

# Reduction of brass model corrosion layers using low-pressure low-temperature hydrogen plasma

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## Introduction

Plasmachemical reduction of corrosion layers is a relatively new method developed by Stanislav Veprek et al. [1] at Institute of Inorganic Chemistry, University of Zürich at the end of the 20<sup>th</sup> century. It has been broadly applied mainly for iron artifacts because optimal conditions for the corrosion removal of other metals are not known yet [1]. The method 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 [1]. Before Veprek, Daniels used a similar method for plasma reduction of silver tarnish on Daguerreotypes [2]. At the beginning of 21st century, K. Schmidt-Ott and her colleagues tried to treat some iron and silver objects and they were successful [3].

Various methods of corrosion removal are used for very old or valuable artifacts, but they tend to be aggressive or even destructive in use. This means that along with the corrosion some of the base metal is also removed. Some methods can remove surface features of the treated object which could contain 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. 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). Moreover, plasmachemical reduction is one step way of corrosion removal from archaeological artifacts, which removes corrosion layers carefully. Only corrosion layers are removed by this method and the object is retained.

Low-pressure low-temperature hydrogen radiofrequency plasma was used for this experiment. Several types of corrosion layers of brass were prepared. The rusted brass sample was placed into plasmachemical reactor where it was treated by plasma. The whole process was monitored by optical emission spectroscopy. Temperature of the sample was measured, too because it is a very important parameter. Too high temperature can change properties such as metallographic constitution of the object and thus historical information can be lost. In case of brass objects, zinc could be removed from object during the heating even at temperature significantly lower than its melting point.

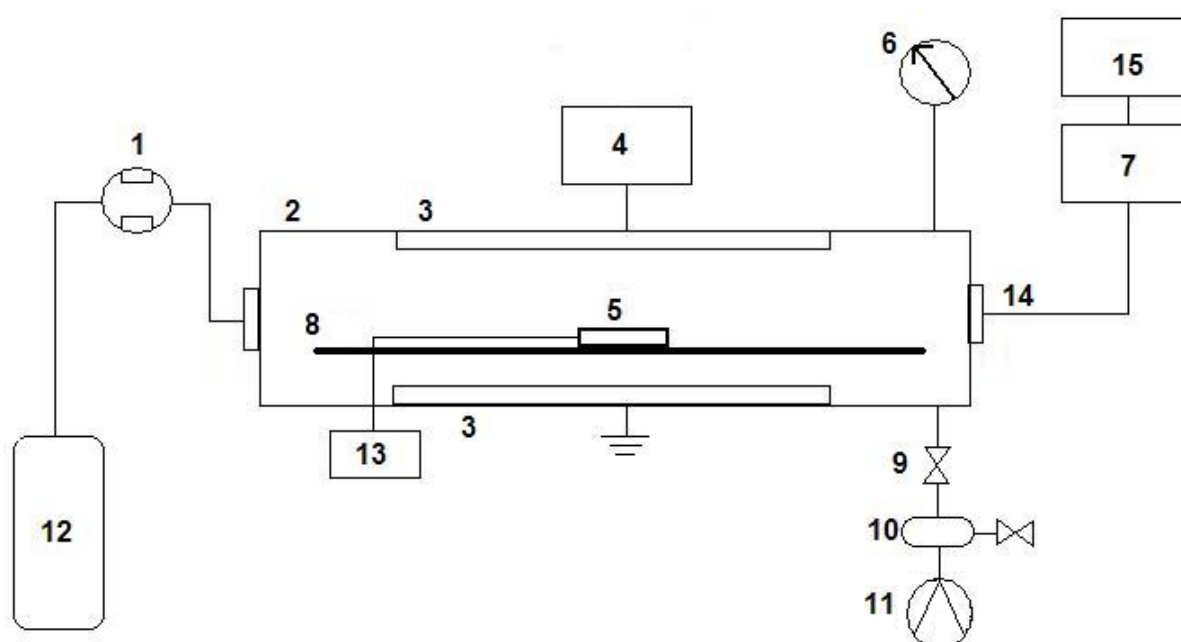
## Experimental set-up

Brass samples (5×1×0.5 cm<sup>3</sup>) were chosen for this study as model samples because it is impossible to obtain a sufficient number of identical originals. Two sets of samples were prepared – samples with a sandy incrustation and without the incrustation. Two corrosion forming atmospheres (alkaline and acidic) were used. Firstly, samples were grinded, after that rinsed in ethanol and dried. Samples were put into desiccator where a Petri dish with chloric acid (acidic atmosphere) or ammonia (alkaline atmosphere) solution was placed at the bottom of desiccators. A half of the samples was additionally covered by sand (*Tab.1*). In all cases, the corrosion layers had been formed for one month.

**Tab.1** Corrosion layer kinds

	Acidic atmosphere	Alkaline atmosphere
Samples with incrustation	4 samples	4 samples
Samples without incrustation	4 samples	4 samples

The plasma treatment of prepared model samples was carried out in a Quartz cylindrical reactor (90 cm long and 9.5 cm in the inner diameter). The reactor (*Fig. 1*) was surrounded by two external copper electrodes supplied by a radio-frequency generator (13.56 MHz) through an automatic matching network. The experiment took place in pure hydrogen at pressure of 150 Pa and constant hydrogen flow rate of 50 sccm. Samples were treated at different plasma power of 100 W, 200 W, 300 W and 400 W in a continuous mode. The treatment duration was up to 120 minutes.



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

The plasmachemical process was monitored by optical emission spectroscopy. An optical fiber was placed at a quartz window of plasma reactor. Data obtained from this method were used to calculate rotational temperatures and integral intensities of OH radicals that were used for the process monitoring according to the procedure described in [4]. Temperature of the sample during the treatment was measured by a thermocouple installed inside the sample 5 mm in its metallic body. To avoid electromagnetic induction influence on the measured temperature, the temperature values were read out at the end of a 5 s discharge break.

During the plasmachemical reduction, hydrogen ions, radicals and excited molecules react with oxygen and chlorine from corrosion layers (corrosion layers are mainly formed by oxides and chlorides). OH radicals and HCl molecules are formed by these reactions. The OH radicals were monitored by the optical emission

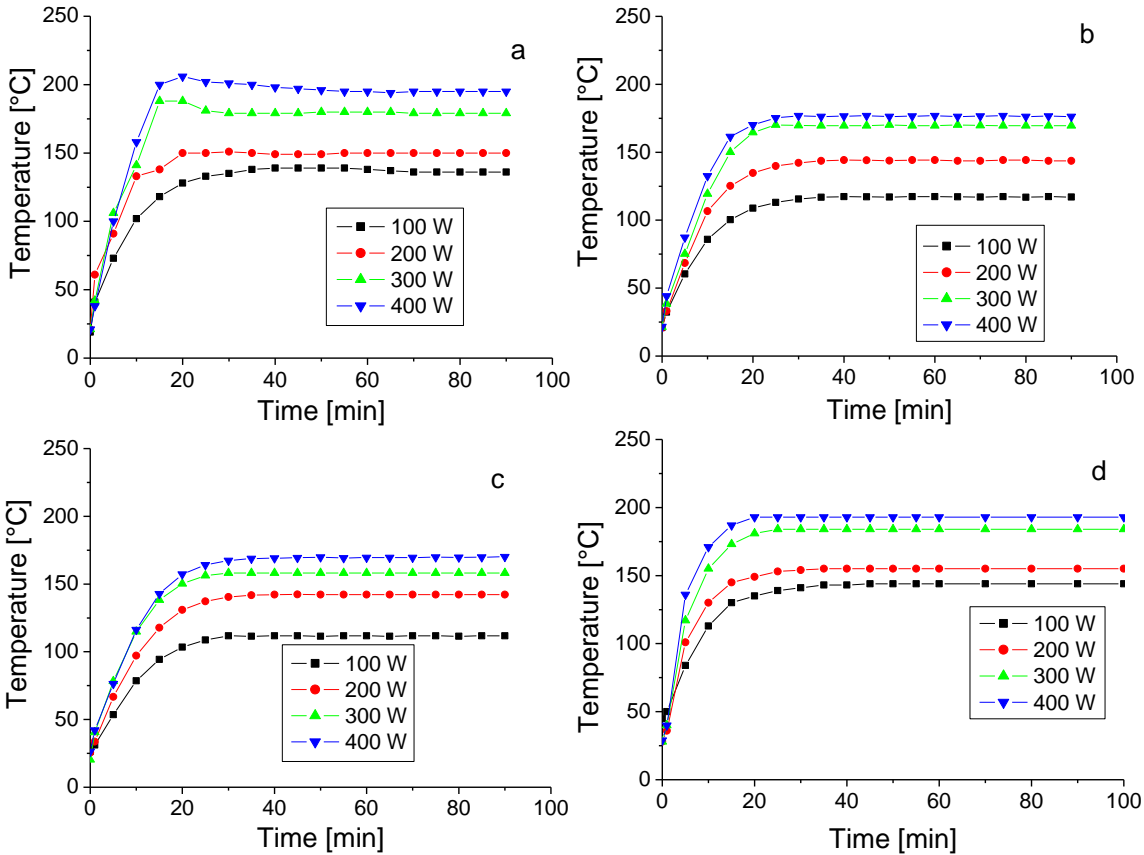
spectroscopy. The HCl presence can be directly confirmed by IR absorption spectroscopy or indirectly by a consequent corrosion downstream of the discharge.

**Results and discussion**

Sample temperature was increasing during the first 30 minutes, after that it remained constant (see Fig. 2). As it was expected, samples treated at the plasma power of 400 W reached the highest temperature (see Tab. 2). In case of corrosion layers obtained in the alkaline atmosphere, samples without the incrustation had higher temperature than samples with the incrustation. 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 could be caused by different thermal resistance of corrosion layers – each corrosion atmosphere had its own corrosion products.

**Tab.2** 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

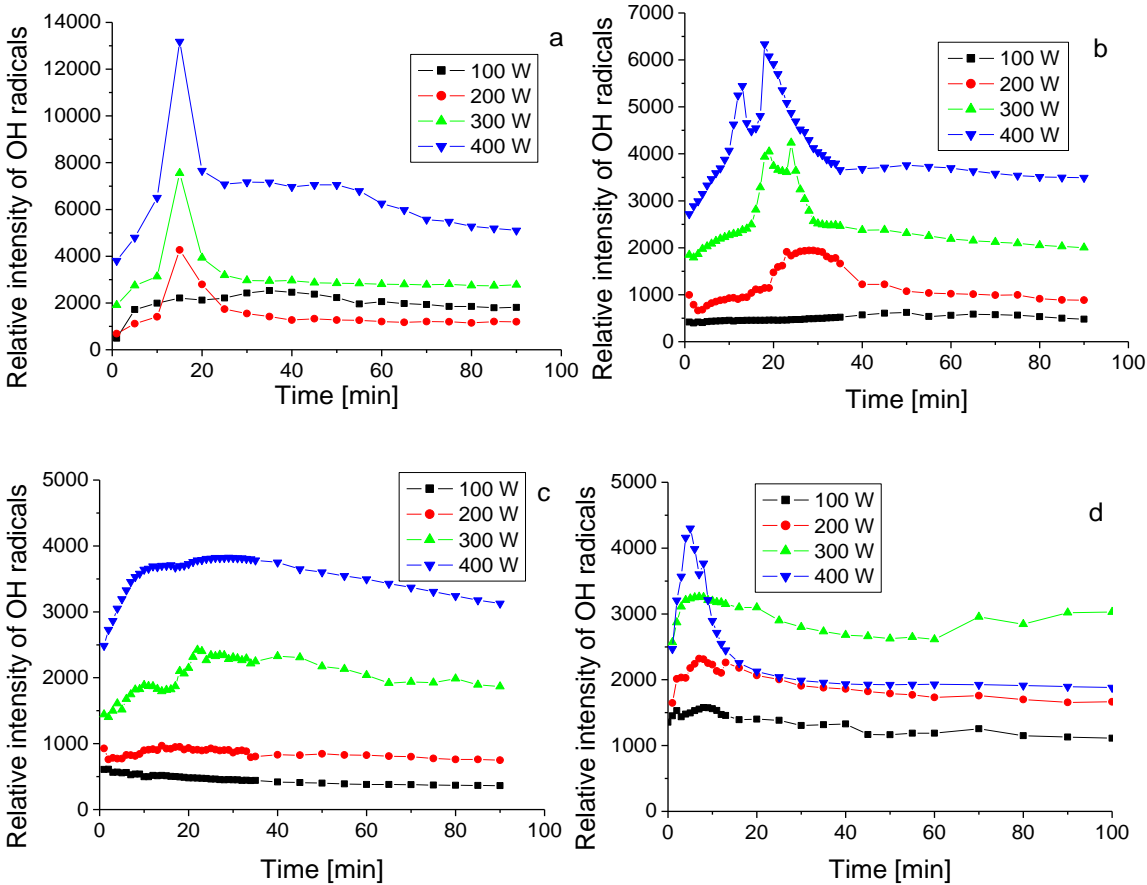


**Fig. 2** Sample temperature evolution during the plasma treatment of alkaline corrosion without incrustation (a); alkaline corrosion with incrustation (b); acidic corrosion without incrustation (c); acidic corrosion with incrustation (d)

The plasmachemical treatment process was monitored by optical emission spectroscopy. From the acquired spectra, the relative intensity of OH radicals was calculated (see Fig.3). 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 [4]. The maximal values of the relative OH radical intensity are presented in Tab.3. In case of samples with the incrustation, there are two dominant peaks of the relative intensity of OH radical (see Fig.3b and Fig. 3d). 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 corrosion products.

**Tab.3** Maximal relative intensities of OH radicals in cts obtained during the samples treatment

Discharge power [W]	Alkaline atmosphere		Acidic atmosphere	
	without incrustation	with incrustation	without incrustation	with incrustation
100 W	2500	600	600	1600
200 W	4300	1900	1000	2300
300 W	7600	4200	2400	3300
400 W	13200	6300	3800	4100



**Fig. 3** Relative intensity of OH radicals during the plasma treatment of alkaline corrosion without incrustation (a); alkaline corrosion with incrustation (b); acidic corrosion without incrustation (c); acidic corrosion with incrustation (d)

At the beginning of each process, intensity of OH radicals increased and then decreased again. Temperature of the sample increased at the beginning of the process (up to about 30 minutes) and then it remained constant. During the treatment of samples prepared in the alkaline atmosphere, higher relative intensities of OH radicals were obtained for samples without the incrustation. But the opposite behavior was observed in case of samples prepared in the acidic atmosphere.

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

## Conclusion

Corrosion layers on brass were prepared in two atmospheres (alkaline and acidic) and with/without the sandy incrustation. These samples were treated in the low-pressure low-temperature flowing hydrogen plasma. The whole process was monitored by optical emission spectroscopy. Relative intensity of OH radicals and rotational temperature of plasma were calculated from the obtained data. At the beginning, relative intensity of OH radicals increased, and after several minutes it decreased accordingly to our previous works. Rotational temperature was about 600 K independently on the treated sample or applied power. The sample temperature was monitored by the thermocouple installed directly inside the sample. Sample temperature increased at the beginning (for the first 30 minutes) and after that temperature remained constant. In case of alkaline atmosphere, the samples without the incrustation had higher temperature than the samples with the incrustation. The opposite behavior was observed for the samples corroded in the acidic atmosphere; the samples with the incrustation had higher temperature than the samples without the incrustation.

## References

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