Journal of Cultural Heritage xxx (2017) xxx–xxx

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Original article

# Reclaiming the image of daguerreotypes: Characterization of the corroded surface before and after atmospheric plasma treatment

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ARTICLE INFO

*Article history:*
Received 18 January 2016
Accepted 17 May 2017
Available online xxx

*Keywords:*
Daguerreotype
Afterglow plasma
Ag-Cu-S corrosion products
Advanced TEM
Super EDX
XAFS

ABSTRACT

Technological developments such as atmospheric plasma jets for industry can be adapted for the conservation of cultural heritage. This application might offer a potential method for the removal or transformation of the corrosion on historical photographs. We focus on daguerreotypes and present an in-depth study of the induced changes by a multi-analytical approach using optical microscopy, scanning electron microscopy, different types of transmission electron microscopy and X-ray absorption fine structure. The $H_2$-He afterglow removes S from an $Ag_2S$ or $Cu_2S$ layer which results in a nano-layer of metallic Ag or Cu on top of the deteriorated microstructure. In case the corrosion layer is composed of Cu-Ag-S compounds, our proposed setup can be used to partially remove the corrosion. These alterations of the corrosion results in an improvement in the readability of the photographic image.


## 1. Research aims and introduction

In the field of conservation there is a continuous challenge to develop new and sustainable treatments, which have no or a minimal impact on the microstructure of the object. Non-thermal remote atmospheric plasma cleaning might be a possible alternative to currently used methodologies. This study investigates the effect of an afterglow generated by atmospheric plasma on the corrosion and deteriorated microstructure of historical photographs.

The daguerreotype, developed by Louis Jacques-Mandé Daguerre, represents the starting era of photography. The image can be seen when light is scattered from clusters of nanoparticles situated on a polished Ag layer on top of a Cu substrate [1]. Due to the fragile surface, daguerreotypes are often presented in protective frames, or cases (Fig. 1A). Previous studies on the deterioration mechanisms of these photographs demonstrated that the, often unknown, history of the object and different storage environments can lead to different types of degradation [1]. However, general observations on the daguerreotype and the efficiency and selectivity of the treatment can still be made. In this investigation plasma treatments, have been performed on 2 different historical daguerreotypes with different types of degradation: (1) the portrait of a women in case 1 (Fig. 1A) shows yellow areas that roughly follows the structure of the drapery; and (2) the portrait of the man (case 2) in Fig. 1B, this daguerreotype has the typical rainbow colours around the edge and a brownish haze in the centre.

There are several reasons why a conservator-restorer decides to remove the corrosion products from the surface of a daguerreotype. In case he/she has decided to perform a cleaning treatment, he or she should select the most appropriate method. The choice of treatment method is influenced by many factors; it should be selective, dry, and non-invasive while the results must be predictable without changing the original and deteriorated microstructure of the object [2]. Several types of treatments were used throughout the years. The first methods were based on immersing the plate in chemical solutions. Although they resulted in the removal of the corrosion, both the cyanide as well as the thiourea treatment

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http://dx.doi.org/10.1016/j.culher.2017.05.008
1296-2074/


**Fig. 1.** A. Daguerreotype of a women presented in a case with yellow areas (case 1). B. Daguerreotype of a man that turned brownish in the centre and has the typical rainbow colours around the edge (case 2). The white rectangles denote the position where samples have been removed for TEM analysis; TEM 1 is the position of the TEM lamella of the blue colour and TEM 2 is the position of the TEM lamella of the orange-brown colour.

caused alterations to the surface properties resulting in an image that appeared faded and introduced compounds, which lead to new degradation [1,3]. Low-pressure plasma and laser cleaning were introduced as alternative methods, however with limited success. Although the corrosion was removed, sputtering by the collision of ions against the original surface of the daguerreotype resulted in a permanent matting effect [1,4–7]. Electrolytic cleaning is another possible treatment method but this technique is limited to objects that are gilded and have not been coloured with water-soluble paints [1,8].

Recently, the use of non-thermal remote atmospheric plasma cleaning was presented as a new method to selectively remove corrosion [9–11]. The concept of the remote plasma treatment is that gas flows through the source where the plasma is created and which then exits through a nozzle and indirectly treats the surface in the afterglow [12]. This means that the highly reactive species such as ions, which were the main cause of the non-selective physical etching of the surface by low-pressure plasmas, are no longer present in the interaction volume [13]. The method also reduces the risk of damage during treatment since there is no mechanical contact with the fragile surface. Additionally, plasma cleaning is an eco-sustainable and healthier "greener" method when compared to conventional conservation-restoration techniques based on chemical solutions. Hence, the method overcomes several of the disadvantages compared to traditional treatments [12]. However, it is still unclear how the chemical etching of the afterglow affects the aged daguerreotype. In this study, the induced changes are characterized through optical, micro-structural and chemical analysis. We evaluated the plasma cleaning at 3 different levels. At the mm-level, visual and statistical analysis has been applied on the photographic image itself. At the μm-level, microstructure and chemical composition was studied by means of scanning electron microscopy coupled to an Energy Dispersive X-ray detector (SEM-EDX) while chemical speciation was determined with X-ray absorption fine structure (XAFS) at the synchrotron facility ESRF. At the nm-level, nanostructure and chemical composition was studied with different types of Transmission Electron Microscopy (TEM). These techniques are described in more detail in the next paragraph.

## 2. Experimental

Two daguerreotypes from the 19th Century were used for this study. The first daguerreotype, case 1, is a portrait of a female presented in an Anglo-American housing system (Fig. 1A). The plate shows an overall yellow sheen with a thick corrosion layer along the edges of the plate. The second daguerreotype, case 2, is a portrait of a man presented in a European housing system (Fig. 1B). The plate shows corrosion along the edges of the passe-partout and which can be recognised as interference colours. Visually, it is not clear if the daguerreotypes have been gilded.

A dielectric barrier discharge commercial plasma jet, type Plasma Spot® [14], was used for the experiments. The power was set to 120 W with a gas flow of 90 slm (standard litre per minute). The nozzle of the torch has a circular opening with a diameter of 10 mm. Inside that opening, a central anode of 6 mm diameter is located. For the removal of corrosion, a reducing gas mixture of 5 vol% $H_2$ in He was used. The plasma jet was mounted perpendicular to the object with a working distance of 5 mm. The treated area is approximately 15 mm in diameter. The treatment was carried out on an automated XY-table that moved the object below the torch at a speed of 2 mm/s. Therefore, each point has a treatment time of about 10 s. In former experiments, the surface temperature with the mentioned parameters had a maximum of 45 °C. However, no temperature measurements could be done because of the close distance between the torch and the object which makes it very difficult to introduce a thermocouple and not damaging the object.

The influence of the plasma was imaged by macro-photography (Nikon D700). Identical settings such as lightning condition, and white balance were set to compare the images [15–17]. The first-order statistical image analysis is based on the value of individual pixels [15]. From the pixel values, the mean, standard deviation, skewness, and kurtosis was calculated while the histogram of pixel intensities (grey scale) gives a graphical overview of image. The mean is a measure to evaluate the brightness of the image and can give an idea on the amount of degradation product present on the object [16]. The standard deviation is a measure of the spread of the pixel values, the larger the standard deviation the greater the contrast. Skewness and kurtosis are associated with the shape of the histogram. Skewness is a measure of the symmetry of the histogram [16,17]. When the histogram is symmetric the skewness is 0. If the distribution of the histogram is skewed, the bulk of the data is towards one side of the histogram. High grey values, which correspond to a negative skewness are associated with a clean surface [16,17]. The last parameter kurtosis is used to study the deviation of the histogram from a normal distribution. An decrease in kurtosis means that the object is less uniform after the plasma treatment [16,17]. The surface was also imaged using an Olympus DSX510 optical microscope in dark field observation. The morphology and chemical composition were characterized with scanning electron microscopy (SEM) in combination with wavelength and energy dispersive X-ray spectroscopy (WDX & EDX) on a FEI Quanta 250. The

Please cite this article in press as: E. Grieten, et al., Reclaiming the image of daguerreotypes: Characterization of the corroded surface before and after atmospheric plasma treatment, Journal of Cultural Heritage (2017), http://dx.doi.org/10.1016/j.culher.2017.05.008