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Nanosecond Nd: YAG Laser Surface Cleaning of Metals and Marbles

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Abstract: Laser cleaning of materials' surfaces implies the removal of deposited pollutants without affecting the material. Nanosecond Nd:YAG pulsed laser, operating at 1064 nm and 532nm, was utilized. Different laser intensities and number of pulses were used on metallic and non-metallic surfaces under O_2 and Ar environments to remove metal oxide and crust. Cleaning efficiency was studied by optical microscope. The results indicated the superiority of 1064 nm over the 532 nm wavelength without any detectable damage to materials' surfaces. Marble cleaned in Oxygen gas environment was better than in Ar gas.

Introduction

Metals and marbles were among many materials used in ancient civilizations and still used nowadays in many industrial and construction applications [1, 2]. The effects of aging, ambient pollutants and different modifications mechanisms make the materials unstable and falling apart [3], which causes damage and affects their preservation [4]. Cleaning represents the process of removing accumulated foreign deposits, oxides and dirt from metallic and non-metallic surfaces [5]. Conventional chemical and mechanical cleaning techniques may harmful to original materials, and the selection of the appropriate technique relies on material type and the foreign-deposited material to be removed. The Conventional cleaning micro-blasting and chemical [3, 6] methods cause some loss of material from the surface; even with careful cleaning [7]. This necessitates the use non-conventional technique (laser in our work) to improve the cleaning results and to protect original materials from damage. There is an increasing use of laser light for surface cleaning of historical objects [8]. Lasers can remove undesirable deposits without any mechanical contact of the original material. [3, 9, 10, 11]. In addition; it is environmentally clean [12] and can work at any material surface [9]. The only waste generated is the pollutants ablated from the surface [11, 13]. Extreme care, however, must be considered in order to optimize the operational parameters and to avoid possible negative effects. Yellowing of marbles is an undesired side effect after laser cleaning [14] that is due to incomplete dirt removal of pollutions, penetration of organic materials through the surface layers [15] or thermally induced chemical transformation of iron in the bulk of the stone surface and within the volume of the crust [16].

Pulsed lasers cleaning is used because it has a great potential to remove surface stains and weathering effects from a wide range of materials and artifacts such as, sculptures, coins, marble, granite, paintings, paper, etc. A successful laser cleaning is when achieving complete removal of foreign contamination without or with a minimal damage to the original material [3]. Laser interaction with metal oxides and crust depends on laser parameters (intensity, laser pulse duration and wavelength) and material parameters such as (reflection and absorption coefficients, melting and boiling points, surface geometry, homogeneity and thermal conductivity). Most of the high intensity laser pulses, incident on the pollutants [3, 17] are absorbed by the surface to generate heat which diffuses into the material [9, 15]. This will lead to a rapid, localized and very short rise in temperature on the material's surface causing melting and vaporization and finally plasma formation with an elevated temperature [18]. This generates mechanical shock waves propagating through the crust or iron oxide; breaking it down and disperses particles of different sizes [14]. In the present work, Nd: YAG laser was employed to clean environmentally affected marbles and iron surfaces.

Experimental

Q-Switched Nd: YAG laser work form (HUAFEI) company working at (1064 nm, and 532 nm) wavelengths, (9 ns) pulse duration and maximum energy per pulse of (0.6J) was employed in this work. Different laser intensities and number of pulses were employed on both oxidized metallic plates (1x1 cm2) and marble (1 cm^3) surfaces covered by thick simulation crust prepared from mixing 49.52% of (CaSO4.H2O), 0.5% of (Fe2O3), and 1% of (carbon) and 48.98% of water. Different laser and environmental (O_2, Ar) gas conditions were tested. A simulation crust layer of 0.4 mm thickness was deposited on the samples and multiple laser spots were focused on the same position to clean the samples. The samples were cut all the way to image the cross section by (400X) optical microscope (super eye). The samples were imaged by 100x magnification; as this was found enough to observe the details of the cleaning process.

Results and discussion

Figure (1) shows a topographic surface view of oxidized iron plate. Larger number of laser pulses at constant low intensity allowed more accurate; but shallower cleaning rate of the iron plate. Most of the crust thickness layer was removed in this way before inflicting any damage to the original surface of the metal. Figure (2) shows the cleaning 0.4mm thick simulation oxide and crust 84 pulses at constant 4.89x1010W/cm2 laser intensity to fully clean the surface. At higher laser intensity (9.17*1010W/cm^2), more effective crust removal was possible at greater depths and less number of laser pulses (16 pulses) but with higher risk of ablating the original metal surface. In this case, the native oxide layer was completely cleared after 16 pulses, as shown in Figure (2).

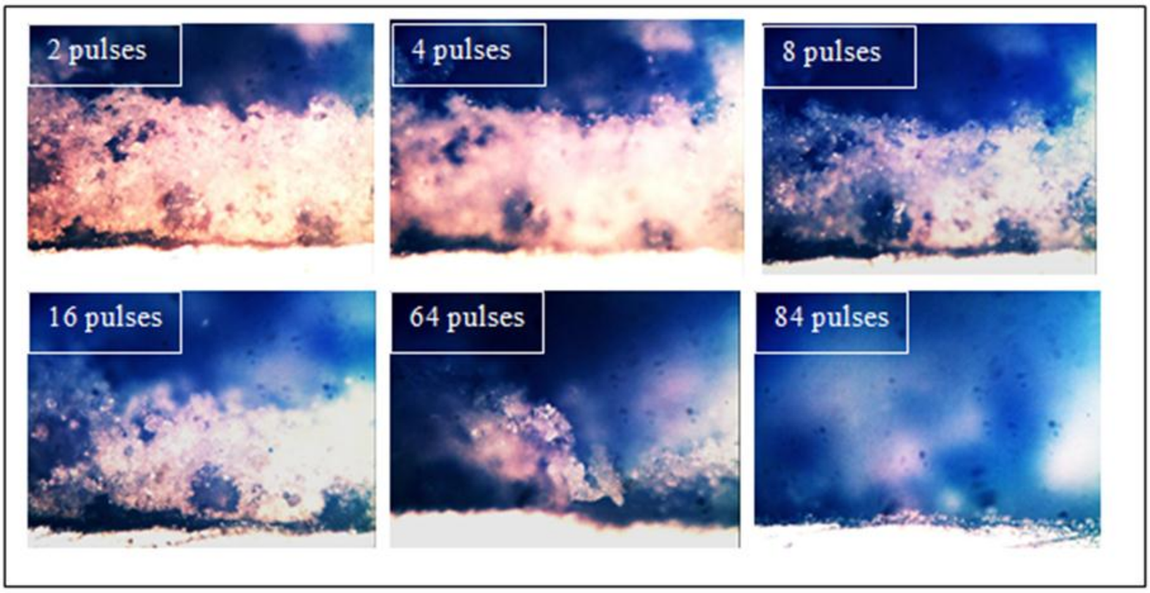

Fig. (1): Microscopic cross section image of iron plate cleaned with different number of Nd: YAG laser pulses and 4.89x1010W/cm2 laser intensity.

Fig. (2): Microscopic cross section image of iron plate cleaned with different number of Nd:YAG laser pulses and 9.17*1010W/cm2 laser intensity.

The effect of laser wavelength on the cleaning process was examined to study the effect of material spectral absorptivity. An optical microscope was used for this purpose. For the purpose of obtaining measurable depth, four laser pulses from the fundamental 1064 nm Nd: YAG laser and its second harmonic (SHG) 532 nm at (4.89x1010W/cm^2) were used. Because of its higher absorption, the optical microscope results of cleaning the iron plate revealed the superiority of the 1064 nm over the 532 nm. The cleaned surface was shiny with clear appearances, and very close to the original surface before oxidation. Figure (3) illustrates the use of SHG (532 nm) wavelength, which resulted in partial cleaning with some changes in its morphology.

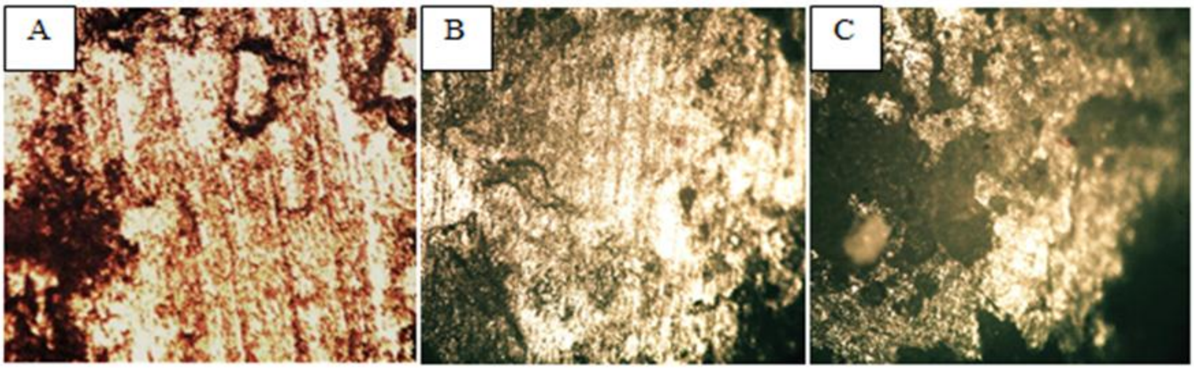

Fig. (3): Microscopic top view images of iron plate A: reference untreated sample, B: cleaned by 4 pulses of 4.89x1010W/cm2 intensity using the 1064nm wavelength and C: cleaned by 4 pulses of 4.89x1010W/cm2 intensity using the 532nm wavelength.

As an application of laser cleaning on real objects, one Jordan Qirsh copper coin was cleaned. The optimum cleaning conditions were reached when using 10 laser pulses of the fundamental Nd: YAG laser wavelength (1064 nm) at (4.89 x1010 W/cm^2) intensity and (50%) pulse overlap. Due to the visual observations and microscopic images, the treated part of the coin was clear from crust and showed bright surface color when compared with the un-treated part as shown in the topographic surface images of Figure (4).

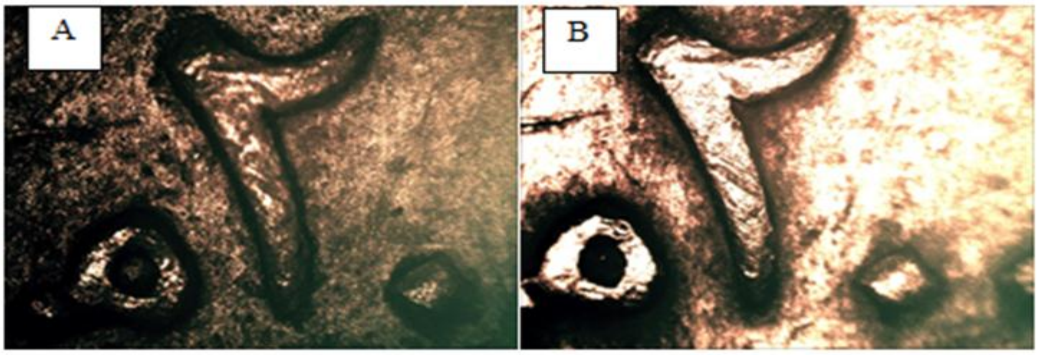

Fig. (4): Topographic surface image (40x) of one Qirsh Jordanian coin A: before cleaning B: after cleaning by ten pulses of 4.89 x1010W/cm2 intensity Nd: YAG laser operating at 1064nm wavelength.

The faster-treated marble samples that we laser-treated showed different response to the Nd: YAG laser when cleaned under different gas atmosphere. The use of ambient O_2 permitted better cleaning; better than Ar, due to its small ionization energy (12.1 eV) and higher thermal conductivity (63.64 x106 Cal/sec.cm.Co). Most of the laser beam energy was used to burn the O_2 in an exothermal reaction which increased the thermal energy at the surface. This has ensured an efficient removal of the crust but not the substrate. The use of Ar ambient, on the other hand, produced the smallest decrease in crust thickness because of its higher ionization energy (15.8 eV) and low thermal conductivity (42.57 x106 Cal/sec.cm.Co**)** [19].

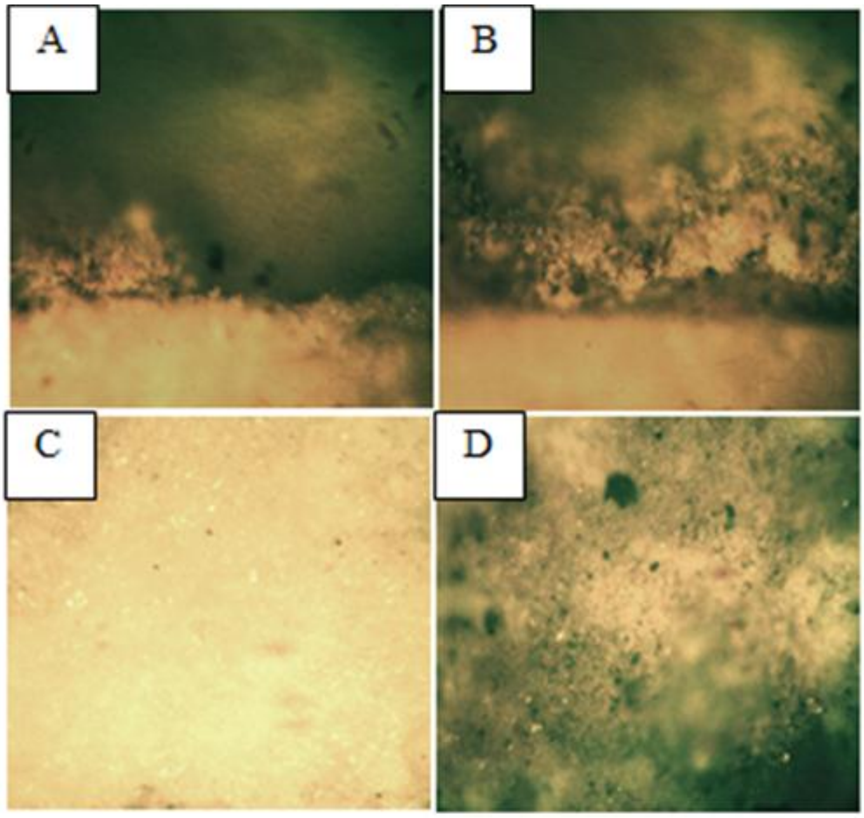

Fig. (5): Microscopic images of marbles (100x magnification), A and B: cross-section of samples cleaned in O2 and Ar respectively; C: and D: top view images of the same samples (using 4 pulses, 6.12 x1010 w/cm2 intensity and 0.1 mm crust thickness).

Conclusion

Within the magnification power of the optical microscope used no detectable damage to metallic and marble samples was notice when suitable laser energy was used. Metal oxides were cleaned effectively using the 1064 nm laser wavelength at minimum laser intensity of (4.89x1010W/cm^2). Higher laser intensity (9.17x1010W/cm^2) allowed faster but risky cleaning. Marble surface cleaning in O_2 gas allowed better results than in Ar gas because it necessitated less number of laser pulses. Clear metal surfaces from oxides were obtained by selecting the suitable laser intensity and number of pulses.

References

[1] K. Watkins, C. Curran, J. Lee, “Two new mechanisms for laser cleaning using Nd: YAG sources” Journal of Cultural Heritage, ***4***, 59s–64s, (2003).

[2] R. Salimbeni,”laser techniques for conservation of artworks”, Archaeometry Workshop, ***1***, p. 34-40, (2006).

[3] Y. Koh, ” Laser Cleaning as a Conservation Technique for Corroded Metal Artifacts” doctoral thesis, Luleå University of Technology, Department of Applied Physics and Mechanical Engineering, Division of Manufacturing Systems Engineering, p. 17-22) , Luleå, Sweden, (2006).

[4] P. Pouli, M.Oujja, M. Castillej.,”Practical issues in laser cleaning of stone and painted artifacts optimization procedures and side effects”, Appl. Phys. A, ***106***, 447–464 (2012).

[5] C. Korenberg and A. Baldwin,”Laser Cleaning Tests on Archaeological Copper Alloys”, Hindawi Publishing Corporation, p. 1, (2006).

[6] M. Cooper, “Laser cleaning in conservation: an Introduction”, p.1, ***3*** Butterworth Heinemann: Oxford, (1998).

[7] J. Marczak, A. Koss, P. Targowski, “Characterization of Laser Cleaning of Artwork”, Sensors ***8***, 6507-6548, (2008).

[8] P. Pasquet, P. Psyllaki, R. Oltra, “Laser Cleaning of Oxidised Metallic Materials”, Laser Techniques and Systems in Art Conservation, Proceedings of SPIE, ***4402***, p. 38, (2001).

[9] John F. Ready “Industrial Applications of Lasers” 2nd Edition, Pp 330, Honeywell Technology Center, Minneapolis, Minnesota, Academic Press (1997).

[10] V. Veiko, T. Mutin, V. Smirnov, ”Laser Cleaning of Metal Surfaces”, Proc. of SPIE ***6985***, p.6, (2008).

[11] P. Ortiz, V. Antúnez, R. Ortiz, ”Comparative study of pulsed laser cleaning applied to weathered marble surfaces”, Applied Surface Science, ***283***, p.193-201, (2013).

[12] T. Rivas, S. Pozo, M. Fiorucci, “Nd: YVO4 laser removal of graffiti from granite-Influence of paint and rock properties on cleaning efficacy”, Applied Surface Science, ***263***, 563–572, (2012).

[13] J. M. Lee and K. G. Watkins, “Laser removal of oxides and particles from copper surfaces for microelectronic fabrication”, Optics Express Special focus issue, ***7***, p. 69-76, (2000).

[14] M. Jasi´nsk, A. Nowak, j. Łukaszewicz, “Colour changes of a historical Gotland sandstone caused by laser surface cleaning in ambient air and N2 flow”, Appl. Phys. A, ***92***, p. 211–215, (2008).

[15] S. Arif and W. Kautek ”Laser cleaning of particulates from paper: Comparison between sized ground wood cellulose and pure cellulose”, Applied Surface Science, ***276***, p. 53– 61, (2013).

[16] S. Siano, J. Agresti, I. Cacciari,”Laser cleaning in conservation of stone, metal, and painted artifacts: state of the art and new insights on the use of the Nd:YAG lasers”, ***106***, p. 421, (2011).

[17] S. Risti, S. Poli´c, B. Radojkovi´c, “Analysis of ceramics surface modification induced by pulsed laser treatment”, Processing and Application of Ceramics, ***8***, p. 15–23,(2014).

[18] A. Koss and J. Marczak, “Evaluation of laser cleaning progress and quality”, Journal of Heritage Conservation, ***32***, p.109-111, (2012).

[19] J. Gross, “Mass Spectrometry: Principles of Ionization and Ion Dissociation”, © Springer-Verlag Berlin Heidelberg, 2nd Ed., p.25-27, (2011).

تنظيف اسطح الحديد و الرخام بأستخدام ليزر النيديميوم-ياك بأمد نبضة نانوية

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الخلاصة: يتطلب تنظيف اسطح المواد إزالة الملوثات المترسبة على اسطح المواد دون التأثير على المادة. لهذا الغرض تم استخدام نبضات نانوية من ليزر النيدميوم – ياك عند الاطوال الموجية ١٠٦٤ نانومتر و٥٣٢ نانومتر. وظفت قيم مختلفة للشدات الليزرية ولعدد نبضات الليزر لازالة اكاسيد معدنية وطبقة الملوثات المترسبة على الرخام في جو من الاوكسجين مرة وفي جو من الاركون مرة آخرى. بينت النتائج تفوق الطول الموجي ١٠٦٤ نانومتر علد الطول الموجي ٥٣٢ نانومتر دون ملاحظة اي تلف لأسطح المواد الاصلية والحصول على نتائج أفضل عند إجراء عملية التنظيف في جو الاوكسجين.