Microchemical Journal 124 (2016) 296–305

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Laser cleaning and laser-induced breakdown spectroscopy applied in removing and characterizing black crusts from limestones of Castello Svevo, Bari, Italy: A case study☆

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ARTICLE INFO

Article history:
Received 15 July 2015
Received in revised form 11 September 2015
Accepted 15 September 2015
Available online 21 September 2015

Keywords:
Monument restoration
Laser cleaning
LIBS
Black crusts
Limestones
Depth profile

ABSTRACT

The laser cleaning process combined with laser-induced breakdown spectroscopy (LIBS) were applied to restore and characterize altered limestones of the ancient jamb of the historic entrance gate of Castello Svevo, Bari, Italy. This area of the masonry blocks of the limestone castle was chosen because of its evident degradation with an apparent deposit of black crusts. The combination of a Q-switched Nd:YAG pulsed laser with the diagnostics typical of the LIBS technique was shown to be very effective for monitoring, controlling and characterizing the laser cleaning process of limestone. The different elemental compositions of the black encrustations covering the stone surface and the underlying stone allowed to evaluate and avoid over-cleaning and/or under-cleaning. Further, coupling LIBS to the cleaning process provided important information about the optimal experimental conditions to be used for evaluating the conservation status and determining the most proper cleaning restoration procedure before operating the consolidation of the blocks. Thus a sufficient removal of unwanted layers could be achieved without modifying the surface underneath and ameliorating the effectiveness of traditional cleaning techniques. In this work, the elemental composition of the ablated black crust and the underlying stone were determined by the spectroscopic study of plasma emitted from either a single pulse (SP) or a double pulse (DP) LIBS configuration. With respect to SP LIBS, a marked enhancement of the signal emission was observed by DP-LIBS used after a previous stratigraphic DP-LIBS assessment of the cleaning depth.

1. Introduction

Laser radiation applied to the cleaning of decayed stones was first investigated on several Carrara marble sculptures in Florence and Venice in a pioneering work by Asmus et al. [1]. Since then laser based techniques have been applied widely for cleaning art objects of various natures, including stones, marbles, metal sculptures, stained glasses, paintings, and icons [2–5]. The cleaning process aims at the controlled removal of contaminant layers, e.g., crusts, soiling patinas, and stains, by mechanical and thermal ablation using nanosecond laser pulses focused on the sample surface. These deposits consist of microparticles of various natures, including fly ashes and fine soots originating from urban traffic and industrial activities, pollens, spores, windborne seeds, generally cemented by gypsum. Thus the material properties, e.g., its absorptivity, roughness, mechanical properties, affect markedly the process [2].

During the cleaning process the high energy laser pulses are absorbed significantly by the dark-colored surface encrustations, whereas the underlying stone, generally white to yellow-colored, is prone to reflect the incident radiation. The very fast processes, of the order of a few billionths of second, occurring during the laser–material interaction depend markedly from irradiation parameters, e.g., wavelength, energy density, and pulse duration [2,6,7]. In particular, short laser pulses in the nanosecond range are likely to produce mechanical damages, microfragmentation and increased porosity of the material surface, whereas longer duration pulses, up to the millisecond range, are expected to induce larger thermal modifications of the surface [6, 8]. For example, the temperature rise of crusts and underlying material impinged by pulsed laser irradiation can be predicted by a few quantitative models [2].

Even though the mechanisms involved are not fully understood, the removal of crusts is ascertained to result from a combination of thermal and mechanical interactions between the absorbed radiation and the irradiated surface [2]. In particular, thermal interaction has been shown to produce a fast, very localized and brief rise of temperature on the material surface, which determines its melting and vaporization. This is followed by the formation of plasma at a temperature of several

☆ Selected papers presented at TECHNART 2015 Conference, Catania (Italy), April 27–30, 2015.

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http://dx.doi.org/10.1016/j.microc.2015.09.011
0026-265X/

thousand degrees, whereas no significant transfer of heat to the stone underneath, i.e., no high-temperature mineral phase transition, has been observed [9]. The dynamic expansion of the plasma formed then generates mechanical shock waves that break down the material dispersing particles of various sizes. Further, the laser induces the explosive vaporization of the water possibly present in the crusts, thus intensifying the mechanical effects and increasing the particle dispersal rate [9]. Several factors, such as the pulse duration, the nature and optical, mechanical, thermal and chemical properties of the material and the presence of water, affect the extent of the thermal versus mechanical effects, and thus the effectiveness of the ablation process [9].

In general, laser cleaning is a very precise and progressive process able to remove layers of few microns for each laser pulse, i.e., it follows the microstratigraphy of the altered layers and can be interrupted at any defined stratigraphic level. A critical aspect to obtain a successful cleaning by any type of cleaning methodology is to determine at which surface depth the process, i.e., the thermal, mechanical and chemical effects operating for the undesired layers removal, must be interrupted. Thus, very weak and highly altered surfaces can be treated successfully.

Besides the actual surface cleaning performance, the laser technique coupled with a spectroscopic system, i.e., laser induced breakdown spectroscopy (LIBS), is able to perform also the evaluation of the extent of contaminant layers removal. This by measuring the distinct differences between the emission spectra of the contaminant layers and those on the sample surface beneath, thus defining properly the end point of cleaning [10–12]. This specific performance adds to the well known advantages of LIBS, which include no sample preparation, destruction of sample areas of the order of few hundreds of microns, automation, selectivity, versatility and a high degree of precision. In particular, despite the higher technological complexity and costs, multi-wavelength Q-switched Nd:YAG laser systems have been used for approaching and solving the problem of the yellow appearance in cleaning whitish substrates [13–21].

One of the most serious problems facing conservation is the deterioration of carbonate stones used in construction, as a consequence of the constant exposure to decay mechanisms. Where stone is severely weakened, some form of consolidation may be necessary to reduce the rate of decay and to reinforce the stone's cohesion. However, even if the use of consolidant products such as exfoliants, and sprays, might stop the degradation, on the other hand it could favor a subsequent fixation of even more dirt on the stones, thus compromising the achievement of an optimal cleaning.

The main aim of this study was to confirm the effectiveness of laser cleaning and LIBS microdestructive stratigraphic analyses by applying an innovative approach for dirt removal before performing the pre-consolidation by adhesion and cohesion of the calcareous stones and quoins of the left jamb of the southern entrance gate to the courtyard of Castello Svevo, Bari, Italy. A qualitative chemical analysis of the bulk samples and their black encrustations was carried out using single pulse (SP) and double pulse (DP) LIBS configurations. In particular, DP LIBS depth profile analyses were performed on the limestone sample covered by black crusts in order to identify the gradual decrease with depth of some specific elements strictly related to the patina, including Fe, Co, Ti, Al and Si.

2. Material and methods

2.1. Sample description and sampling procedure

The sample studied was a selected area of the limestone masonry blocks of the left jamb of the southern entrance gate to the courtyard of Castello Svevo, Bari, Italy. The castle is an historic multilayered building featuring a quadrangular shape and square towers built originally by Roger the Norman in 1131 on the remains of a Byzantine structure, and followed by several successive building phases from the twelfth to the sixteenth century.

The area selected showed a very complex surface and structural degradation of limestone blocks (Fig. 1). In particular, the surface degradation featured a layer of black crust and incoherent and coherent surface deposits, whereas the structural degradation was characterized by several cracks with solutions of continuity in the quoins and widespread spalling with irregular shapes and consistent thickness. Some spallings showed the total detachment of the stone material with subsequent fall and loss, whereas others showed a partial detachment which needed proper consolidation. Several areas of disintegration and erosion appeared, especially where the black crust experienced a structural change with the passage of calcium carbonate to gypsum which resulted in the pulverization of the constituent material of the building stone.

The experimental samples collected in the central area of the masonry showed apparent fractures and detachment of material, which resulted from the heavy load crushing probably accentuated by the mechanical properties of stone blocks. The masonry featured different types of limestone, thus the various quoins showed different compactness and porosity. Officials of the Superintendence of Fine Art and Landscape for the Provinces of Bari, Foggia Barletta–Andria–Trani have suggested the possibility that an old protective treatment ("scialbaturas") would have been present under the thick layer of the black crust.

In order to decide the degree of cleaning and the procedures to be used for conservation, four areas of the blocks showing a macroscopic different texture and firmness were sampled for analysis (Fig. 2).

2.2. Optical and scanning electron microscopy and X-ray diffraction analysis

In order to characterize the sequence of layers, the encrustation/limestone interface and the textures of each sample, thin polished cross sections of the four samples were prepared and examined by an optical polarizing microscope (ZEISS Axioskop 40 POL) equipped with a micrometer particle size device and a digital camera. The depth crater image was obtained by a JEOL (JSM-6510, Thermo Scientific) scanning electron microscope (SEM).

X-ray diffraction analyses were conducted on micro-samples using a Philips powder diffractometer PANalytical Pro PDM (CuK, 40 kV, 40 mA) equipped with an X'Celerator detector. Sampling of layers showing a coarse texture was performed using the finer portion enriched in binder. Diffraction spectra were acquired in the angular continuous scanning mode from 3° to 70° of 2θ at a speed of 0.07° 2θ/s.

2.3. Laser cleaning

The cleaning was performed by a portable pulsed Nd:YAG Q-switched laser mod. Thunder Art of Quanta System at a pulse width of 8 ns (Fig. 3a) is equipped with a multi-articulated arm with seven folding mirrors that enable the laser beam to travel into an aluminum tube. The choice of the optimal experimental parameters for the laser was made after comparison of results obtained using two different wavelengths, i.e., 1064 nm and 532 nm, different pulse repetition frequencies (from 10 Hz to a maximum of 20 Hz), and varying the energy (maximum energy per pulse, 900 mJ at the wavelength 1064 nm and 400 mJ at 532 nm).

2.4. Laser induced breakdown spectroscopy

The LIBS technique was used to analyze the concentrations of key elements related to the formation of alteration layers at various depths and in the limestone underneath. The LIBS system used consisted of two Nd:YAG lasers operating at different wavelengths, i.e., 1064 nm (IR) and 532 nm (VIS) (Fig. 3b). The IR pulse was generated by a Nd:YAG Q-switch Ultra (Quantel) at a maximum energy of 75 mJ, and a width of 6 ns. The VIS pulse was generated by a Nd:YAG Q-switch Brillant