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Spectroscopic and surface analysis of the laser ablation of crust on historic sandstone elements

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Abstract

The plasma emission spectra obtained due to pulsed laser ablation of crust from the sandstone surface allow to identify the K and Na, and also Al, Ca, and Si in the removed material and in the substrate, respectively. The crust removal progress is observed through the changes in respective peak intensities of successive spectra and agrees with ablation measurements under pulsed irradiation at 1064 nm. The differences in surface morphology examined by means of scanning electron microscopy images confirm the ablation and spectroscopic data.

Keywords: Laser ablation; Gotlandic sandstone; Diagnostic; LIPS and SEM techniques

1. Introduction

The pulsed laser ablation applied for restoration of the historical monuments represents numerous advantages in comparison with conventional methods. This laser technique allows for removal of the surface encrustation without damage of the underlying bulk (Gobernado-Mitre et al., 1996). For some materials such as the Gotlandic sandstone it seems to be the best conservator's tool. This sandstone widely used for masonry of historical buildings, e.g. in Toruń, Chełmża, Chełmno, Gdańsk and Malbork (Poland) in the past represents a serious conservation problem (Jarmontowicz et al., 1994). The Gotlandic sandstone is characterised by a green-greyish hue, and composed of quartz grains joined by loam–limestone cement (Majdzińska, 2001). Under influence of sulphates contained in atmospheric pollution the sandstone decomposes on the surface, where transformation of indissoluble calcium carbonate in hydrated calcium carbonate occurs. Due to this process and also in consequence of deposition of burning products a dark, hard to remove, tight encrustation covers the substrate surface being in contact with the aggressive environment.

In this work an analysis of the laser-induced plasma emission (LIPS) is used for diagnostic of the encrustation removal from the sandstone due to pulsed laser ablation. The elemental analysis is utilised for identification of the material composition. For the ablation process the acoustic detection is used. Moreover, the surface images obtained by means of the scanning electron microscopy (SEM) for the laser-treated and non-treated samples are compared and discussed.

2. Experimental

For experimental studies the samples of façade elements and fragments of elevation made of gotlandic sandstone were used. They originated from a collection of sculptures and architecture details in the St. John's church in Gdańsk (Poland), and were originally covered by black encrustation of thickness of about 100 μm due to interaction with the polluted environment.

Measurements of the crust removal parameters were performed in order to define the optimal parameters of laser cleaning process of sandstone. For representative samples the LIPS spectra were recorded in situ during

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processing and also the SEM surface inspection was performed.

For sample irradiation the pulsed Nd:YAG laser (Quantel) operating in a Q-switched, single pulse mode and characterized by the pulse duration of 6 ns (FWHM) was used. The selection of the 1064 nm wavelength followed from own experimental results in agreement with literature. The laser beam was directed onto the sample surface by two bending mirrors. A telescope composed of two lenses (BK-7, $f_1 = 250$ mm, $f_2 = 150$ mm) assured the control of the beam position and focusing. During experiment a constant pulse energy of 330 ± 10 mJ was applied and measured by an energy meter (Gentec). The arrangement assured an exact selection of the laser fluence that was varied in the range from 0.1 to 3 J cm^{-2}, by changing the distance between sample and telescope. For the crust removal measurement the samples were irradiated perpendicularly to the surface and the selected area was laser treated until the crust was completely removed.

The process speed and ablation rate were measured by means of the acoustic detection. An electret microphone measured the snapping sound amplitude accompanying the laser pulse interaction. The angle of signal incidence onto the detector has been kept constant and close to the normal to the stone surface. After extraction of the background acoustic noise the signal was recorded by a digital oscilloscope TDS 3012 (Tektronix) and the signal traces were stored and processed by the PC-based data acquisition unit. It was assumed that the recorded sound intensity was independent on the frequency spectrum.

In order to observe the changes in chemical composition of the remaining crust layer during laser ablation the LIPS spectra were recorded. The visible spectral region was selected for detection of the plasma emission because such results were not published yet (Marakis et al., 1998; Maravelaki et al., 1997; Maravelaki-Kalaitzaki et al., 1999). The emitted light was collected by collimating optics and directed by an optical fibre to the entrance slit of the 0.5 m spectrograph (Acton Res. Corp., Spectra Pro 500) equipped with a grating of 300 grooves/mm (blaze at 500 nm). The overall system resolution was about 1 nm. The dispersed light was registered by a Peltier-cooled CCD camera (CVI) and the respective synchronisation of the excitation pulse, light detection and recording of the spectra was assured by means of the delayed pulse generator DGD 535 (Stanford Res.).

The SEM studies were carried out so for the laser cleaned as well as for crust-covered standstone surface, and also the cross-sections of processed and non-processed samples were inspected. Observations were performed by means of the Scanning Electron Microscope XL30 (Philips) and with regard to the transient conductivity of sandstone the samples were kept in the water vapour atmosphere during recording of the scans.

3. Results and discussion

The spectroscopic study and SEM surface inspection were preceded by extensive measurements in order to optimise the interaction parameters of the ablative crust removal from the contaminated surface of the Gotlandic sandstone. First, the ablation threshold, i.e. the highest value of laser energy per pulse and unit surface which does not result in the material removal due to photoablation was measured for previously untreated original sandstone elements. The measurements were carried out for dry and moistened surfaces. The threshold values for irradiation at 1064 nm were equal to 0.40 J cm^{-2} (dry) and 0.10 J cm^{-2} (wet). Values corresponding to the 532 nm wavelength laser were equal to 0.10 and 0.06 J cm^{-2}, respectively. These results characterising the original crust are comparable with those reported for removal of a dendrite-like black crust from limestone by the pulsed Nd:YAG laser at 1064 nm (Lee and Watkins, 2000). Due to higher ablation rates the fundamental wavelength and fluences from the range of 0.5–3 J cm^{-2} were selected for further measurements.

Results summarised on Fig. 1 show the dependence of the acoustic signal amplitude due to the laser pulse

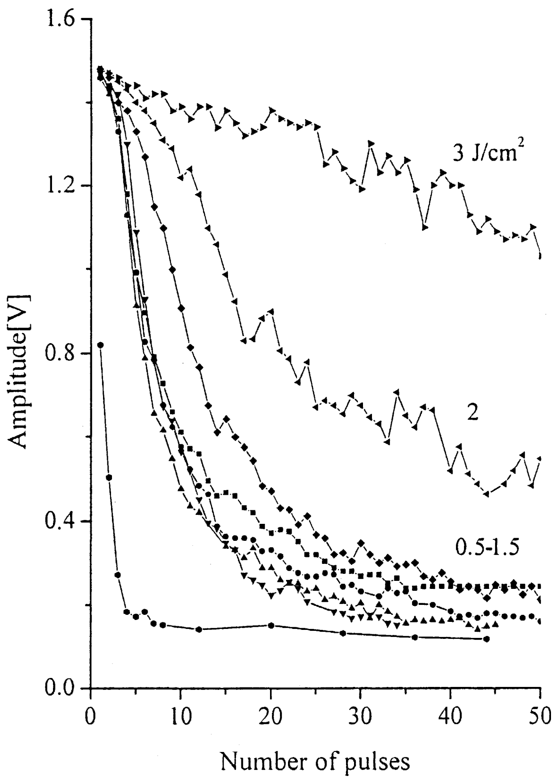


Fig. 1. Laser ablation of crust from the sandstone surface: the dependence of the acoustic signal amplitude on the pulse number measured at energy fluences in the range 0.5–3 J cm^{-2}; laser wavelength 1064 nm, dry surface.

interaction with the ablated surface on the total energy deposited on given location expressed as the pulse number. The observed, strong correlation of this acoustic signal with the thickness of the removed layer was utilised for detection purposes. The sets of data points represent series of experimental data obtained for different laser pulse energy fluencies applied. The lowest curve gives the reference level obtained for the crust-free sandstone cleaning. An extensive discussion of this experiment can be found elsewhere (Jankowska and Śliwiński, 2003). Finally, for the set of processing parameters the values of: wavelength of 1064 nm, laser pulse duration 6 ns, and the laser fluence of $0.5\,J\,cm^{-2}$ (moistened surface) were selected. For the black, porous encrustation of a thickness of typically 100–200 μm the surface was completely cleaned after 10–15 laser pulses.

For the sandstone surface originally covered by a tight crust layer of about 100 μm thickness, the SEM images taken prior to laser processing are shown in Fig. 2. At lower magnification the particles of an irregular shape of dimensions between several and 20 μm can be identified—see Fig. 2a. In some locations the quartz grains being the main component of the sandstone are visible. Also a melt-like collections of these grains are visible indicating traces of damage. It is confirmed by an image of the same area at larger magnification where cracks and crumbling of the grain's surface accompanied by the fracture characterised by sharp edges can be observed—Fig. 2b.

Additional SEM images of the sandstone cross-sections confirm the expectation, that for the degraded sandstone surface just below the crust layer the natural cement is not present. Absence of it is due to prolonged interaction of the aggressive environmental pollution. The cement can be found again at larger distances from the surface. This difference between contents of cement in the sandstone structure can be concluded from comparison of Figs. 3a and b. At the depth of 1 mm (Fig. 3a) the cement-free intergranular spaces are clearly visible, and at larger depths from surface (1 cm) the cement is present among grains which corresponds to the original sandstone composition—Fig. 3b. In contrary, on the top layer of the stone surface the empty intergranular spaces are filled up with crust.

The effect of laser interaction on the morphology of sandstone surface can be observed by comparison of the processed and non-processed regions. The close-up of the interface area between both regions is shown at two different magnifications in Figs. 4a and b. On the left hand side of both images the surface of the stone covered by encrustation is visible and on the right-hand side the cleaned fragment is shown, respectively. The encrustation is removed and the external layer of sandstone is set apart. The substrate is cement-free and the grains are loose. It is worth mentioning that in the crust-free region neither the top layer removal nor damage of the grains can be observed.

The plasma emission spectra recorded during laser ablation characterise well the crust because the plasma plume contains ions of elements present in the removed material. These ions recombine and emit a characteristic radiation allowing for elemental analysis. Also the progress of the crust removal process can be concluded from spectra obtained for successive laser pulses and results supporting the above conclusions are presented in Fig. 5. The strongest peaks are ascribed to potassium, silicon, aluminium, natrium and calcium and are centred at 766.5–769.9 (K I), 810.3–819.1 (Si III), 515.1 (Al III), 589.0 (Na I), 849.8–854.4 nm (Ca II). Besides, two broad bands of maximum around 650 and 750 nm are observed in the spectrum, too. Under prolonged laser irradiation these bands and also lines originating from potassium and natrium disappear after about 20 pulses, in contrary to the other peaks which are still present in spectrum, even after 50 pulses. This allow to conclude that Ca, Si and Al are natural components of the gotlandic sandstone whenever K and Na occur only in the encrustation. The confidence of assignment of the other

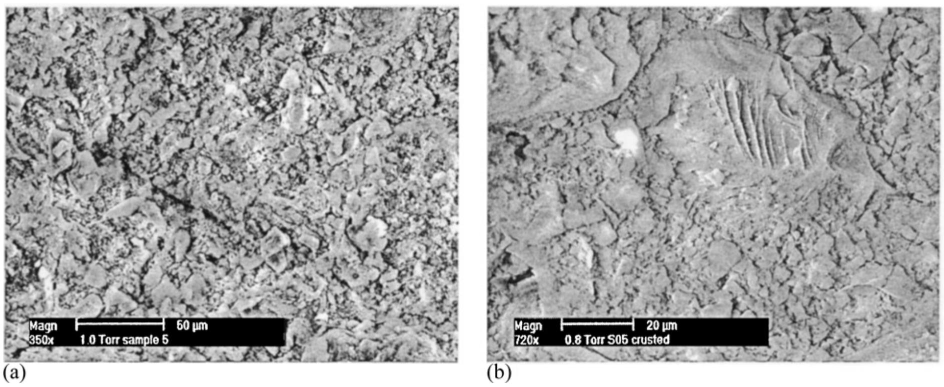
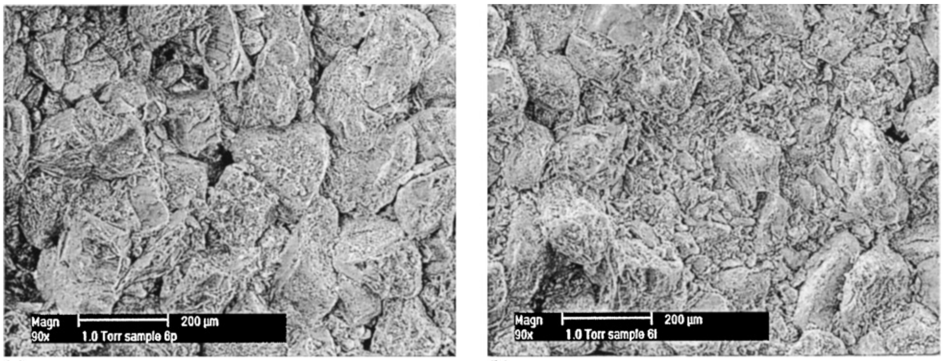
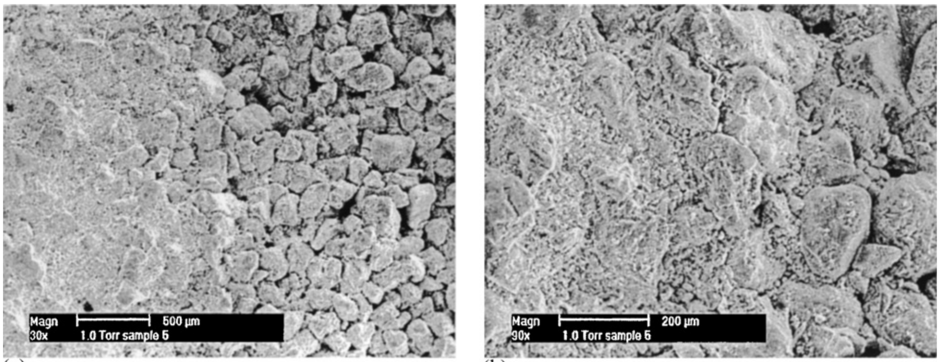


Fig. 2. SEM pictures of the sandstone surface before ablative cleaning: magnification 350× (a) and 720× (b).



(a) (b)

Fig. 3. SEM images of the sandstone cross-section: on the depth of 1 mm (a) and 1 cm (b) from the contaminated surface; magnification 90×.



(a) (b)

Fig. 4. The interface region between the non-treated (image parts on the left-hand side) and the laser-treated sandstone surface (right parts) at two magnifications: 30× (a) and 90× (b).

peaks visible in the spectrum require more experimental data and this work is in progress.

Finally, it can be concluded that the in situ spectroscopic analysis delivers results which are consistent with the SEM observation and also with the ablation data obtained by means of acoustic detection. This confirms that the LIPS technique can be used as a simple and reliable diagnostic method. Also monitoring of the laser encrustation removal can be possible and a schematic of the proposed procedure completed by an additional element required for analysis of data is shown by a dashed line in Fig. 6. Intensities of peaks originating from certain elements due to ablated material can indicate on continuation or stopping of the cleaning of a given surface fragment. A compact, industrial spectrometer together with the data acquisition and processing unit may assure sufficient capabilities for the safe performance and a careful choice of laser interaction parameters which are both the main requirements when working with objects of historical value.

4. Conclusions

The LIPS spectra due to pulsed laser ablation and the pre- and post-processing SEM surface scans were recorded and analysed for samples of Gotlandic sandstone in order to check the diagnostic possibility of the laser removal of surface pollutants. The work was carried out on elements from the St. John's Church in Gdansk (Poland). Results confirm the possibility of laser cleaning of gotlandic sandstone with the instantaneous, on-line analysis of chemical composition of removed material by means of spectroscopic measurement in the visible region. Comparison of SEM images of samples originally covered by crust and the laser-cleaned ones confirms the cleaning result obtained without any observable damage of the material. In order to support confidence of this conclusion it is necessary to study the mechanical properties and ageing of the laser processed stone. Also the plasma emission in the UV spectral region during laser cleaning is of considerable interest in spite of the optimal diagnostic conditions.

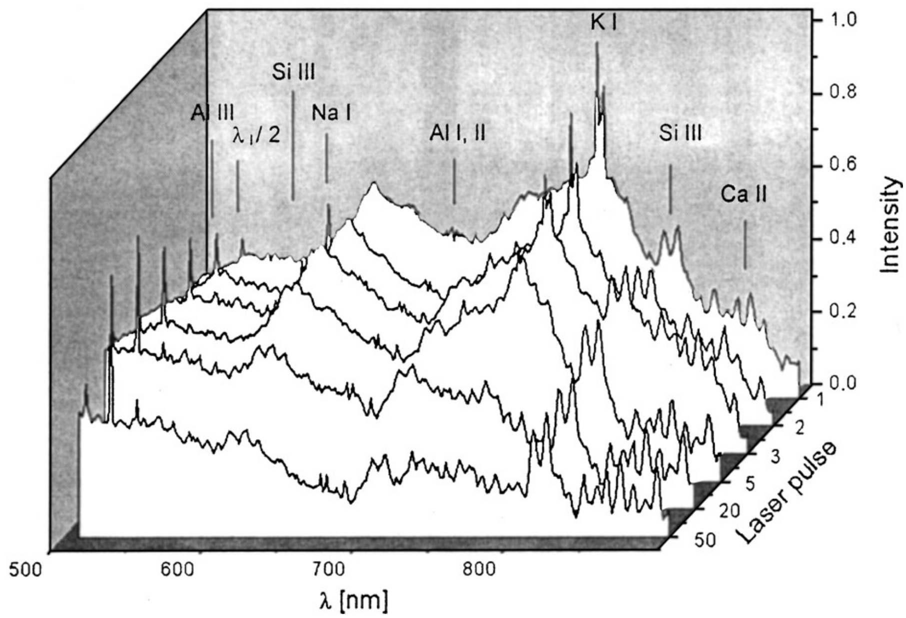


Fig. 5. Successive LIPS spectra recorded during laser ablation of the black crust.

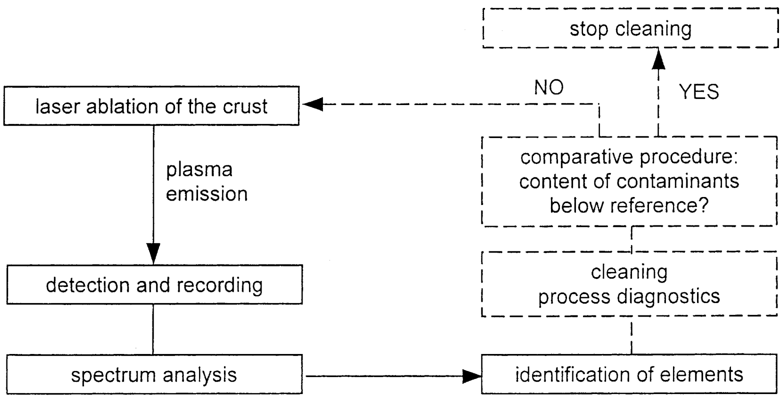


Fig. 6. Schematic of the LIPS procedure for diagnostic of the ablative laser cleaning of sandstone surface.

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