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Cleaning of iron archaeological artefacts by cascaded arc plasma treatment

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Abstract

An effective and fast way of restoration and preservation of archaeological artefacts is described. In this method a high intensity atomic hydrogen source plasma is used which expands in a low pressure treatment vessel. By nuclear techniques the removal of chlorine and the reduction of oxides to stable forms is monitored. It proves that both hydrogen atom reduction and thermal decomposition are important. In trial experiments with artefacts from a shipwreck followed by post-treatment a successful preservation has been shown. Also the removal of the dirt crust of the excavated artefacts was greatly facilitated in the treatment.

Keywords: Plasma cleaning; Archaeological artefacts; Expanding thermal plasma

1. Introduction

Two problems are encountered in the conservation of iron archaeological artefacts. The first problem concerns encrustation, a hard agglomerate layer that covers the artefact, consisting of soil and migrated oxides. The second is to prohibit any further corrosion. It has been argued in an earlier paper [1] that hydrogen plasma treatment of the artefacts is very effective for overcoming both problems. A short exposure (about 10 min) to a hydrogen plasma loosens the encrustation from the artefact and it can be removed with a simple tool like a scalpel. Compared with conventional techniques such as sanding there is a huge time advantage. Also finer surface details can be preserved.

The second problem, to stop post-corrosion of the artefact, is strongly related to chlorine contamination on the artefact, which catalyses the corrosion process [2]. The removal of chlorine from corrosion layers is the subject of this paper.

2. Plasma machine

The plasma machine is depicted in Fig. 1. The plasma is generated in a cascaded arc source under near-thermal conditions and expands at the anode size of the source through a nozzle into the vacuum chamber. Downstream

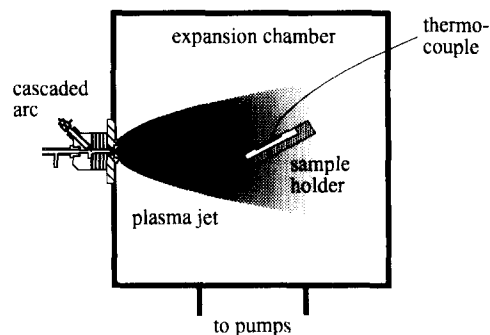


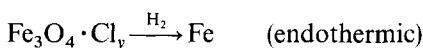
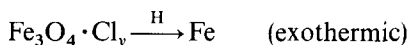
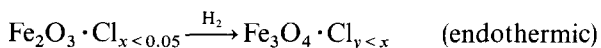
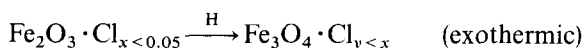
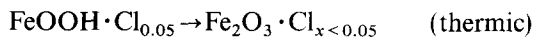
Fig. 1. The plasma machine, consisting of the cascaded arc plasma source and a low pressure chamber in which the sample holder was placed.

of the beam that emanates from this nozzle, the sample holder is placed. A detailed description of the set-up can be found in [3].

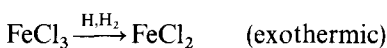
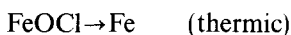
3. Reduction of chlorides

A definite description of the corrosion layer including all compounds in which chlorine can be bound and processes that result in chlorine removal is not available at present. However, akageneite or β -FeOOH.Cl_{0.02–0.05} is generally considered to play a key role in post-corrosion of artefacts [2,4,5]. The reduction of

akageneite in a hydrogen plasma can involve a number of reactions:



with possible intermediate compounds



As there is no definite answer to which structures are obtained after dehydration of akageneite, various options are given. The reduction of FeCl_3 to FeCl_2 is exothermic for both atomic and molecular hydrogen. The reduction of FeCl_2 is strongly endothermic with molecular hydrogen and therefore requires atomic hydrogen.

In addition to reducing reactions involving hydrogen, thermal decomposition of chlorides is also possible. FeOCl , a possible intermediate product in the decay of akageneite, decomposes thermally to FeCl_3 . At temperatures above 350°C FeCl_3 evaporates. The reduction of chlorine from a corrosion layer can therefore occur both thermally and by chemical processes.

4. Results

The effect of the plasma treatment was investigated using proton induced X-ray emission (PIXE). The PIXE measurements were taken with 3 MeV protons from the EUT AVF cyclotron. X-rays were detected with a 30 mm^2 Si(Li) detector (Canberra, energy resolution 165 eV) positioned at an angle of 165° with respect to the direction of the incoming beam. The Cl concentration was calculated with the PANEUT computer code which amongst others accounts for X-ray absorption along the outgoing path [6]. For this nuclear analysis technique, the samples must be smaller than $3 \times 3\text{ cm}^2$ and have a thickness of less than 3 mm. Therefore we used substitute artefacts, platelets cut from contemporary steel containing predominantly akageneite, for analysis. As the chlorine that is hosted in akageneite is the most problematic to remove, a method capable of removing chlorine from

platelets is expected to be successful on real artefacts too. Results of the treatment of real artefacts will be described in a forthcoming paper.

The PIXE spectra in Figs. 2 and 3 show the composition of the top $10\ \mu\text{m}$ of an untreated and a plasma treated standard platelet. The plasma settings for the latter were 10% H_2 in a total Ar– H_2 flow of 3.5 standard l min^{-1} , arc current 70 A, and reactor pressure 2 mbar. The temperature at the surface of the platelet was measured to be 560°C . This temperature was measured with a thermocouple mounted on the surface of the samples. At these settings the best results so far on chlorine reduction were found. The chlorine peak in the spectrum of the untreated platelet corresponds to a chloride to iron ratio of 5:100. This corresponds to the composition of akageneite. In the spectrum of the treated platelet the Cl peak has disappeared; this corresponds to a Cl fraction of less than 10^{-5} . Fig. 4(a) shows the chlorine reduction vs. treatment temperature for a series of standard type platelets. In this series the platelets were mounted on a heated sample holder at an angle of 60° with respect to the plasma beam in the centre of the reactor. This was done to prevent stagnation of the plasma beam in front of the samples. The total gas flow was kept at 3.5 standard l min^{-1} in all treatments, and the reactor pressure was held constant at 0.45 ± 0.05 mbar. The discharge current was varied from 30 to 70 A and the hydrogen fraction of the total flow from 0% to 100%. The treatment temperature is the temperature measured on the platelet at the end of the plasma treatment. The temperature generally rises slowly to its end value, which is reached within 10–15 min. Data points that correspond to a treatment temperature below 410°C did not have additional heating from the sample holder. These platelets were treated for 20 min. Data points that correspond to temperatures above 410°C had preheating with the sample holder. The plasma treatment time after preheating was 10 min. The residual chlorine fraction decreases with increasing treatment temperature. Furthermore, at the same temperature better chlorine removal is obtained in a hydrogen plasma than in an argon plasma. There is no apparent correlation between the seeded hydrogen fraction and chlorine removal in hydrogen-containing plasmas, Fig. 4(b). This can indicate that already at a seeding fraction of 5% hydrogen in the plasma hydrogen is abundant. In a previous paper another explanation is argued [1]: the relation between the hydrogen fraction seeded in the source and the atomic hydrogen fraction downstream the plasma beam is not clear. Especially at a high hydrogen fraction, recirculating (molecular) background gas is mixed into the plasma beam and lowers the dissociation degree drastically. The inaccuracy in the figures is determined by the inaccuracy in the peak area determination in the PIXE spectrum. The standard deviation in this determination is about 15%.

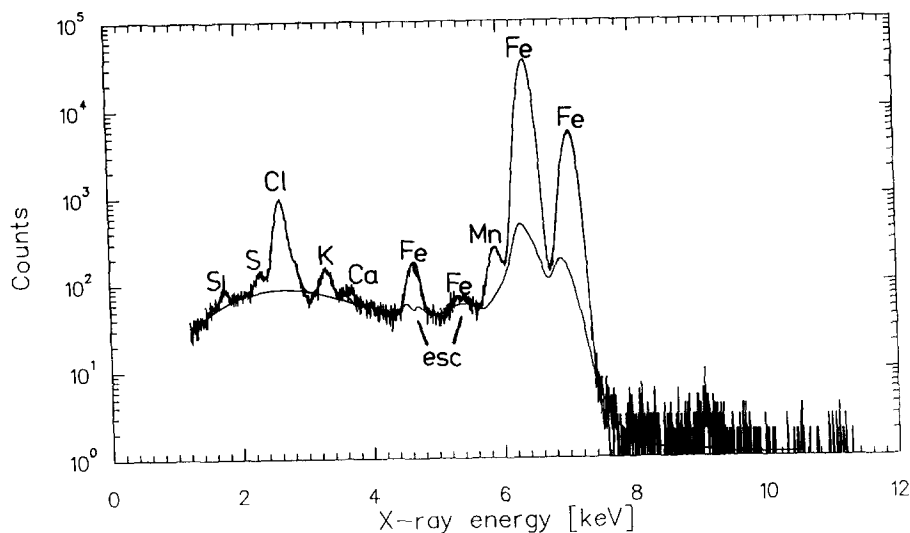


Fig. 2. PIXE spectrum of an untreated standard type platelet. A strong Cl peak is observed in the spectrum. The iron-to-chlorine ratio determined from this spectrum is 1:0.05. This is the stoichiometry of Cl saturated akageneite, $\text{FeOOH}\cdot\text{Cl}_{0.05}$. The lower curve in the figure represents a background fit.

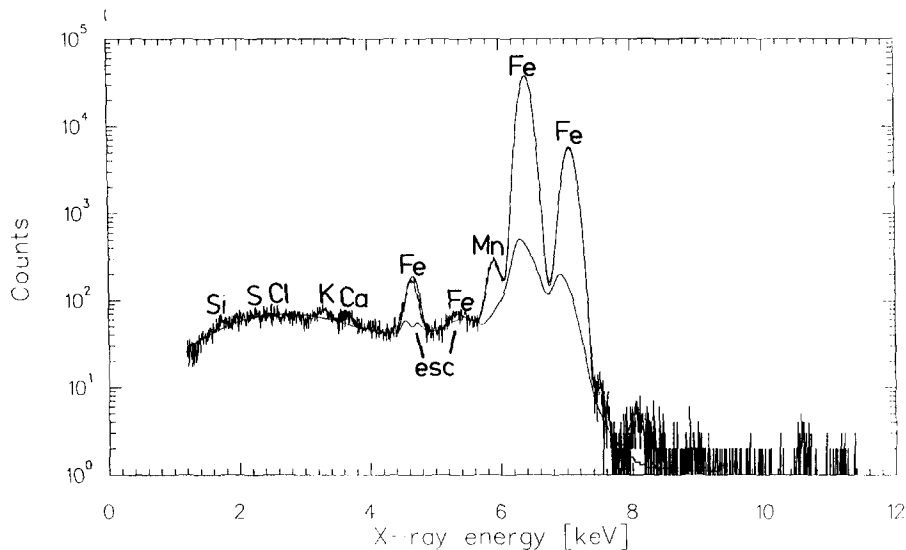


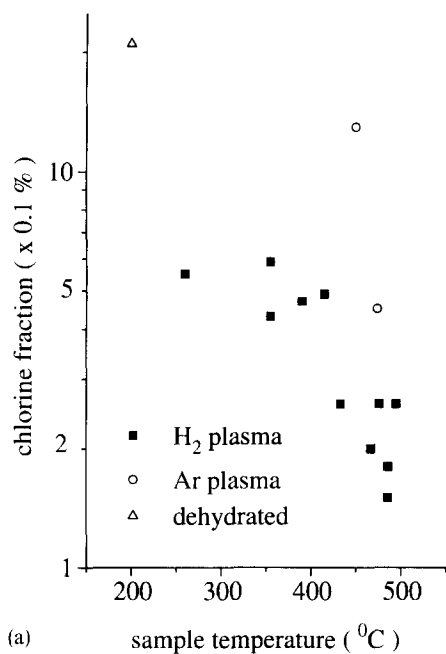
Fig. 3. PIXE spectrum of a standard type platelet after 20 min plasma treatment. The Cl peak has disappeared from the spectrum.

5. Discussion

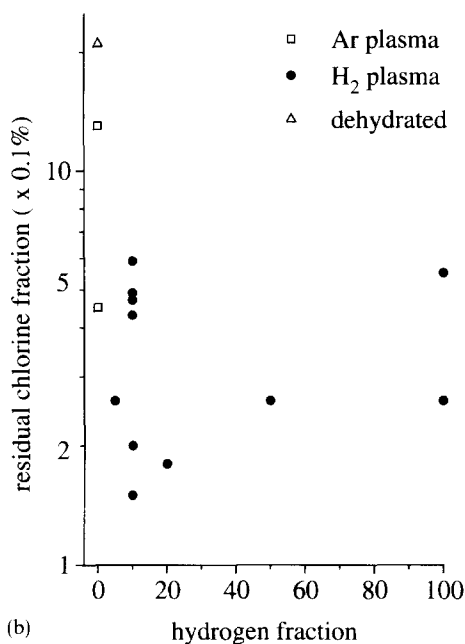
The removal of chlorine is dependent on the sample temperature. The picture that arises from the PIXE data on treated samples is that chlorine removal is better in a hydrogen-containing plasma than in an argon plasma or a vacuum oven for similar treatment temperature and duration.

What residual chlorine concentration is acceptable for long-term conservation? There is no clear answer to this question yet. The way the chlorine is distributed over the artefact and the chemical form are important factors. Sjøgren and Buchwald [5] have observed chlorine infections in test chambers when the local chlorine concentration relative to iron was 0.8%. Below this

value the artefacts are considered to be safe. For argon plasma or heat treated samples this is critical; hydrogen plasma treated samples generally have residual chlorine concentrations below this value. An exceptional reduction is found for samples treated at high temperatures (above 550 °C) in a hydrogen plasma. Under these conditions removal of chlorines to below the detection limit of PIXE (100 ppm relative to iron) was achieved. These conditions also yielded almost full oxide reduction [7]. As a treatment at equally high or higher temperatures in an argon plasma did not yield full removal, it is likely that full chlorine removal demands oxide reduction as well. This could mean that the oxide lattice structure has to be dismantled before all the chlorine can be removed. However, on many artefacts under the



(a)



(b)

incrustation a corrosion layer several millimetres thick is found, which has to be preserved. As full chlorine removal over the full corrosion layer demands a change in the crystalline structure of this layer, damage may not be avoided. A better strategy may be therefore to apply limited chlorine removal, to a value below the above mentioned 0.8%, followed by a post-treatment that covers the artefacts with an anti-corrosion layer.

A final remark is made on the treatment time of artefacts. In the Eindhoven machine the pretreatment time needed to facilitate removal of the incrustation is 10 min. The chlorine removal takes another 20 min. This is even more favourable than the fastest alternative so far, the Vepřek method [8], with a total time including post-treatment of 20–24 h, while more conventional chemical methods such as the alkalide sulphite treatment take months of treatment time.

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Fig. 4. (a) Chloride content in standard platelets as a function of temperature. All platelets were treated at approximately the same pressure (0.4–0.5 mbar) and were mounted on a heated sample holder. (b) The same data as in (a) but now plotted as a function of the hydrogen fraction seeded to the plasma.