APPLICATION OF LOW TEMPERATURE PLASMAS FOR THE TREATMENT OF ANCIENT ARCHAEOLOGICAL OBJECTS

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Abstract. The plasma chemical removal of the corrosion layers from archaeological artifacts by RF hydrogen low pressure plasma is a relatively new technique discovered at mid 80's. Because each object is original with the unique composition of corrosion layers as well corrosion history the model corroded samples were used for the presented study. The different duty cycles were applied to keep low temperature of samples. The second plasma application in the conservation is deposition of thin layers protecting the objects from the secondary corrosion. The organosilicone and parylene thin films were applied.

1. INTRODUCTION

Reduction of corrosion layers using hydrogen plasma is a relatively new method, which should be used for conservation and restoration of archaeological artifacts. The conservation of artifacts represents a serious problem because of post-corrosion which occurs after excavation [1]. At the first, Daniels used a glow discharge in hydrogen gas to reduce silver tarnish back to silver [2]. He used it for Daguerreotype too, and his process was successful [2]. The method of plasma treatment for metallic artifacts was developed at the end of the 20 century at Institute of Inorganic Chemistry, University of Zürich. The method was successfully applied to the treatment of more than 13 000 historical objects from various periods (400 B.C. until 19th Century) and places of excavation [3]. This technology is used mainly for iron objects, because the optimal conditions for the corrosion removal of other metals are not known yet [3].

Because each archaeological object is original with the unique composition of corrosion layers as well corrosion history it is necessary to study the influence of processes and discharge conditions using the model corroded samples. Samples of the most frequent ancient metallic materials (iron, bronze, copper, brass) were prepared usings anorganic acid vapors (HCl, ammonia) or by dipping into the acid solution (H_2SO_4, HNO_3) and after that they were stored in dessicator for 2-4 weeks. The longer time storage was realized in in polyethylene ziplock bags up to application of plasma.

2. EXPERIMENTAL

The corrosion removal is realized by low pressure RF hydrogen plasma where different duty cycles are applied to keep low temperature of samples. The treatment was carried out in a Quartz cylindrical reactor (length 90 cm, i.d. 9.5 cm). Radio-frequency electric field (13.56 MHz) was applied by two external copper electrodes using automatic matching network and capacitively coupled RF discharge was generated. The reactive hydrogen particles (atoms, ions, molecules) were formed in plasma and reacted with the corrosive layer containing oxygen. This reaction leads to sputtering of corrosion layer and creates the OH radical, which emitts light in the region of 305–320 nm that is used as process monitoring quantity [4], example of results is given in Fig. 1. The data were not recalculated with respect to the discharge on time.

3. RESULTS

Rotational temperatures and integral intensity of OH radicals were determined from obtained data. The sample temperature was measured by thermocouple installed inside the sample volume. Temperature was readed out when discharge was stopped for 5 s to eliminate RF field influence on this measurement. The corroded samples were usually less warm in pulsed mode than in continuous mode (see at Figure 2). The sample temperature is one of the critical treatment parameters because elevated temperatures (even over about 120°C depending on material) can initiate the metallographic or composition changes in objects.

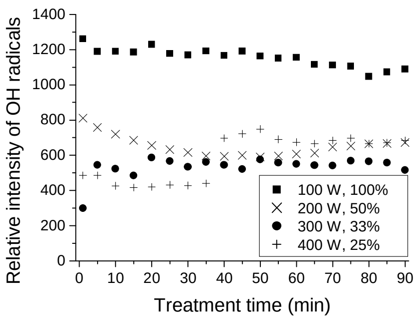

Figure 1: Relative intensity of OH radicals (brass, ammonia atmosphere).

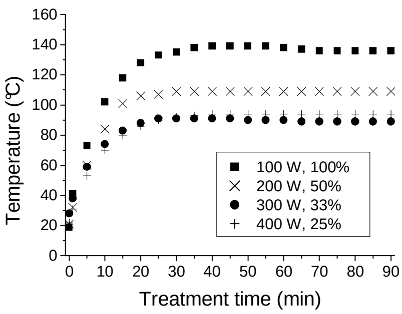

Figure 2: Temperature of samples during treatment (brass, ammonia atmosphere).

XRD pattern has shown that the corrosion layer in case of brass corroded in ammoniac atmosphere was formed by zinc chloride hydroxide (ZnOHCl), ammonium chloride (NH_4Cl) and zinc hydroxyl chloride hydrate ($Zn_5(OH)_8Cl_2 \cdot H_2O$). The corrosion layer was redish brown with black crystals on the surface. The same compounds were observed after the plasma treatment, but their abudance was different and the samples color was brown with white cover on the surface.

After the plasma chemical corrosion layers removal, the surface is highly reactive and inclines to secondary oxidation. To prevent this process, it is necessary to protect the surface with a barrier film preventing the penetration of oxygen a humudity (as well as the other corrosion agents) to the surface.

We tested possibilities of the archaeological artefacts model samples protection by a thin film deposition of SiO_x and Parylene (poly-para-xylylene) thin films. Parylene coatings are chemically inert, conformal and transparent with excellent barrier properties [5] but relatively small adhesion. These all properties determine parylene to be a perfect material for protection of archaeological artefacts. Parylene coatings are prepared by the standard chemical vapor deposition (CVD) method [6]. SiO_2-like high density films were prepared by PECVD in a low pressure reactor with capacitively coupled plasma discharge (13.56 MHz). Mixture of Hexamethyldisiloxane with oxygen was used as a precursor of plasmachemical reactions.

The coatings were characterized by various methods in order to obtain information about their thickness (ellipsometry), chemical structure (FTIR) and elemental composition (XPS), surface morphology (LCSM, SEM) and barrier properties (OTR) - examples of results see in Figs. 3 and 4. To verify applicability of our prepared thin protective layers, the standard corrosion tests were performed. Example of such test is shown in Fig. 5 where standard protected brass samples (protected by Paraloid B44 varnish) and parylene coated samples were exposed in salt chamber according to the ISO 9227 norm.

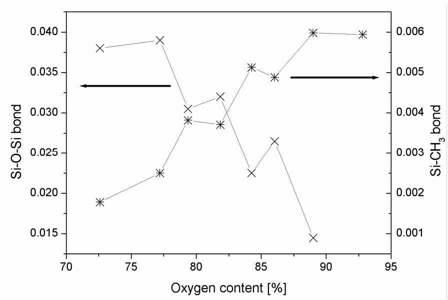

Figure 3: Content of Si-O and $Si\text{-}CH_3$ in dependence on oxygen content in $HMDSO\text{-}O_2$ reacting gas mixture.

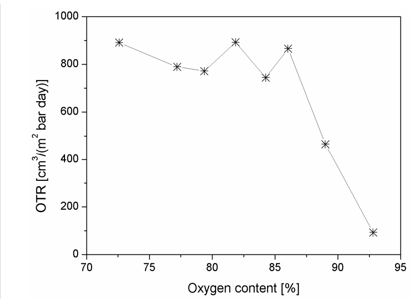

Figure 4: Oxygen transmission rate on SiO_x thin films (substrate has value of about 600).

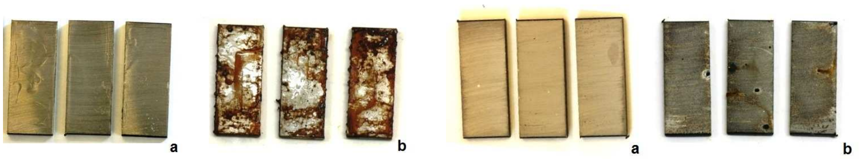

Figure 5 Comparison of classically protected brass samples (left) and parylene coated samples (right) before (a) and after (b) 300 hours test in salt chamber.

4. CONCLUSION

The presented contribution clearly demonstrated the applicability of pulsed RF hydrogen plasma for the removal of surface corrosion from ancient archaeological objects. The decrease of the mean applied energy led to the significant decrease of the samples temperature, on the other hand the plasma process was nearly the same effective at all cases. This result is very important mainly for the treatment of temperature sensitive objects made from bronze or for objects with broken structure (neerly fully corroded objects). The application of both SiO_x and parylene thin films showed very good barriere properties in contrary with classical conservation procedure. The possibility to protect more objects at the same time is the main advantage of their application but their removal must be studied because all protecting procedures must be reversible.

Acknowledgements

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