [10]. The results of element masses are also depicted in Fig. 6 for better comprehension of the positive effect of plasma chemical reduction.

4 Conclusions

Plasma chemical reduction of artificially prepared corrosion layers on bronze samples was performed. Results from OES, measurement of the sample temperature and SEM and EDX microanalysis showed that plasma chemical reduction had a positive effect on the corrosion layers removal. OH radical emission intensity that reflects corrosion removal showed two maxima; the first one corresponded to the removal of oxygen from incrustation, the second one corresponded to the removal of bulk corrosion. The better reduction effect was observed on samples treated at effective power of 200 W. The sample's temperature did not exceed the value of 160°C that was estimated as the protection temperature for the bronze damage under the plasma treatment. The plasma treated corrosion layers start to be more brittle and also their composition was changed. The real bronze corrosion products (chlorides and oxides) were partially removed. The full corrosion removal by plasma was not possible because the remaining corrosion layers blocked the direct interaction between plasma and sample surface. Thus, the process used in practice should be carried out in more plasma stages separated by the mechanical removal of corroded layers.

The rotational temperature calculated from OH radical spectra was nearly independent on the plasma conditions.
except for its slight increase during the first few minutes of the plasma chemical treatment.

Our further work will be focused on the measurements of the cross section corrosion profile of the samples before and after the plasma chemical reduction, as the X-ray diffraction analysis will be performed.

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