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PLASMACHEMICAL REDUCTION FOR THE CONSERVATION OF ARCHAEOLOGICAL ARTEFACTS

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Abstract. This work deals with the plasmachemical treatmant influence on the chlorides removal from the corrosion layers that are present on the surface of an archaeological artefact. The plasma was analysed by optical emission spectroscopy. The OH, N_2 CN, NO band integral intensities as well as hydrogen line intensities were observed as a function of the treatment time. It was found that OH band intensity measurment is sufficient for the reduction process monitoring in practice. Results obtained with a real artefact were compared with the other from model samples treatment. Moreover, the corrosion layer analyses were carried out by means of X-ray diffraction. These results confirmed that the plasmachemical method is very effective.

1. INTRODUCTION

It was proved that the using of hydrogen plasma allows reduction of chlorinated products as well as oxides from the corrosion layers of archaeological objects [1, 2, 3]. Plasmachemical treatment is much more shorter than the mechanical or chemical treatment that have been commonly used till this time. The main advantage of this method is the fact that it is possible to treat the artefact of big size, the hollow artefacts or artefacts with broken relief [2, 4, 5].

Furthermore, it could be appreciated that the plasmachemical treatment is regardful of the artefacts. Obviously, the effect of UV radiation should not be neglected.

Internal corrosion layers of steel objects, surrounding the metalic core, are mainly made of magnetite Fe_3O_4. External corrosion layers consist of oxides, chlorides, α-FeOOH, β-FeOOH, α-Fe_2O_3 in combination with other minerals such as FeOCl, $FeCl_2$, Fe_2SiO_4, $Fe_3(PO_4)_2$ $8H_2O$, and many other compounds.

Corrosion layers of copper or bronze artefacts include for example Cu_2O, CuO, $Cu(OH)_2$, $Cu_2Cl(OH)_3$, CuS, Cu_2S, $CuFeS_2$, etc… It is well known that especially chlorinated products are dangerous in term of new corrosion occurance. The chlorinated products can be decomposed to the chlorides which cause the active corrosion. Our aim is to remove the corrosion layers and to protect the artefacts against new corrosion. Besides the corrosion products, the real corrosion layers contain also many other compounds originating in the artifact surrounding. Thus, for example, the sand grains are build up in the corrosion layer structure and they furthermore complicate the conservation procedures.

Mechanical and chemical treatment in alcaline sulphite bath is often used to eliminate the chlorides from the layers. The main disadvantage of this method is its long duration which can take several months. In 1980, the plasmachemical method was developed [1, 2, 3]. This method is based on the reduction processes by means of low-pressure hydrogen plasma and it included:

1. Partial reduction of external corrosion layers in the mixture of hydrogen with 25 % of methane. Duration of this step was about 2 h and the gas temperature increased up to 300 °C.

2. Mechanical removing of the corrosion layers.

3. Reduction corrosion layer from the artefact bulk. It taked about 20 houres, the temperature was about 400 °C. The mixture of 39 % of hydrogen, 17 % of metane, 22 % of nitrogen a 22 % of argon was applied. Besides reduction, the carbonitridation and passivation of the object surface was provided.

4. The conservation using the commonly used hydrophobic wax.

The original method of prof. Veprek was changed and improved on the basis of further experience. Presently, it is given priority to pure hydrogen utilization and in some cases, the argon and much lower temperature is used (up to 250 °C) to decrease the negative higher temperature effects, especially in case of sensitive archaeological objects their composition is not fully known..

The reduction process is based on the presence of atomic hydrogen created in the plasma. The main reactions in pure hydrogen plasma are as following:

$e + H_2 \rightarrow e + H + H$
$e + H_2 \rightarrow e + H_2^*$
$e + H_2 \rightarrow 2e + H_2^+$
$e + H_2 \rightarrow 2e + H + H^+$

Depending on the corrosion layer character, the reduction can be fully completed up to the metal. For example, the reduction of ferrous corrosion products can be described by following reactions:

$10\ FeOCl + 3H_2 \rightarrow 2Fe_3O_4 + 4FeCl_2 + 2HCl + 2H_2O$
$FeCl_3\ H_2O \rightarrow FeOCl + 2H_2O$
$2FeCl_3 + H_2 \rightarrow 2FeCl_2 + 2HCl$
$FeCl_2 + 2H + \rightarrow Fe + 2HCl$

Many corrosion layers contain also the ammonia complexes. The amonium is liberated under the plasma conditions and by photolysis it can be the additional source of atomic hydrogen:

$h\nu + NH_3 \rightarrow NH_2 + H$
$h\nu + NH_3 \rightarrow NH + 2H$

2. EXPERIMENT

The plasmachemical treatment was carried out in two reactors that differed from each other by their dimensions. The simplified scheme of the experimental set up is shown in Fig. 1.

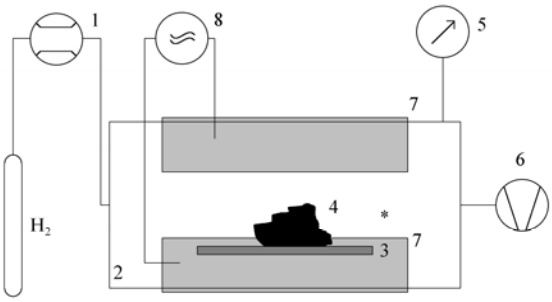


Fig. 1. 1 – mass flow controller; 2 – Pyrex glass reactor (length 100 cm, inner diameter 10 cm); 3 – Pyrex artifact holder; 4 – the treated archaeological artifact; 5 – baratron gauge; 6 – rotary oil pump; 7 – outer cylindrical copper electrodes; 8 – RF power supply; * – point of spectroscopic measurements.

Both reactors consist from a Pyrex glass tube with a pair of outer copper electrodes. The created capacitivelly coupled RF discharge has a good spatial homogeneity and thus it could be applied for treatment of objects with large range of dimensions. The main part of presented results was provided in the simplified small model device with inner diameter of 10 cm and length 100 cm. Fig. 2 shows the real wiev on this small scale device. The working pressure was kept between 100 and 110 Pa, hydrogen flow rate was 100 sccm. The capacitively coupled RF power supply gave the total power of 400 - 450 W, and the sample temperature was estimated at 280 °C. The second experimental device uses a Pyrex tube of 40 cm in diameter with length of 150 cm. This device is continualy developed and improved.

The optical emission spectroscopy was applied to study the processes during the plasma treatment. The spectra emitted from the discharge were recorded by spectrometer Jobin Yvon 550 with CCD detector.

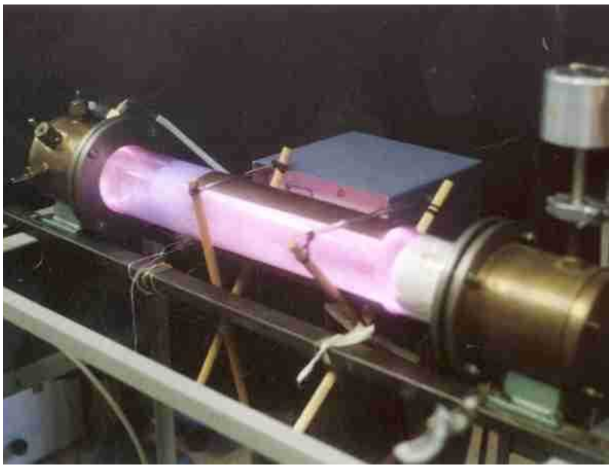


Fig. 2. Photography of the small scale experimental device during the operation.

3. RESULTS AND DISCUSSION

The optical emission (OE) spectra were recorded with and without an artefacts inside the reactor.

In the spectra, various lines and bads were found, as it is shown in Fig. 3. The hydrogen lines and bands as well as OH radical bands were the most intensive. The band and line intensities were observed as a function of the treatment time.

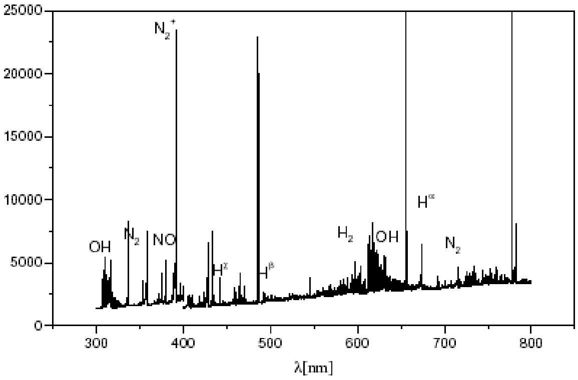


Fig. 3. An example of the optical emission spectra obtained during the plasma treatment of archaeological bronze coin.

It was found that the integral intensity of OH is changed during the reduction process. The plasmachemical reduction was carried out in several stages. Each of them consits of the reduction in the discharge and mechanical removal of the rest of corrosion layer. At the begining of the cyclus, the small increase was observed first, and then, the intensity decreased, as presents Fig. 4. The relation between oxides reduction and OH intensity was found. It could be appreciated that its integral intensity decrease to the value of 10 % of its maximum corresponds to the „end“ of the cyclus of the redution process. For the removal of corrosion layers and for their reduction to the metal it is necessary to apply several treatment steps which are combined with the soft mechanical cleaning and desalination in the LiOH solution or in the distilled water. The desalination process was controlled by the determination of chloride concentration in the solution using the titration method. The Fig. 5 shows that plasmachemical treatment influence the desalination process. The chloride amount in the layer is lower than in the case of classical mechanical treatment and besides, the desalination time is much shorter.

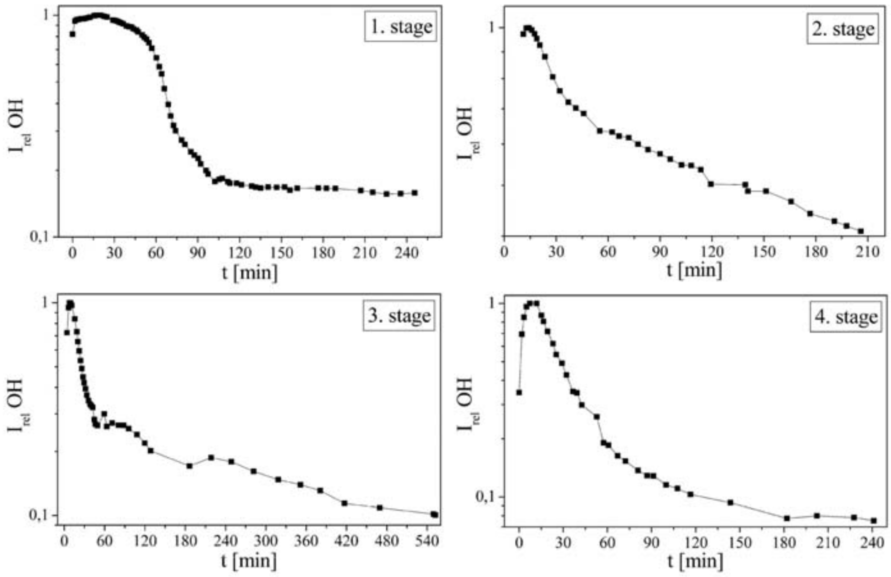


Fig. 4. The dependence of the OH band integral intensity as a function of the treatment time during four different stages.

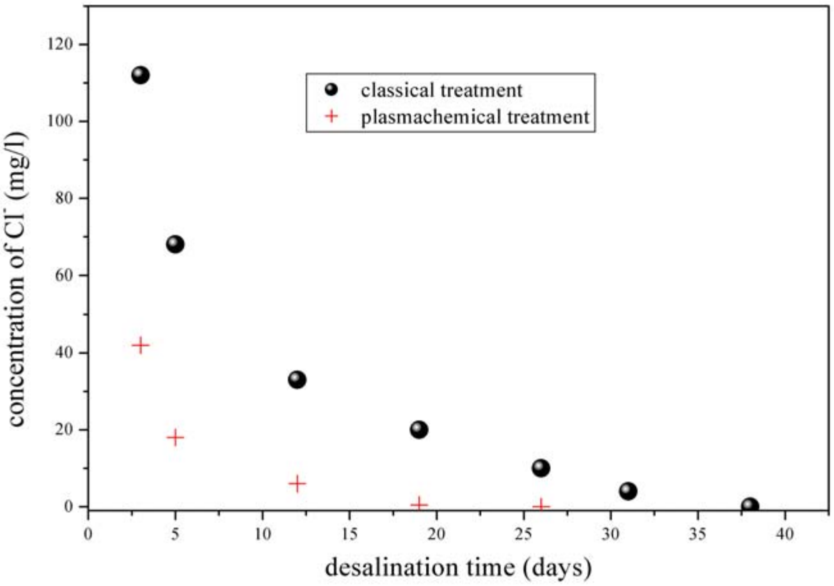


Fig. 5. The dependence of the concentration of Cl^- as a function of the desalination time in the case of classical and plasmachemical treatment of iron artefacts. The concentration was determined by titrimetric (mercurimetric) method.

Moreover, the model samples of corrosion layers were made and treated in our experiments, too. Two sets of copper corroded samples were prepared for the study. First one was created in acid atmosphere that consisted of 18.5% HCl, 32.5 % HNO_3 and mixture of HCl, Na_2CO_3 + Na_2SO_3. So, theree different corrosion layers were obtained (chloride, sulphate and carbon). For the other set of samples, basic atmosphere of ammonia was applied. The diameter of copper samples was 70x100x0.6 mm. Initially, they were cleaned by an alkaline galvanic solution and they were placed on a glass grating in the dessicator at the temperature of 20 °C. The sampels were removed after six days and dried at ambient air. The $CuCO_3$, $CuCO_3$ $2Cu(OH)_2$, $CuSO_4$ $Cu(OH)_2$ compounds were dominant in the corrosion layers. The CuO, CuO_2 represented only about 10 %.

The emission spectroscopy was used to find out all changes those had been resulting from plasmachemical reactions in a hydrogen RF discharge. Identification of the atomic lines and the molecular bands was the first step to be done. After that some atomic and molecular spectrograms were chosen to be suitable for later studies of plasma catalysed reactions. $OH(A^2\Sigma \to X^2\Pi)$ (305 – 320 nm) and $N_2(C^3\Pi_u \to B^3\Pi_g)$ 0-0 (337 nm) bands and H^β (486,1), resp. H^γ (434,0 nm), lines were chosen as the best describing makers of their intensities, those had changed mostly in the spectra during whole plasma operation. Those emitted spectra intensities were measured as a function of treatment duration and results were enregistered into diagrams. Spectra emitted from the discharge during the plasmachemical treatment were measured also as a function of the treatment time. The hydrogen lines and OH, N_2 CN, NO bands were the most intensive in the spectra. The bands of metal were observed, too.

The results obtained during the treatment were compared with the results obteined using real archeological artefacts. The results show, that the OH radical intensity slowly decreases in the both cases while nitrogen bad intensities decrease very fast (almost exponentially). In the case of hydrogen lines, it was found the difference during the „basic“ corrosion treatment and the acid corrosion treatmnet. During the basic corrosion reduction, the hydrogen line intensity increases and then it is constant or it slowly decreases. But during the acid corrosion layer reduction, this intensity decreases, first and then strongly increases.

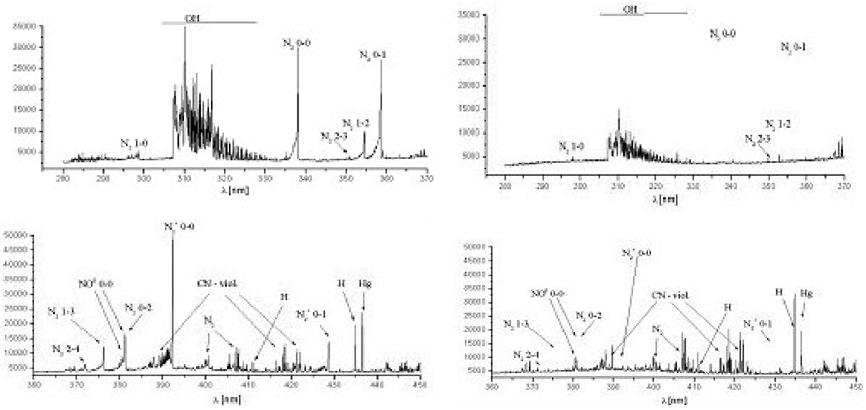
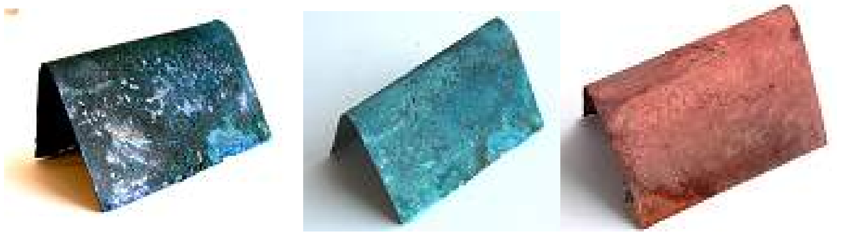


Fig. 6. An example of the OE spectra obtained during the plasmachemical treatment of model samples with created corrosion layers [7]. The pictures on the left side show the emitted spectrum recorded at the begining of the treatment. The pictures on the right side present spectra emitted after 1 hour of treatment.



Green layers : $CuCO_3$, $CuCO_3.2Cu(OH)_2$
Green-blue layers: $CuSO_4$, $CuSO_4.Cu(OH)_2$
Dark blue layers: NH_3 complex compounds
Brnown layers: CuO, CuO_2

Fig. 7. Various kinds of corrosion on model copper layers.

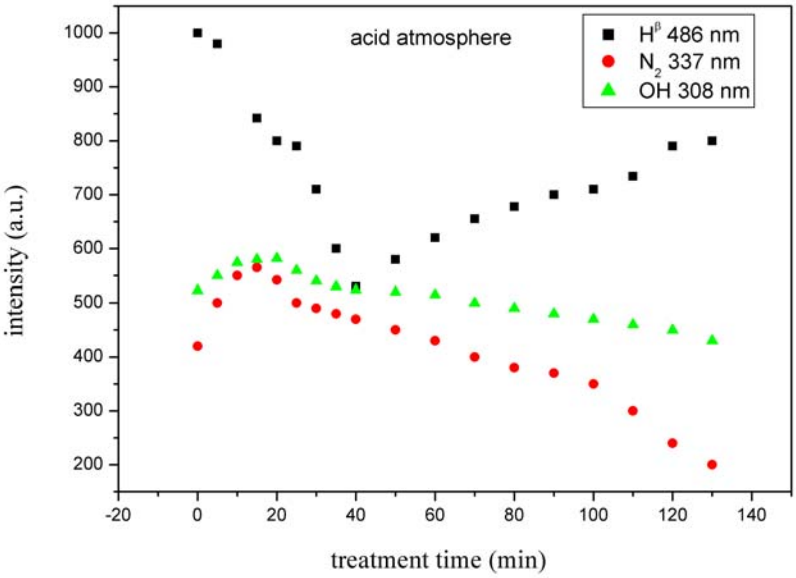


Fig. 8. The dependence of the spectral band integral intensity as a function of the treatment time during the plasma model samples treatment. The corrosion layer was made in acid atmosphere.

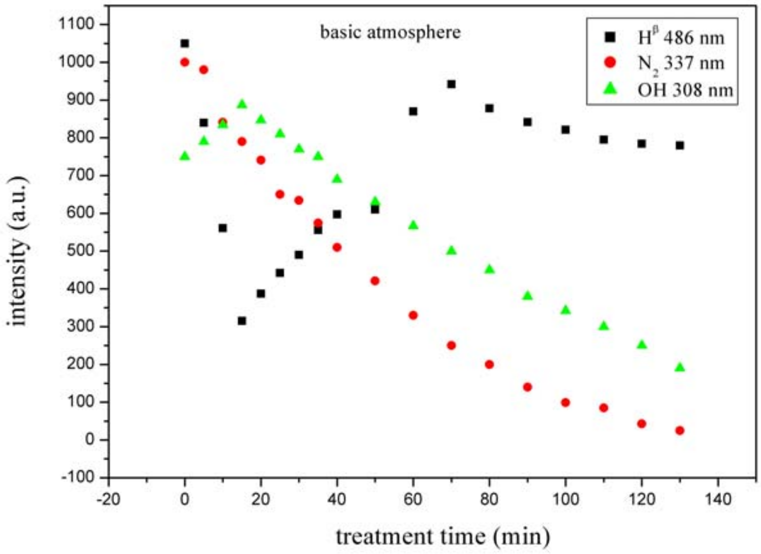


Fig. 9. The dependence of the spectral band integral intensity as a function of the treatment time during the plasma model samples treatment. The corrosion layer was made in basic atmosphere.

Outcome graphs (Figs. 8 and 9) showed explicitly that nitrogen is removed from the corroded samples as first. Its intensity maximum was in the time of about 5 to 10 minutes after the treatment beginning and in time of 1 hour it became extinct at latest. Intensity of OH radical had its maximum in time period 10 to 25 minutes, depending on the corrosion character and it is decreasing to constant minimum level in time about 180 minutes after start of measurement. In the case of iron object, the treatment time of 120 minutes for each step is sufficient.

These results proved that copper oxides reduction took longer time than removal of the other elements contained in the corrosion compounds. Due to detected facts, monitoring of the OH radical spectrum could be suitable for the plasma treatment of more types of corrosions than only the oxide ones.

It was also found that the simplified monitoring device would be useful for the purpose of practical conservation in the museum. The device consists of lens, interference filter, UV sensitive photodiode, low noise amplifier, AD converter, grounded box and digital signal output [4, 7].

Furthermore, the X-ray diffraction analysis was provided during our experiments. The results shows the strong decrease of the chloride content in the layer during the treatment. We also observed the difference between the layer composition at the begining of the treatament and the composition identified after several hours of treatment. The diagrams obtained from X-ray diffraction are given in Figs. 10 and 11. The chlorine removal from the corrosion layer is shown in Fig. 12 as a function of hydrogen discharge treatment time.

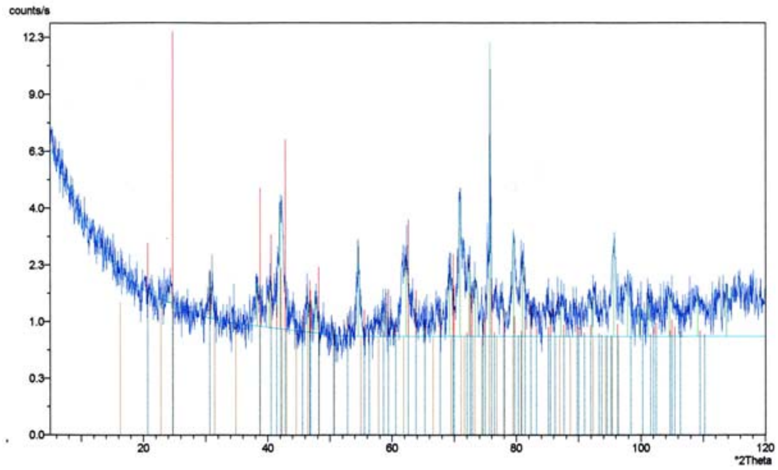


Fig. 10. X-ray diffraction diagram of corrosion layers on the surface of iron object before plasma treatment. The main peaks correspond to the geothite FeO(OH), lepidocrocite Fe_2O_3 H_2O and FeOCl

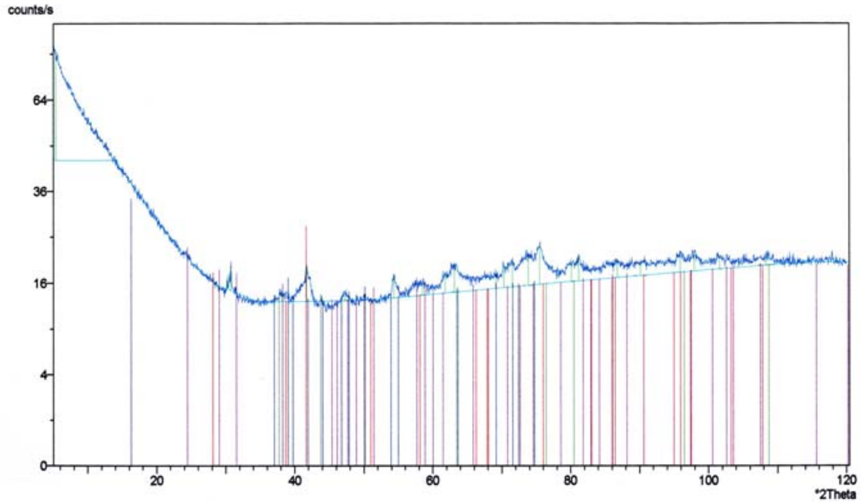


Fig. 11. X-ray diffraction diagram of corrosion layers on the surface of iron object after 60 minutes of the plasma treatment. The main peaks correspond to the magnethite,Fe_3O_4, hematiteFe_2O_3 and calcium iron oxide $CaFe_3O_5$.

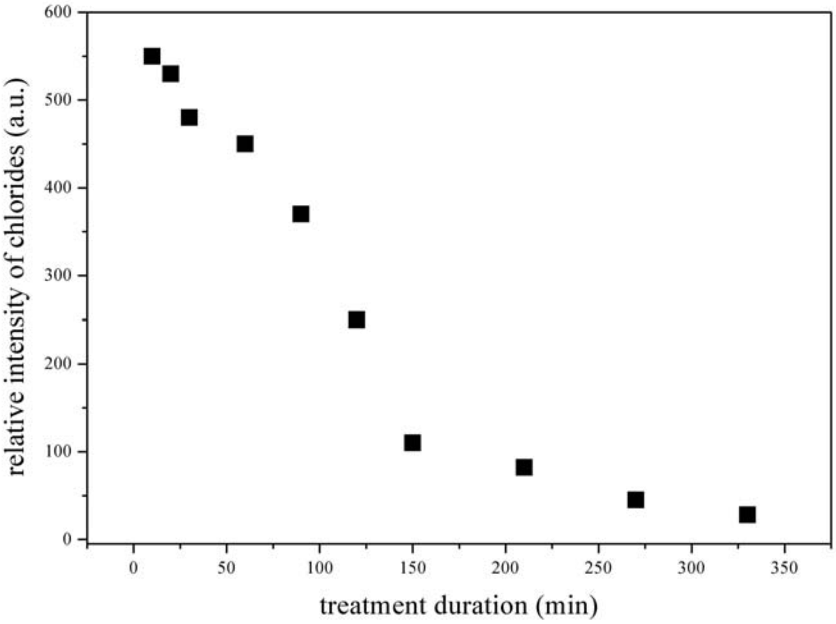


Fig. 12. The intensity of chlorides in the corrosion layer of silver coin as a function of treatment duration in the hydrogen discharge. The chloride content was determined using X-ray diffraction analysis.

4. CONCLUSION

The low pressure plasma chemical treatment of various metallic archaeological objects and model samples was studied. It was found that the whole process can be monitored by using optical emission spectroscopy. Mainly the OH radical band intensity is useful to observe. The plasmachemical treatment consists of several steps and it is possible to determine the end of the reduction in the each step according to the OH integral intensity decrease. Moreover, the gas temperature can be estimated from the rotational spectrum of this band. The N_2 second positive band intensities can also interesting for this purpose. It was found that plasmachemical treatment has positive influence to the chloride ions removal from the corrosion layers. Thus, the deionisation time is shorter than during classical mechanical treatment.

Furthermore, the X-ray diffraction analysis was carried out before and afret plasmachemical reduction. The results show that the reduction process is very effective and in some cases, the reduction to the pure metal was observed.

In the second part of the experiment, the model corrosion layers were created to better comprehension of reduction processes in the plasma. With defined corrosion it was much more simple to observe and to distinguish the bands in the spectrum. The evolution of nitrogen and hydroxyl radical intensity was similar like in the case of real archaeological artefacts. Due to the fact that OH radical monitoring is sufficient during the plasmachemical treatment, the simple monitoring device was presented in [4]. For the practical application, the exact plasma conditions for the treatment are required in dependence on the metallic treated material. So, the searching these condition on the basis of the results from corrosion layer and plasma diagnostics will be aim of further studies for the other materials.

The plasmachemical method is still developed and upgraded. Up to now, it was used mainly for the iron objects treatment. But one of the objective of our work is to find the working conditions for plasma treatment of the other metals, wood and textile materials. Those materials require low temperature up to 80 °C. The pulse plasma utilisation could be very useful to solve the problem with the low temperature keeping. The plasmachemical method is still developed and upgraded. Up to now, it was used mainly for the iron objects treatment. But one of the objective of our work is to find the working conditions for plasma treatment of the other metals, wood and textile materials. Those materials require low temperature up to 80 °C. The pulse plasma utilisation could be very useful to solve the problem with the low temperature keeping.

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