Lasers Cleaning of Patrimonial Plasters

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Abstract. The use of the lasers Q-switched Nd:YAG to remove the dust of the stone monuments especially sculpture gradually replaces the more abrasive technique of sandblasting. This tendency made us consider the lasers as solution for the cleaning of ceramics and the plasters. Indeed in museums, these materials are often covered with dirty mark (dust, grease, etc.) which is difficult to remove without damaging the object. This paper deals with the impact of different types of lasers (Nd:YAG first and third harmonic) irradiation on plaster and with the effects on its morphology and its crystallography. Plaster is an interesting material because of its typical acicular crystals altered at low temperature. That is why synthesis samples were prepared, constrained in temperature then analysed by various processes (SEM, XRD, TGA. . .). These results were compared with samples cleaned by laser. That enabled us to conclude that plasters cleaned by UV-laser (third harmonic of the Nd:YAG) underwent neither yellowing, nor morphological or crystallographic changes. It has to be opposed to the intense yellowing, and sometimes morphological destruction, which appears with an infrared wavelength (first harmonic of the Nd:YAG).

1 Introduction

Numerous plasters are found in museums (original sculptures, fine copies or simple casts). Plaster ends to get dirty very quickly what is due to its mineralogical and physical characteristics (dielectric constant. . .). Because of its natural fragility and sensitivity to moisture and physical actions, the removing of greasy dust is ordinary based on peeling methods or rubbing-out. Sometimes these traditional techniques turn out to be ineffective or damaging especially when fineness of details exclude physical operation or when the dust layers are too hard. In those cases, the use of lasers, already employed for stone [1], has then been considered.

2 Choice of the Wavelength

The first tests have shown that after cleaning with an infrared Nd:YAG laser an intense yellowing appeared (Fig. 1a) while the use of the third harmonic of the Nd:YAG laser permits to recover a surface colour close to the initial

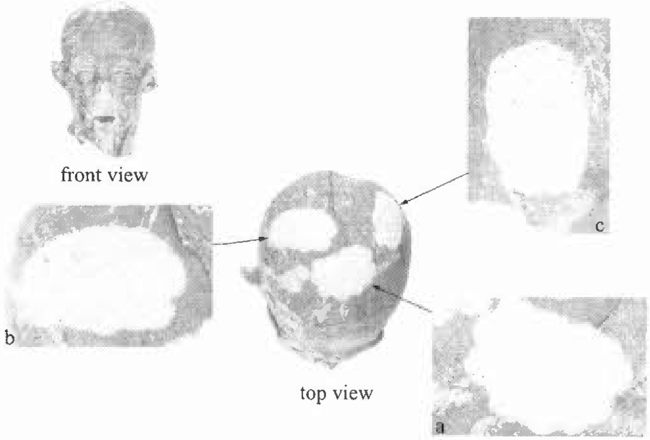

Fig. 1. Plaster écorché cleaned by Nd:YAG, (**a**) 1st harmonic, (**b**) 2nd harmonic, (**c**) 3rd harmonic

one (Fig. 1c). Nevertheless, this method seems to give out a too white surface (Fig. 1c) compared to the traditional methods of cleaning. The yellowing obtained following cleaning by the infra-red Nd:YAG laser [2, 3] is reversible by using the third harmonic of the Nd:YAG laser without apparent damage for the surface. The cleaning of the plaster by the third harmonic of the Nd:YAG laser gave very good results but we must check out that neither morphological nor crystallographic modification will occur. Therefore, we made some measurements on some plaster samples.

3 Preparation of the Samples

The diversity and the complexity of the plaster artworks and the dirty marks which cover them are not taken into account, the results obtained in this study will be only indicative. We chose a plaster of the Molda 3 type, typically used for moulding (impurity rate lower than 1%) and mixed the powder and water without any additive. However, it is common that the sculptors or the moulders complex this formulation (by addition of milk to improve texture, for example). The plaster was versed in metal moulds of approximately $20\,cm^3$. The samples were dried at 50°C, without causing any transformation of phase or fast desiccation [4].

All the analyses presented below are related to the face in contact with the air during drying. The gypsum crystals of this kind of surface are less organized there Fig. 2 than those on the faces in contact with the mould, where the phenomenon of growth is directed. Thus, the possible effects of the laser will be more easily observable and the damage on surface will be maximized.

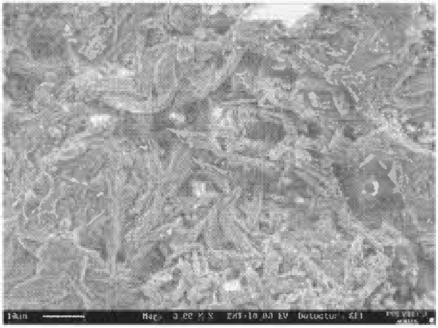

Fig. 2. Crystal morphology of the face in contact with the air

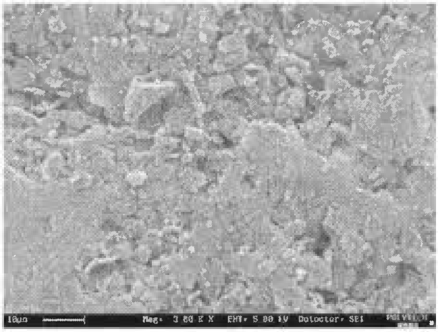

Fig. 3. Deposit of carbon graphit

A natural dust contamination would be too long and insufficiently reproducible. We thus chose a deposit of carbon graphite reduced to powder and applied to the brush (Fig. 3). This powder forms part of porosities and makes it possible to obtain a fine and homogeneous layer.

4 Treatment in Temperature

Laser ablation induced a fast but localized rise in temperature in the medium. However the modifications of phase of the plaster occur for temperatures ranging between 100°C and 1200°C Fig. 4. Plaster is an interesting material because of its typical acicular crystals ($CaSO_4.2H_2O$ β) altered at low temperature (120°C = $CaSO_4.0{,}5H_2O$ β) [4]. In order to detect possible modifications of phases of the plaster cleaned by laser, samples were first thermally treated, at various temperatures, then they were observed with the SEM and, eventually they were reduced to powder and analysed by x-rays diffraction (Fig. 5). These data will be employed as references and will be compared with the results obtained after the laser cleanings. The fine grains

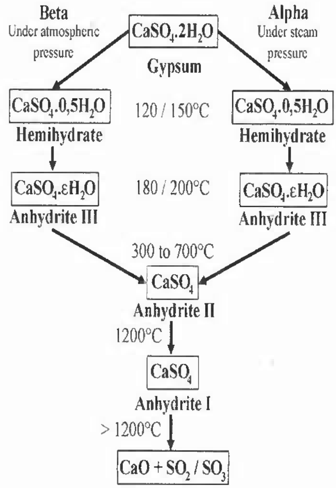

Fig. 4. Dehydration of the gypsum function of the temperature

observed at 300°C (Fig. 5) may be attributed to transformation of the sample to anhydrite.

5 Laser Cleaning

Because of problems of yellowing in the use of the fundamental wavelength of the Nd:YAG laser [2], we studied also the method of cleaning by the third harmonic of the Nd:YAG laser [3]. Each sample was dirtied and cleaned on half of its surface to preserve a part for comparison (Fig. 6). The energy used at the 1064 nm wavelength is 360 mJ (2.88 J/cm^2) and 90 mJ (0.72 J/cm^2) at the 355 nm (10 Hz).

Cleaned surfaces were compared with the samples treated in temperature using SEM and x-rays diffraction as shown in Fig. 7

According to this figure, the plaster cleaned by UV does not undergo any morpho-logical or crystallographic modification. Moreover, this method of cleaning by the third harmonic of the Nd:YAG laser shows clearly that the restored colour is the same one as the original colour. On the other hand, it is interesting to note that the surface cleaned by the fundamental wavelength of the Nd:YAG laser presents a morphological modification of its surface, that is due to a too significant abrasion and maybe the influence of the heat on the phase (Fig. 8).

The ablation thresholds of the dirt was estimated at 0.16 J/cm^2 for the UV and 0.23 J/cm^2 for IR. The alteration threshold of the plaster is around 1.41 J/cm^2 for IR. Following these experiments, tests were carried out on real works so as to validate these first results.

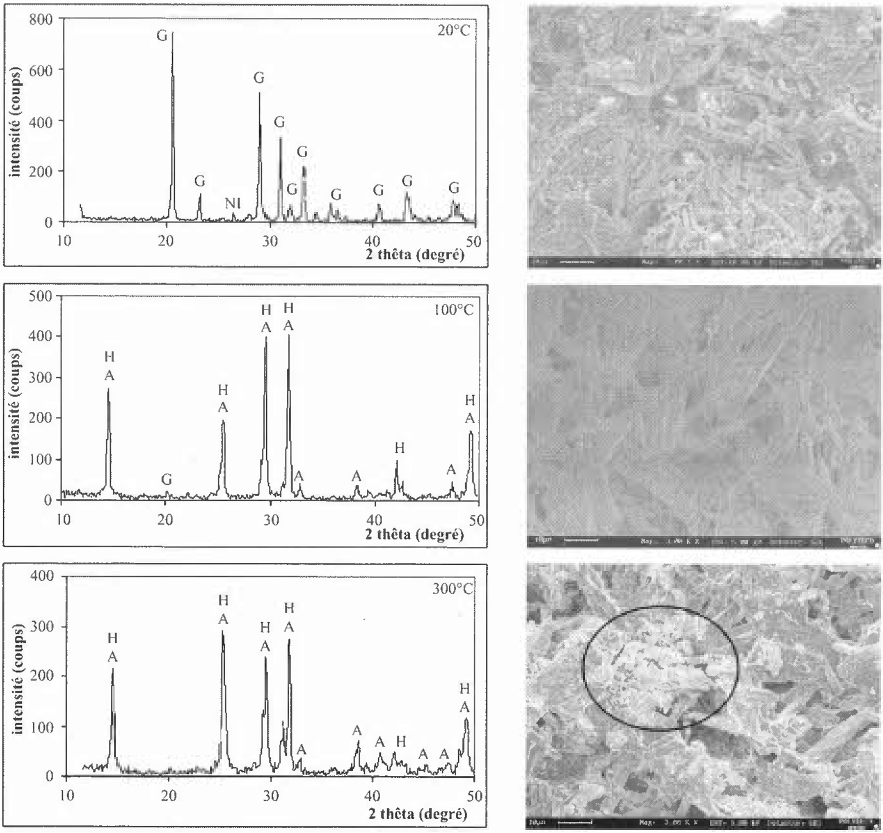

Fig. 5. Modification of the plaster phases versus temperature at 20, 100 and 300°C (DRX – SEM), G: gypsum, H: hemihydrate, A: anhydrite

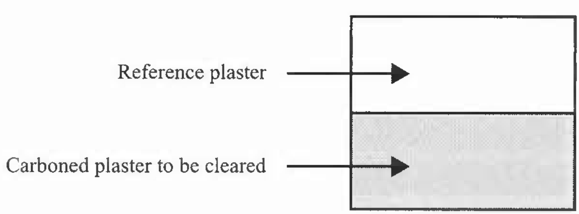

Fig. 6. Sample before cleaning

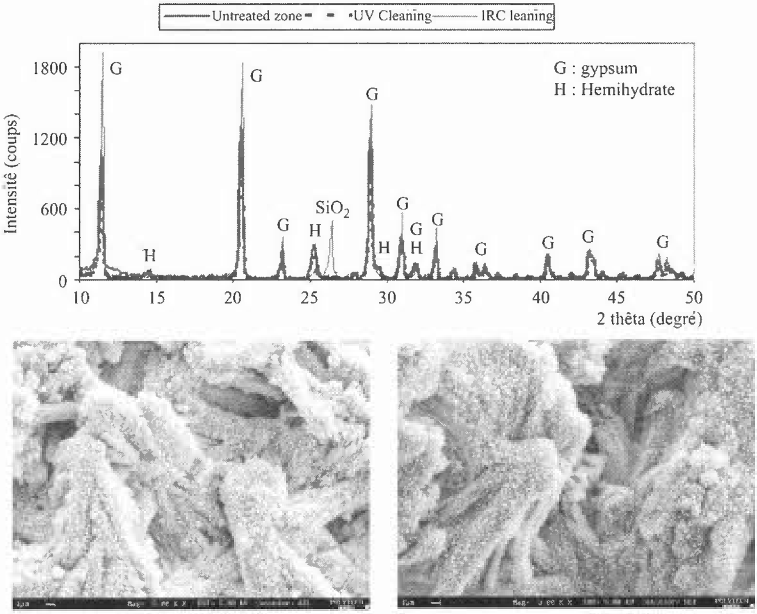

Fig. 7. Sample after and before cleaning with UV wavelength at 0.72 J/cm^2 (DRX – SEM)

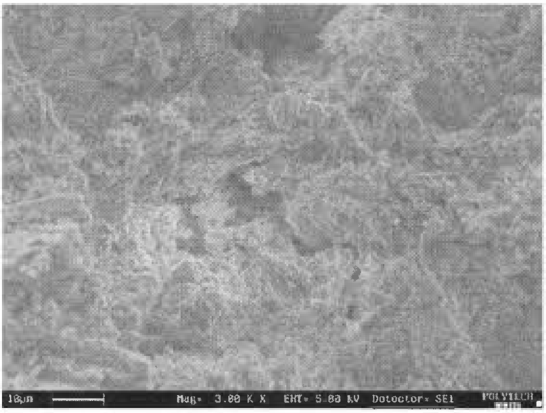

Fig. 8. Sample after cleaning with 1064 nm wavelength: fractionation of the crystals

As it can be seen in Fig. 9, an intense plasma is formed on the surface of the object under the impact of the laser beam.

As can be seen in Fig. 10, we cleaned part of a pieta using UV laser at 0.41 J/cm^2 with satisfactory results. Indeed, surfaces are perfectly cleaned

Fig. 9. plasma formed on the surface

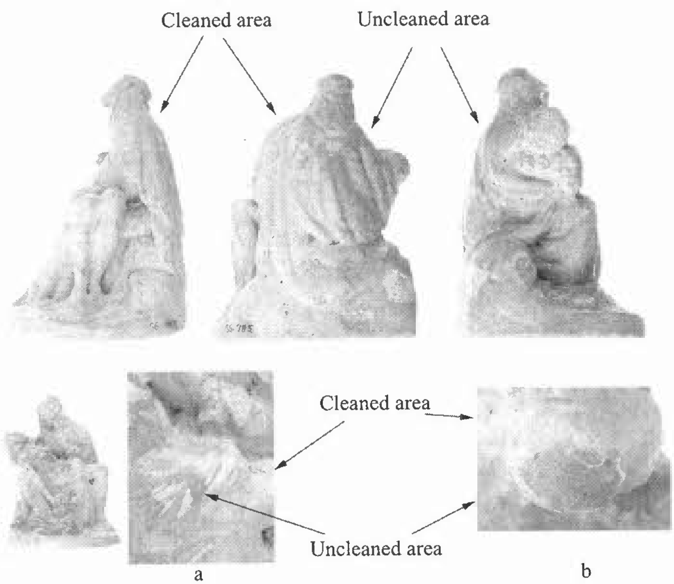

Fig. 10. Pieta partially cleaned by UV laser

and the fine structure of the moulding or the surface quality is still preserved, even the fragile white coating.

6 Conclusion

The cleaning of the plaster using the third harmonic of Nd:YAG laser modifies neither the colour, neither the crystallo-graphic structure nor the phase of material. This technique appears as an interesting alter-native to the traditional methods of cleaning of the plasters as well for ceramics.

The researches have to be continued on a variety of historical plasters as well as on comparisons with the traditional methods of cleaning and their potential damages on morphological structure of the material.

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