A systematic study of laser ablation efficacy as a low-invasive cleaning technique for Cu-based alloys

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A SYSTEMATIC STUDY OF LASER ABLATION EFFICACY AS A LOW-INVASIVE CLEANING TECHNIQUE FOR CU-BASED ALLOYS

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Summary

This dissertation is focused on a systematic study of the efficacy of laser ablation as a low-invasive cleaning procedure for Cu-based alloys. On one hand, the research was motivated by the increasing use of lasers in our society in recent decades and in a specific and important field like Cultural Heritage conservation. On the other hand, little information is available within the literature on laser-surface material interactions during the ablation process on metals and, in particular, on Cu-based archaeological and historical artefacts. Furthermore, no systematic studies have been done on both laser parameters and material composition.

There are two innovation in this research. The first is the use of a near-infrared (1064 nm) pulsed laser coupled with a galvanometric scanner. The laser scanner is coupled with a vector graphic editor, with CAD-*like* capability, which enables the user to perform rapid, precise and complex surface treatments in a repeatable way. The other innovation is the preparation of artificially-corroded coupons that mimic some of the possible corrosion scenarios found in archaeological Cu-alloys to favour the study of laser interaction mechanisms.

The main issue in laser-cleaning procedures for Cu-based materials in the Cultural Heritage field is the proper setting of laser parameters, in order to *ablate* (remove) only the unwanted materials (e.g. reactive corrosion products), leaving a protective layer (e.g. copper oxides corrosion products) and without affecting the

metallic substrate. A problem arises when both the unwanted materials and the protective layer have similar ablation thresholds, due to the similarities in their absorption values. Proper setting of both laser (i.e. power, fluence, irradiance, pulse duration) and geometrical parameters due to the scan system (i.e. interlining, scan speed), makes it possible to ablate only the reactive corrosion products, avoiding thermal diffusivity in the metallic bulk, that could result in structural transformation and even melting phenomena.

Screening tests to investigate and optimise the effect of laser power, pulse duration and scan speed were carried out on artificially-aged Cu-based samples. Then, the optimised parameters (in terms of best ablation without affecting the metallic substrate) were applied on archaeological bronze coins in order to validate the treatments as a low-invasive procedure.

A second issue was also studied: the possibility of re-oxidation phenomena during the ablation process. To this aim, more intense laser conditions were applied in order to force the possible laser-material interactions between the outer layers and the oxygen present in the air. Tests were performed in a vacuum chamber filled with synthetic air marked by the presence of ^{18}O (a less common oxygen isotope) at atmospheric pressure. This way, if interactions with the oxygen present in the air occurred, the re-oxidised products would be traced with the ^{18}O isotope. Results show that no abnormal amount of ^{18}O % was detected by means of an advanced spectroscopic technique (ToF-SIMS). This phenomenon was also verified for the optimised condition used on the coins.

Results show that the scanning laser system has proven to be a powerful tool in performing rapid, precise and complex surface treatments in a repeatable way and that a low-invasive laser-cleaning procedure on complex stratified corrosion layers, present in archaeological Cu-based alloys, is possible. Furthermore, no substantial phenomenon of re-oxidation occurred; only slight incremental trend was found when laser intensity was increased, in extreme conditions far from optimal. This shows that lasers, applied in optimised conditions on Cu-based archaeological artefacts, do not induce re-oxidation interactions at a sufficient level to be detectable by advanced spectroscopic techniques. A model of the laser-surface material interaction mechanisms during the ablation process is therefore proposed.