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Comparison of the performances of nanosecond and femtosecond Laser Induced Breakdown Spectroscopy for depth profiling of an artificially corroded bronze

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ABSTRACT

Single Pulse Laser Induced Breakdown Spectroscopy (SP-LIBS), performed by nanosecond and femtosecond laser sources has been applied to the study of the depth profiling of the artificially obtained patina of a bronze sample. The results show improved performances of femtosecond LIBS compared to nanosecond one. The differences found in the analyses are related to the different laser–matter interaction processes induced by the different time duration of the laser pulses.

1. Introduction

Copper and its alloys have been widely used through the centuries, from the Chalcolithic up to the present. The reasons of this importance, for both utilitarian and artistic purposes, are related to copper good ductility, shining coloring and mechanical resistance. The conservation and preservation of copper alloys in general, and of bronze items in particular, and their protection from corrosion phenomena are considered a primary necessity. As a consequence, the study of corrosion is still of interest for conservators, scientists, art historians and collectors [1]. From this point of view, the characterization of the patina which covers the bronze surface, which is due to the influence of different atmospheric conditions and components or originally intentional, could be relevant. In particular, two of the most important parameters for any patina characterization are both its thickness and compositional depth profile. Several techniques can be used to measure these parameters, including Scanning Electron Microscopy, electrochemical and spectroscopic methods [2–5] and Laser Induced Breakdown Spectroscopy (LIBS). The latter method is becoming increasingly utilized, mainly because of its experimental simplicity and micro-destructive sampling. LIBS is an atomic emission spectroscopy technique which uses a highly energetic laser pulse as sampling and the excitation source. The laser is focused on the sample to produce a plasma, formed mainly by atomic, neutral and ionized, excited species. This technique can be used for many qualitative chemical–physical applications, including patina characterization, laser ablation, thin film study application and depth profiling [6–12]. In particular, the application of LIBS to depth profiling analysis of materials which composition changes strongly with depth, is related to the possibility of evaporating very small quantities of material hit by the laser spot, without modification of the surrounding area. From this point of view, copper based alloys are particularly difficult to be analyzed by LIBS, due to the large differences in the physical-chemical properties of the metal constituents. In fact, the different vapor pressures of the elements present on the surfaces, do not always guarantee the stoichiometry correspondence between the laser induced plasma and the starting material [13–15]. In addition, the high thermal conductivity of the alloy [16] could produce melting of the material surrounding the ablated area,

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adding a further complication. Several routes are possible to minimize these drawbacks, including Double Pulse LIBS [17–19] and Single Pulse LIBS (SP-LIBS) performed by ultra-short pulse lasers. The latter is easier to be performed, since it does not require the use of two temporized laser sources, and its performances are related to the particular characteristics of the laser–matter interaction when the laser pulse duration is in the sub-picosecond regime [20]. Several studies have already compared the features of SP-LIBS, performed by both short (ns) and ultra-short (sub-ps) pulse lasers, for the analysis of copper alloys obtaining different, and sometimes contrasting, results [13,15,20,21], but in this paper we have used SP-LIBS performed by lasers with different pulse duration to verify the performances of this technique in detecting the presence and the composition of the patina formed on the surface of a copper-tin alloy. From this point of view, the aim of our work is different from that of the other studies, which compared, by theoretical or experimental approaches, the LIBS data that can be conveyed either by fs or ns laser beams in terms of ablation rate and analytical quantification of single components copper based materials. Finally, the results obtained using both short (10 ns) and ultra-short (250 fs) pulse lasers have been compared and interpreted considering the different laser–matter interaction phenomena involved.

2. Experimental

The sample to be investigated was realized starting from a binary alloy (Cu–Sn: 88–12 wt%), similar in composition to that of the Greek ancient statuary, selected for its good strength and resistance to corrosion properties. The cast bronze specimens have been realized starting from pure elements. Copper and tin have been melted in an electric furnace at 1150 °C with borax protective slag. The molten metal has been cast in a graphite die, then homogenized in an electric furnace at 600 °C for 72 h [3,22]. Wet & Dry technique as weathering method has been performed with the aim of simulating the effect of natural acid rain on bronze and to investigate the degradation of alloy specimens exposed to corrosion conditions. The wet test (Kesternich Corrosion Test) simulates a severe corrosion condition with a solution reproducing acid rain and the subsequent dry test simulates the outdoor dry condition of exposed materials. The corrosion tests were carried out in an Erichsen Mod. 519/AUTO cyclic corrosion chamber following the indication of DIN 50018 standard. Bronze specimens have been exposed to an atmosphere containing about 200 ppm of SO2 at 40 °C and 100% RH for 8 hours (wet cycle), subsequently they have been exposed to room condition for 16 h (dry cycle). Each wet and dry cycle has been repeated 15 times [3].

The general LIBS instrumental set-up consists of a laser source, a spectroscopic system, pulse generators and a target holder allowing micrometric adjustment of the target position as described in previous works [15]. Two different laser sources with pulse duration of 7 ns and 250 fs have been used. The ns source was a Handy Quanta System Nd:YAG laser which provided pulses with a repetition rate of 1 Hz and a fixed fluence of 5.0 J cm^{-2} at 532 nm. The ultra-short pulses were provided by a Twinkle Light Conversion Nd:glass laser (λ = 527 nm), running at 1 Hz repetition rate, an energy of 3.0 mJ and a relative fluence of 4.2 J cm^{-2}. Either ns or fs laser beams were perpendicularly conveyed on the target surface by a 150 mm focusing lens. All experiments were performed in air at atmospheric pressure. The target holder was placed on a remote-controlled *x*,*y* translation stage (resolution 0.1 μm). A spectroscopic system consisted of a 500 mm focal length spectrograph (ARC 500i mounting a 2400 g/mm grating) and connected to a fast ICCD detection system (Princeton PI Max II, 1024 × 1024 pixels) has been used. The plasma emission was imaged directly by a fused silica 7.5 cm focal length biconvex lens on a bundle of 19 fused silica fibers connected to the spectrograph entrance slit (80 μm width) achieving, at 500 nm, a spectral resolutions of 0.008 nm/pixel.

The bronze patina has been characterized in backscattered configuration by using a Horiba Jobin-Yvon LABRAM HR 800 micro-Raman spectrometer, equipped with two gratings (600 g/mm and 1800 g/mm) and with an Olympus microscope supplied with 10×, 50× and 100× objectives. Raman spectra were acquired using the 600 g/mm grating and the 100× objective. In these conditions, the estimated resolution was around 4 cm^{-1}. Excitations were performed by 632.8 nm radiation from a He–Ne laser source. The laser power was maintained at 20 mW.

Scanning Electron Microscopy (SEM) and Energy Dispersion X-ray Spectroscopy (EDX) analyses, performed by a Philips-FEI ESEM XL30 apparatus, have been used for characterizing the morphology and the composition of the target ablated surface. SEM micrographs of the cross section of the sample have been used to estimate the patina thickness.

3. Results and discussion

3.1. Patina analysis.

Although the altered bronze sample surface shows a green color, the analysis, performed by the Olympus microscope connected to the micro-Raman spectrometer, shows the presence of areas with different colors, suggesting the presence of different compounds. In particular, despite the large majority of the surface presents green crystals, some zones display a brownish color. The micro-Raman analyses have been performed in the different zones, with a spatial resolution of few microns and the results are reported in Fig. 1a and b. Fig. 1a shows the Raman spectrum obtained from one of the green zones of the patina, which can be assigned to brochantite, a copper(II) hydroxyl-sulfate ($Cu_4SO_4(OH)_6$) [23]. Brochantite is a well known patina constituent and it is the main corrosion product detected on outdoor copper and bronze [24,25]. The Raman spectrum reported in Fig. 1b, which refers to one of the brownish zone, can be assigned to antlerite ($Cu_3SO4(OH)_4$) [23], another possible patina constituent which can be formed under more acidic conditions than brochantite [26].

3.2. LIBS depth profiling

The LIBS technique, successful used for assessing the bulk composition of bare and artificially aged copper based alloys by the use of either calibration curves or calibration free approach [27], has been here exploited providing a depth profile analysis of the sample. Since the patina is irregular and formed by different components, the measurements have averaged by been carrying out analyses on six different sample positions. For both ns and fs LIBS measurements, the ratios between the intensities of copper and tin signals have been reported as a function of the number of successive laser pulses, obtaining in this way a relative concentration profile. On each position, the depth profile datum has been obtained by 100 laser pulses. When the measurements have been carried out to study the effect of the laser radiation on the surface, the number of pulses has been varied between 2 and 40, without performing any contemporary acquirement of the emission spectra.

The emission peaks used for LIBS analyses were λ = 282.35 nm and λ = 283.94 nm, for copper and tin, respectively. These wavelengths were chosen for several reasons. First of all, both peaks are in the same spectral interval, avoiding in this way possible differences in the apparatus sensibility. In addition, the detected signals do not present self-absorption and the transition upper levels have very similar values [28]. In order to evaluate the emission signals obtained, Voigt line profile functions subtracted of the

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