

SAMPLE TEMPERATURE DURING CORROSION REMOVAL BY LOW PRESSURE LOW-TEMPERATURE HYDROGEN RF PLASMA*

L. ŘÁDKOVÁ, P. FOJTÍKOVÁ, Z. KOZÁKOVÁ, F. KRČMA, V. SÁZAVSKÁ, A. KUJAWA

Brno University of Technology, Faculty of Chemistry, Purkyňova 118, 612 00 Brno, Czech Republic
E-mail: xcradkova@fch.vutbr.cz, krcma@fch.vutbr.cz

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Abstract. The plasma chemical reduction of corrosion layers from archaeological metallic objects is developing since the late 70th. Contemporary, it is used in some museums, but the optimal treatment conditions are not fully known yet. Treated object temperature is one of the most critical points because metallographic changes can be initiated by elevated temperatures and thus the unique historical information can be lost. Temperature increases due to the direct inductive heating in the discharge as well as by the interaction of the surface with plasma active particles. In the case of samples prepared in acidic corrosion environment, the maximal temperature of the samples with the incrustation was lower than of samples without incrustation treated under the same conditions because the incrustation layers decrease the direct interaction of plasma active particles with the corrosion layers. In contrary, in the case of brass samples prepared in the ammonia atmosphere, the incrustation had an opposite effect due to intense heating of the sample during the reaction with oxygen presented in the outer corrosion layers. The maximal sample temperature was directly proportional to the linear size (or the third root of weight) of the treated sample.

Key words: plasma surface treatment, metallic corrosion removal, hydrogen RF plasma, processing temperature.

1. INTRODUCTION

Various classical methods of corrosion removal are used for very old or valuable artifacts. Sanding or application of dental drill belongs to these techniques. It is clear that they can tend to be aggressive or even destructive in use. This means that along with the corrosion, some of the base metal is also removed. Moreover, some methods can remove surface features of the treated object which

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could content important information (*e.g.* fine details, etc.). All these classical methods need high manpower because one person can treat only one object at the same time [1]. On the other hand, application of low temperature low pressure plasma allows simultaneous treatment of many objects (up to thousands depending on their shape and size) [2]. Moreover, plasma chemical reduction is one step way of corrosion removal from archaeological artifacts which can remove corrosion layers carefully as well as completely in some cases. Only corrosion layers are removed by this method and the object is retained.

Plasma chemical reduction of corrosion layers is a relatively new method developed by Stanislav Veprek *et al.* [3, 4] at Institute of Inorganic Chemistry, University of Zürich at the end of the 20th century. However, it has been broadly applied mainly for iron artifacts and the optimal operation conditions were estimated empirically [2, 5–8]. The optimal conditions for the corrosion removal from the other metals are not known yet however, some works have been done already [9–11]. The plasma chemical process was successfully used for the treatment of more than 13 000 historical objects from various periods (since 400 B.C. until 19th century) and places of excavation [2]. Before Veprek, Daniels used a similar method for plasma reduction of silver tarnish on Daguerreotypes [12]. At the beginning of 21st century, K. Schmidt-Ott and her colleagues successfully applied this procedure for the treatment of some iron and silver objects [13, 14].

Low pressure low temperature hydrogen plasma operating in a continuous regime was used for the presented experiment [15]. It is impossible to carry out any comparative study using original archaeological objects because each of them is an original by its manufacturing as well as corrosion and storage history, and they have a very high historical value. Due to these facts, several sets of corrosion layers were prepared. The rusted sample (one for each experimental conditions set up) was placed into plasma chemical reactor where it was treated by plasma. The whole process was monitored by optical emission spectroscopy according to [16]. Samples temperature during the plasma treatment was continuously monitored to prevent samples overheating that can cause significant metallographic changes and thus, historical information can be lost. In case of brass objects, zinc could be removed from the object during the heating even at temperature significantly lower than its melting point is.

2. EXPERIMENTAL

Model samples were prepared from the most common archaeological metals using hydrochloric acid vapor (for iron, copper, bronze and brass samples) and

ammonia solution (for brass samples). Two different sets were prepared: The first one with a pure corrosion layer, the second one with a sand incrustation for a better simulation of the real situation of an excavated archaeological artifact. Firstly, metallic samples (typically $0.5 \times 1 \times 5 \text{ cm}^3$) were grinded, after that rinsed in ethanol, and dried. Consequently, they were put into a desiccator where a Petri dish with chloric acid or ammonia solution was placed at the bottom of the desiccator. A half of the samples were additionally covered by sand. In all cases, the corrosion layers had been formed for one month. Each corroded sample was dried under vacuum and stored individually in a protecting package (Art for Life foil) with humidity and oxygen absorbers to keep the same corrosion conditions of all samples up to their plasma treatment.

The composition of the formed corrosion layers is typically very complex [17]. Various oxides and chlorides (both also hydrogenated or with crystalline water) were detected by XRD analysis. The elementary abundance was obtained by SEM-EDX analysis. The preliminary results as well as the influence of plasma treatment on the surface composition were described in detail in [18, 19]; the full paper containing this information is under preparation, now.

The plasma treatment of the prepared model samples was carried out in a Quartz cylindrical reactor (90 cm long and 9.5 cm in the diameter). The reactor (see Fig.1) was surrounded by two external copper electrodes supplied by a radio-frequency generator (13.56 MHz) through an automatic matching network. Sample was placed onto glass grid holder at the middle of a Quartz cylindrical reactor as it is marked in Fig.1. This sample holder consists of two parallel Pyrex tubes (outer diameter of 6 mm) fixed at the ends of reactor. The experiment took place in pure hydrogen (99.9 %) at low pressure (160 Pa) and constant hydrogen flow rate of 50 sccm. Samples were treated at different applied RF plasma power of 100 W, 200 W, 300 W and 400 W in a continuous mode. The treatment duration was up to 120 minutes.

A special series was carried out using non-corroded brass samples to verify the role of the object mass. The samples used for this study had nearly cubic shape with its mass of 11–1046 g.

The plasma chemical process was monitored by optical emission spectroscopy using the Ocean Optics HR4000 spectrometer with 2400 g/mm grating. An optical fiber was placed at a quartz window mounted at the reactor axis. Data obtained from this method were used to calculate integral intensities of OH radicals that

were used for the process monitoring according to the procedure described in [16]. The plasma rotational temperature was calculated from the same spectra, too. Temperature of the sample during the treatment was measured by a K-type thermocouple installed 5 mm inside the sample metallic body. To avoid electromagnetic induction influence on the measured temperature, the temperature values were read out at the end of 5 s discharge break.

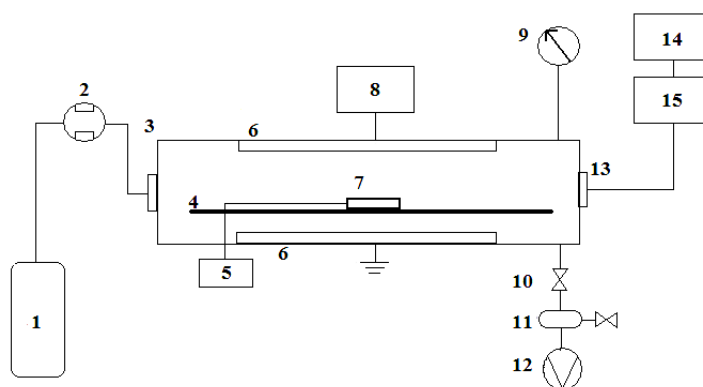


Fig. 1 – Schematic drawing of the experimental set-up: 1–hydrogen; 2–mass flow controller; 3–Quartz discharge reactor; 4–sample glass grid holder; 5–thermocouple; 6–outer copper electrodes; 7–sample; 8–RF power supply and matching network; 9–capacitance pressure gauge; 10, 11–valves; 12–rotary oil pump; 13–optical fiber; 14–PC; 15–OES-spectrometer.

During the plasma chemical reduction, hydrogen ions, radicals and excited molecules react with oxygen and chlorine that are the main elements of the corrosion layers (see above and in [18–20]). OH radicals and HCl molecules are formed by these reactions. The OH radicals were monitored continuously by the optical emission spectroscopy. The HCl presence was directly confirmed by IR absorption spectroscopy, no HCl bands were found in the emission spectra. HCl presence was also confirmed indirectly by a consequent corrosion of aluminum parts downstream of the discharge.

3. RESULTS AND DISCUSSION

In general, sample temperature was increasing during the first 30 minutes of the plasma treatment. After that, it remained constant (details see below in Figs. 3–6). As it was expected, samples treated at the highest applied plasma power of 400 W reached the highest temperature as well. The following subsections describe the plasma chemical treatment in details depending on the corrosion layers kinds.

3.1. IRON, COPPER, BRONZE AND BRASS SAMPLES WITH ACIDIC CORROSION LAYERS

As it was already mentioned above, the non-incrusted samples temperature increased during the first 30 minutes of the plasma treatment, and after that it remained constant (see Fig. 2). During the treatment of the incrusted samples, much faster but only a temporal increase of temperature was observed. After that, the temperature was significantly lower in contrary to the non-incrusted samples as it can be seen from Fig. 2. The maximal temperature in this case was even higher than maximal temperature of non-incrusted sample but this is non-typical as it is demonstrated in Tables 1 and 2.

The maximal temperatures reached during the process are listed in Table 1 (non-incrusted samples) and Table 2 (incrusted samples) for the treatment in the continuous regime at selected applied powers. It can be noted that the maximal temperatures is significantly lower at the lowest applied powers. This is due to the fact that no temperature peak at the process beginning is observed.

We are suggesting that the strong temperature enhancement observed at the beginning of the incrusted samples treatment is connected to the removal of slightly bounded outer corrosion layers. This is clearly visible from Fig. 2. The OH radical intensity (that is produced by reaction of active hydrogen atoms with surface bounded oxygen) increases much faster in the case of incrusted samples. When the slightly bounded oxygen at incrustation layers is removed, the rest of incrustation plays a shielding role and thus the plasma active particles do not interact directly with the corroded surface. Consequently, the OH radical intensity drops down. The sample temperature decreases because the reduction of corrosion products is slower.

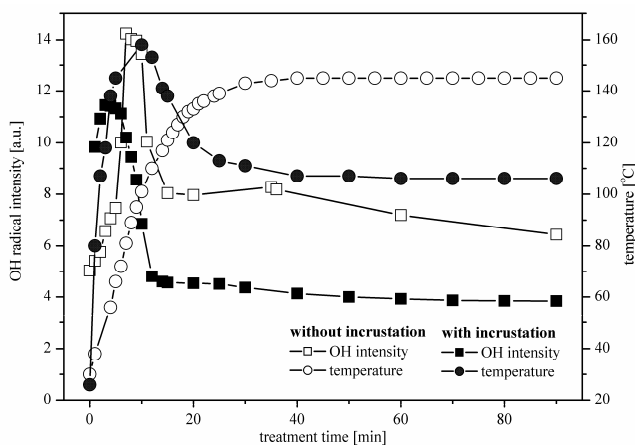


Fig. 2 – Temperature and OH radical intensity during the plasma treatment of iron samples at applied power of 400 W.

Tabel 1

Maximal temperatures of samples without incrustation

Power [W]	Maximal temperature [°C]		
	iron	bronze	brass
100	119	134	139
200	150	164	170
300	173	185	188

Tabel 2

Maximal temperatures of samples with incrustation

Power [W]	Maximal temperature [°C]			
	iron	bronze	brass	copper
100	40	73	142	41
200	97	159	162	179
300	-	153	182	195

3.2. BRASS SAMPLES WITH ALKALINE CORROSION LAYERS

In case of the brass corrosion layers obtained in the alkaline atmosphere, samples without the incrustation had higher temperature than samples with the incrustation (Tabel 3). The opposite behavior was observed for samples corroded in the acidic atmosphere; samples with the incrustation had higher temperature than samples without the incrustation. These different temperatures are caused by different thermal resistance of corrosion layers – each corrosion atmosphere had its own corrosion products. The exothermic character of the plasma active particles reactions with corrosion products differs, too and thus we suppose that the final sample temperature combines either described effects or even some other effect which is unknown up to now.

Tabel 3

Sample maximal temperatures in °C

Discharge power [W]	Alkaline atmosphere		Acidic atmosphere	
	without incrustation	with incrustation	without incrustation	with incrustation
100 W	139	117	112	144
200 W	151	144	142	164
300 W	188	170	158	184
400 W	206	177	170	193

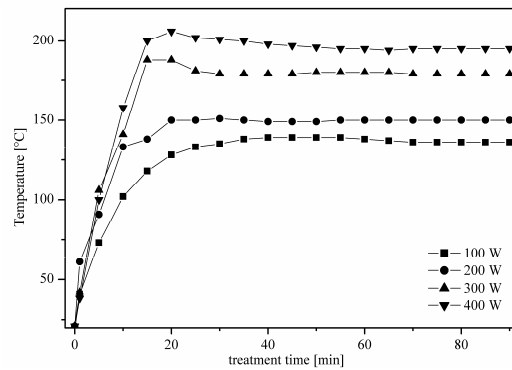


Fig. 3 – Sample temperature evolution during the plasma treatment of alkaline corrosion on brass without incrustation.

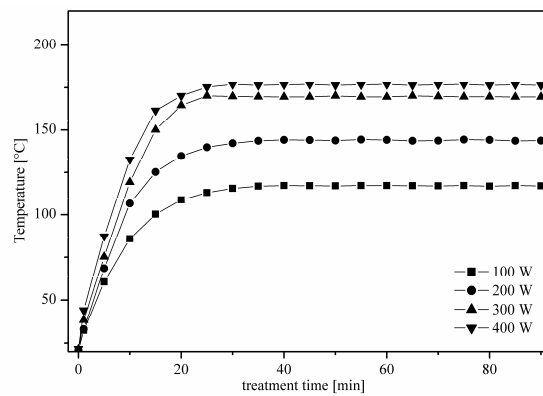


Fig. 4 – Sample temperature evolution during the plasma treatment of alkaline corrosion on brass with incrustation.

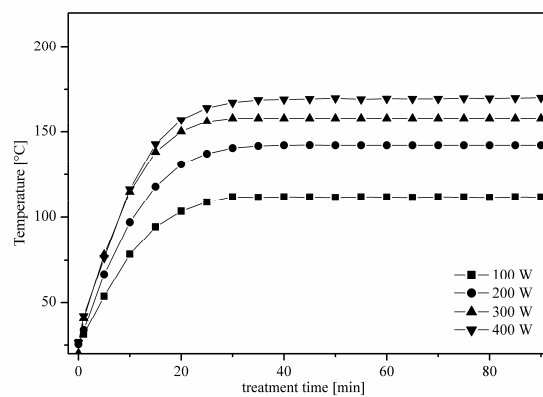


Fig. 5 – Sample temperature evolution during the plasma treatment of acidic corrosion on brass without incrustation.

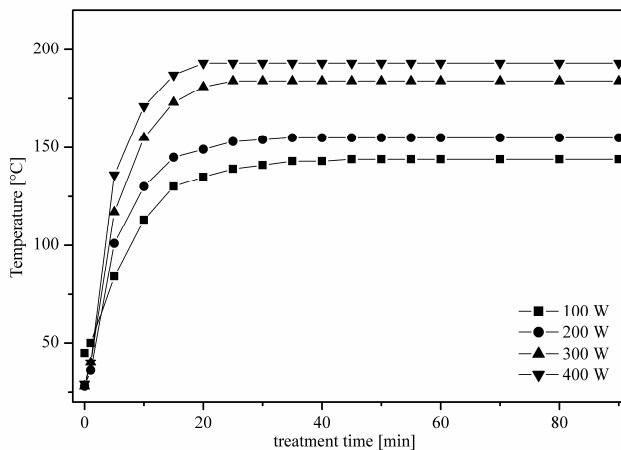


Fig. 6 – Sample temperature evolution during the plasma treatment of acidic corrosion on brass with incrustation.

The optical emission spectra (focused mainly on OH radicals) were taken during the treatment simultaneously with sample temperatures. The relative intensity of OH radicals in the interval of 305–312 nm was calculated (Figs. 7–10). The process is considered to be terminated when the relative intensity of OH radical reaches 10 % of its maximal value or when it is constant [16]. As it can be seen from Figs. 7–10, the intensity of OH radicals increased at the beginning of each process and then decreased again.

In the case of samples corroded in the acidic atmosphere (Fig. 7), the process is very fast and the OH radical presence remains nearly constant after the first 20 minutes of the plasma treatment. This well correlates with the sample temperature that increases rapidly and remains nearly constant after the same treatment time (Fig. 3). The samples covered by corrosion with the incrustation (Fig. 4 and Fig. 8) show the same correlation between OH radical intensities and sample temperatures. The presence of two peaks of the OH relative intensity (Fig. 8) can be explained by a consequence of two processes. The first of them corresponds to the reaction of hydrogen active particles with oxygen bounded in the sandy layer. The second one reflects the reactions with metal (brass) corrosion products.

The correlation between sample temperatures and OH radical intensity is observed also in the case of samples prepared in the ammonia atmosphere. The non-incrusted corrosion removal is much slower in comparison with the samples prepared in the acidic atmosphere because chlorides react with active hydrogen faster than amino compounds. Due to this fact, the maximal sample temperature is also lower than in the case of samples prepared in the acidic environment. OH radical intensity during the treatment of samples covered by the incrustrated corrosion shows only one maximum at the short treatment time that also corresponds to the reaction of hydrogen active particles with oxygen bounded in the sandy layer.

There is no other OH emission maximum because of much slower removal of inner corrosion layers. The maximal temperature of incrustated samples is higher because they are effectively heated during the outer layers reduction (also the temperature increase is faster in comparison with the non-incrustated corrosion) and this elevated temperature is kept for the long time due to very limited thermal conductivity under the low pressure conditions.

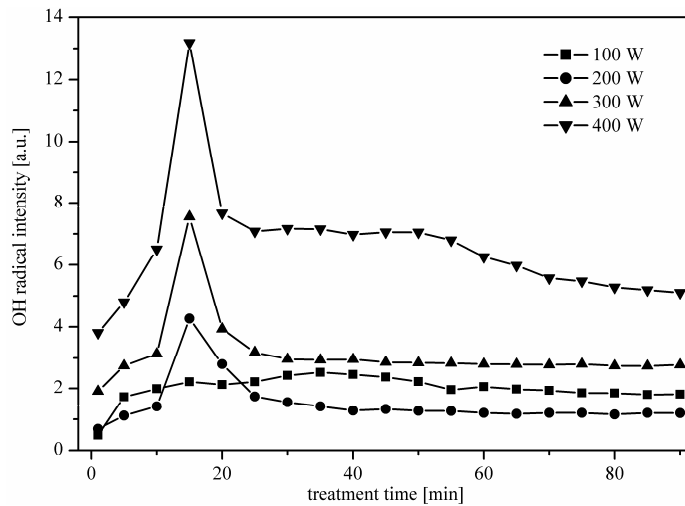


Fig. 7 – Relative intensity of OH radicals during the plasma treatment of alkaline corrosion on brass without incrustation.

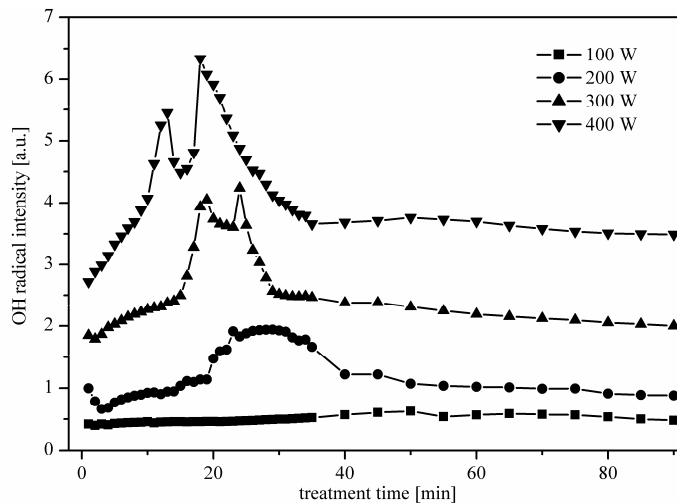


Fig. 8 – Relative intensity of OH radicals during the plasma treatment of alkaline corrosion on brass with incrustation.

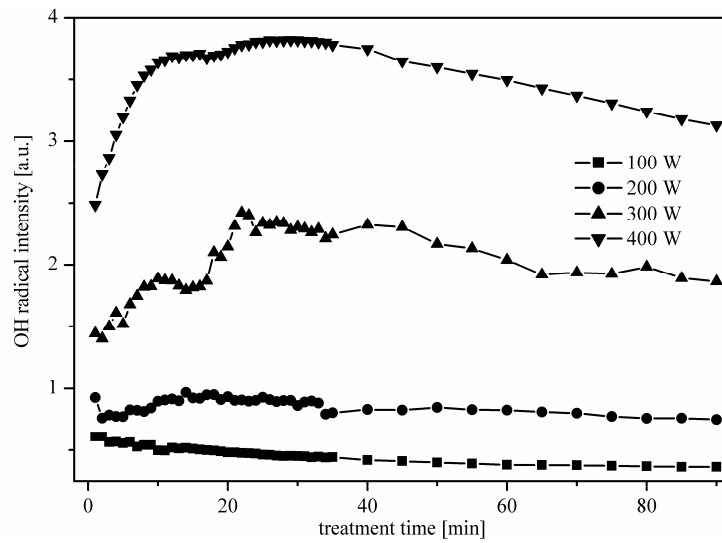


Fig. 9 – Relative intensity of OH radicals during the plasma treatment of acidic corrosion on brass without incrustation.

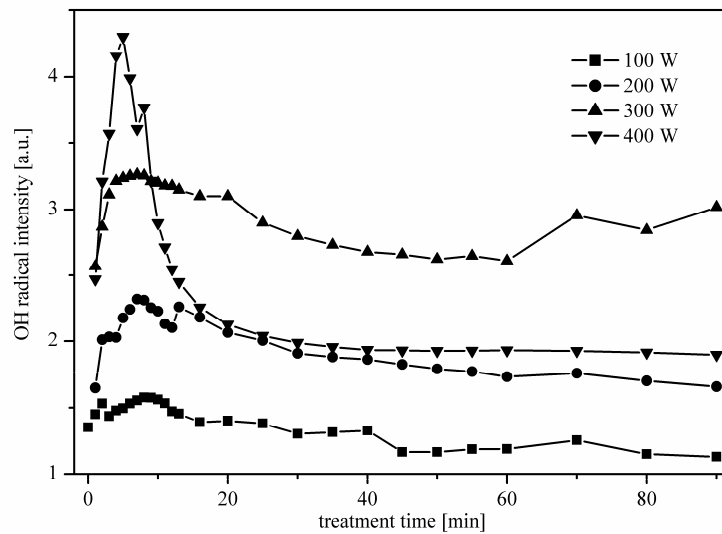


Fig. 10 – Relative intensity of OH radicals during the plasma treatment of acidic corrosion on brass with incrustation.

The OH radical spectra were simultaneously used for the plasma rotation temperature calculation. Rotation temperatures (calculated from obtained emission spectra) were estimated of about 600 K independently on applied power or on the type of the corrosion layer.

3.3. TEMPERATURE DEPENDENCE OF NON-CORRODED BRASS SAMPLE ON ITS SIZE

To separate the influence of exothermic reactions heating from the other processes (plasma particles impact and inductive heating), the set of non-corroded samples of different weight and of almost cubic shape was prepared (see Tab. 4). These samples were treated in plasma under the standard conditions described above (pressure, hydrogen flow) at applied power of 300 W in the continuous regime. Temperature evolution of selected samples is shown in Fig. 11. As it can be seen, the temperature increase is slower if a bigger sample is treated, and the thermal stabilization takes longer time directly proportional to the sample size. Maximal temperatures of these samples are listed in Tab. 4, too and they are plotted as a function of the sample mass in Fig. 12. The sample maximal temperature is directly proportional to the linear size of the sample; deviations are caused by a non-ideally cubic shape of the used samples. Note that sample C is nearly equivalent (by its weight) to the samples presented in section 3.2.

Tabel 4

Maximal temperature of differently sized brass samples without corrosion layer

Sample	A	B	C	D	E	F	G	H
Weight [g]	11	27	40	78	90	293	535	1046
Maximal temperature [°C]	144	141	152	170	173	184	185	201

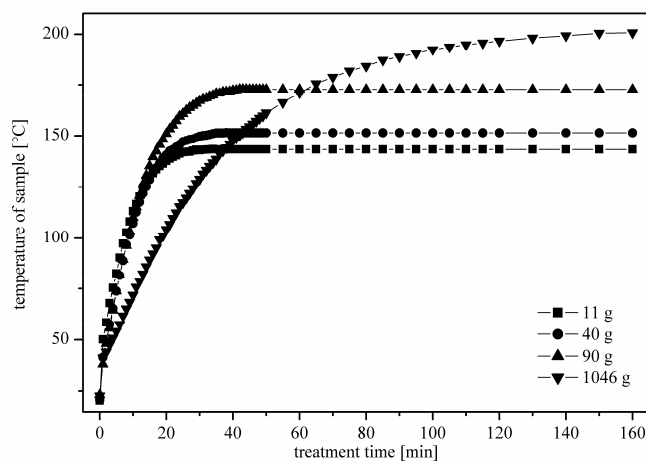


Fig. 11 – Temperature of selected differently sized brass samples without corrosion layer.

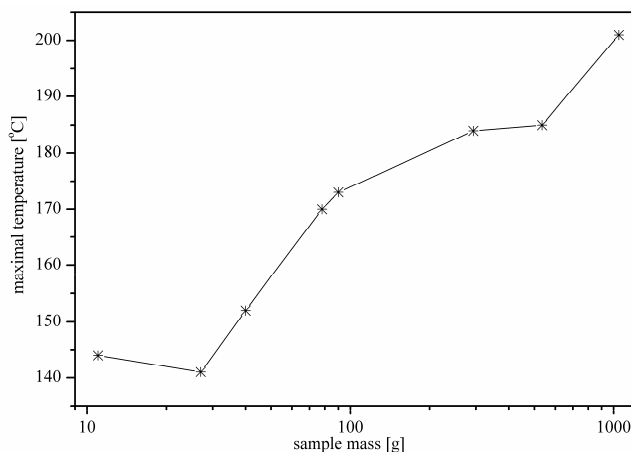


Fig. 12 – Maximal temperature of brass samples without corrosion layer in the dependence on their mass.

4. CONCLUSIONS

Several types of corrosion layers of four metals (iron, copper, bronze and brass) were prepared. These samples were treated by low-pressure low-temperature hydrogen RF plasma. This method can be very important step in the restoration of archaeological artifacts in future.

In the first part, samples of mentioned metals with or without sandy incrustation were treated by plasma at selected applied powers in continuous regime. The maximal temperature of the samples with the incrustation was lower than of samples without incrustation under the same conditions. This difference is due to shielding effect of the incrustation grains, by other words, incrustation decreases the direct interaction of plasma active particles with the corrosion layers.

In the second part, corrosion layers on brass were prepared in acidic or alkaline atmosphere with or without sandy incrustation. The whole process of plasma treatment was monitored by optical emission spectroscopy. Relative intensity of OH radicals and rotational temperature of 600 K were calculated from the obtained data. The sample temperature was monitored by the thermocouple installed directly inside the sample. The correlation between OH radical intensity and sample temperature was observed. The incrustation at samples prepared in chloric acid vapor decreased the maximal temperature due to the shielding effect that decelerates the plasma chemical removal of corrosion layers. On the other hand, in the case of samples prepared in the ammonia atmosphere, the incrustation had an opposite effect due to intense heating of the sample during the reaction with oxygen presented in the outer corrosion layers (mainly at sandy grains).

In the last part, temperature effect on the non-corroded brass samples with different size was monitored. The maximal sample temperature was directly proportional to the linear size (or the third root of weight) of the treated sample.

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