Sudan University of Science and Technology
College of Graduate Studies

Cleaning Rust of Iron using Pulsed CO_2 Laser

تنظيف صدأ الحديد بإستخدام ليزر ثاني أوكسيد الكربون النبضي

A Dissertation Submitted as Partial Fulfillment of the Requirements for the Degree of Master of Laser Applications.

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بسم االله الرحمن الرحيم

﴿ وَقُلِ اعْمَلُوا فَسَيَرَى اللَّهُ عَمَلَكُمْ وَرَسُولُهُ وَالْمُؤْمِنُونَ ﴾

صدق االله العظيم

(سورة التوبة : 105)

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Thanks for institute of laser, Sudan University for all given to us..

Special thank for:

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To guiding me to right way

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Dedication

To my Dear Mather

To my Dear Father

To Dr. Ibrahim Abass Ahmed

To my brother & fellow worker

To Rasha Abass Ahmed

ABSTRACT

As general laser properties it's unique, are used in a wide variety of applications in all walks of life. The common problem to metal industrial is rust. The rust is a layer coated surfaces of metallic object which decreases the performance of metal in its applications.

In the thesis work,CO_2 laser used to remove rust from the surfaces of ironic objects by focusing a laser beam on the surface of two samples (flat and carved). The output power of the laser was selected in such a way that the beam cannot melt or evaporate the surface of the metal, and the energy of the pulse was 0.3 J, while the pulse frequency was approximately 400 Hz.

The experimental results indicate that the beam of laser causes evaporation of rust, and better cleaning was obtained in booth flat and curved surface.

Laser beam can be used to clean regions that are difficult to clean by common method, saved time and exertion.

المستخلص

بصورة عامة خصائص الليزر الفريدة تجعل ضوء الليزر يستخدم في شتى نواحي الحياة.من أشهر المشاكل التي تواجه الصناعات المعدنية هي الصدأ،هو طبقة تغطي أسطح المعادن تقلل من أداء المعادن في التطبيقات .

في هذا البحث تمت إستخدام ليزر ثاني أوكسيد الكربون لإزالة الصدأ من سطح الحديد بتركيز شعاع الليزر بصورة متتابعة على سطح عينتين معدنيتين (مسطحة ومنحنية) ، الطاقة الخارجة من الليزر تم إختيارها لتبخير الصدأ مع إحتمالية عدم إحداث أي تغير أو إذابة أو تبخير لسطح المعدن ، قدرة النبضة كانت في حدود 0.3 جول, تردد النبضة في حدود 400 هيرتز.

النتائج التي تم الحصول عليها عملياً أظهرت أن هذا الليزر يسبب تبخير للصدأ ويتم بذلك تنظيف المعدن. تم الحصول على نتائج جيدة في أسطح كلٍ من العينة المسطحة والمنحية.

يمكن بواسطة شعاع الليزر الوصول لأماكن يصعب الوصول إليها بالطرق التقليدية كما انه يوفر في الوقت والجهد .

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Chapter One

Introduction

Chapter One

Introduction and Literature Review

1-1 Introduction:

Modification of surface properties over multiple length scales plays an important role in optimizing a material's performance for possible applications. For instance, the physical and chemical properties of any surface can be controlled by altering its texture, morphology, structure as well as type of impurities (Matthew S. Brown and Craig B. Arnold, 2010). Also, one can consider the frictional, adhesive, and wetting forces acting at a material interface as being strongly influenced by the size and shape of the micro and nano scale features present .As such, multi scale surface modifications are a critical factor in the development of new material structures and in engineering the detailed interactions that occur at surfaces and interfaces (Matthew S. Brown and Craig B. Arnold, 2010).

One of the major advantages of the laser as a tool for material processing is the ability to precisely control the laser beam where in the material and at what rate energy is deposited. This control is exercised through the proper selection of laser processing parameters to achieve the desired material modification. Laser ablation is a process by which material is removed from a surface (Matthew S. Brown and Craig B. Arnold, 2010). At lower laser energy, this occurs as a pulsed laser immediately transitions a material from solid to gaseous phases, a process called sublimation (Matthew S. Brown and Craig B. Arnold, 2010).

1-2 Removing rust from metals:

The rust is formed as layer on the surface of metals due to the interaction between water and metals and this is actually happens when metals exposed to moisture (I.e., Fe^{+} $+H_2o$ $\rightarrow$FeOH + H^{+}). Laser system can use as a tool to remove the rust from surface of metal under certain conditions. If the laser pulses don't have enough energy per pulse, they might simply melt the rust (United States Patent, 27Oct1980) while at higher laser energy the pulses may convert the material to plasma instead of vapor. Therefore, the reason for using pluses laser is that the time between two pluses is too small to produce heat to diffuse into the metal, and therefore the metal does not melt, but instead only thin layer will be removed. Thick layer can be removed by pulsing multiple times in each spot (United States Patent, 27Oct1980).

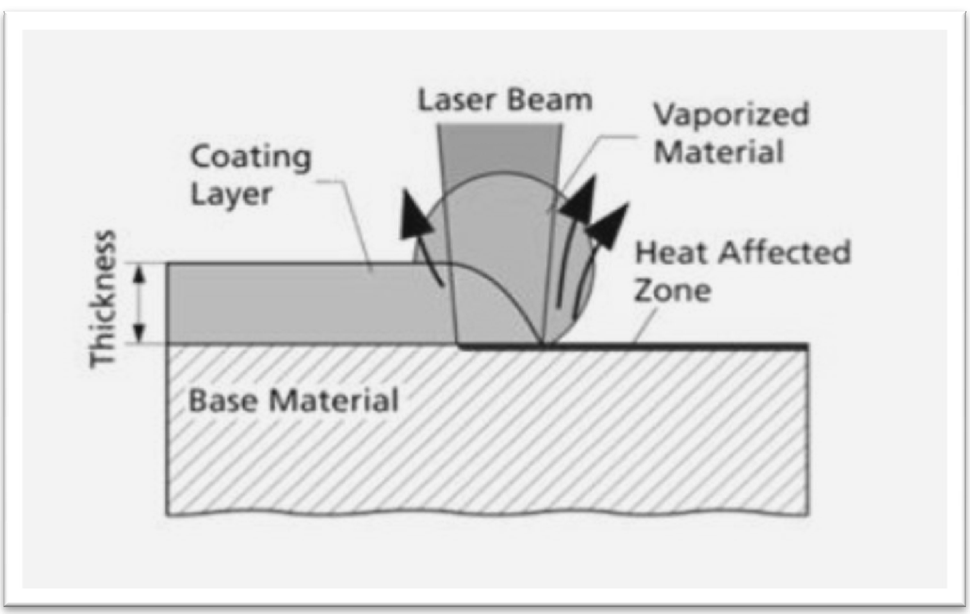

Fig (1-1): schematic diagram showing how to remove the rust using Laser (United States Patent, 27Oct1980).

Laser (Light Amplification by Simulated Emission of Radiation) cleaning is a good solution for removal of rust from surfaces, because the laser beam has unique characteristics than normal light, such as a single wave length (monochromaticity), is extremely parallel, it produces high power per unit area, coherence and it is highly directional. Furthermore, the laser cleaning process itself has several advantages, such as no mechanical contact, selectivity, and localized action, no introduction of foreign contamination, less waste, flexibility, reliability and immediate feedback (William T.Silfvast, 2004). However, laser cleaning process has some disadvantages as well, for example the cost is high and the laser cleaning should be done by the specialized trained workers.

The selection of appropriate laser is the important role in the laser cleaning process. There are several parameters that should be considered for laser cleaning such as energy, wavelength, pulse duration and number of pulses, scanning speed (for continuous wave) etc. There are different types of lasers that can be used for laser cleaning such as CO_2 laser, Nd:YAG laser, high power diode laser and a number of excimer laser systems. The laser cleaning can occur photothermally, photochemically or both. In the photothermal process, the rust is removed by vaporization and it normally happens when the laser cleaning is done in the range of visible and infrared wavelengths. In the case of photochemical process, breaking of direct covalent bond of rust occurs. It happens when the laser cleaning is done in the range of ultraviolet wavelength (William T.Silfvast , 2004).

1-3 Research Problem:

Clean surface of ironic object from rust by use CO_2 laser beam and prove the laser beam can be clean faster a better than common method .

1-4 Literature Review:

In April 2011 S. Siano and et.al. present work the application of laser cleaning in the conservation of cultural assets is reviewed and some further developments on the interpretation of the associated laser-material interaction regimes are reported. Both the state of the art and new insights mainly focus on systematic approaches addressed to the solution of representative cleaning problems , including stone and metal artifacts along with wall and easel paintings. The innovative part is entirely dedicated to the extension of the application perspective of the Nd:YAG lasers by exploiting the significant versatility provided by their different pulse durations. Besides extensively discussing the specific conservation and physical problems involved in stone and metal cleaning, a significant effort was also made to explore the application potential for wall and easel paintings .The study of the latter was confined to preliminary irradiation tests carried out on prepared samples. Characterized the ablation phenomenology, optical properties, and photo mechanical generation associated with the irradiation of optically absorbing varnishes using pulse durations of 10 and 120 ns. Further results concern the nature of the well-known problem of the yellowish appearance in stone cleaning, removal of biological growths and graffiti from stones ,cleaning of bronze andiron artifacts and related aspects of laser conversion of unstable minerals, removal of calcareous stratification from wall paintings, and other features (S. Siano·J. Agresti·I. Cacciari·D. Ciofini· M. Mascalchi·I. Osticioli·A.A. Mencaglia, 2011).

In 2016 Mahmoud Kamal Ahmadi and Blaine A. Pfeifer presented experiment in Iron oxidation, known as rust formation, causes enormous loss in term of property damages and associated economic risks. Depending on the degree of formation, rust consists of several layers of iron in different oxidation states.

The brownish top layer is mostly iron (III) oxide-hydroxide [FeO(OH), $Fe(OH)_3$] while the deepest black layers possess iron oxide ($Fe_2O_3.nH_2O$). The flaky nature of surface rust meditates diffusion of oxygen and water to inner material sections which can lead to total disintegration of iron mass. As a result, it is desirable to remove rust and protect fresh surface from oxidizers. The common rust removal reagents are mainly based on complex formation of ferric ion with organic and inorganic acids such as citric acid, oxalic acid, and phosphoric acid. Rust removal ability is typically a qualitative observation which makes direct comparison between treatment options cumbersome if not impractical. In this work we have developed a colorimetric assay to measure ferric concentration in rust removal treatment media using a bacterially-produced siderophore in comparison to a commercial rust removal reagent. In this approach, ferric concentration is correlated to the mass of rust being dissolved in the presence of different removal agents. This assay is based on a modification of the 1, 10-phenanthroline assay to enable detection using a 96-well plate format for higher throughput screening and assessment.(Mahmoud Kamal Ahmadi and Blaine A. Pfeifer, 2016).

In 2006 Wolfgang Kautek present this paper is focused on the systematic investigation of the layer-by-layer removal of corrosion products on artificially corroded metal coupons aiming to introduce a methodology for the optimum laser cleaning approach of historical metal objects. Thus, it is very important to determine the chemical composition of the studied surfaces before and after irradiation. A series of laser cleaning studies has been performed on test coupons (reference and artificially corroded). Wavelength and pulse duration e□ects are investigated. Initial studies were focused on the use of infrared (1064nm) and ultraviolet (355nm and 248nm) radiations of nanosecond (ns) pulse duration. Damage and removal threshold values were determined for the substrates and the corrosion layers, respectively. The irradiated surfaces are evaluated microscopically under the optical and the scanning electron microscope, while the mineralogical and chemical composition of the various layers is determined with X-ray di□raction and SEM-EDAX analyses, respectively. The results obtained are providing a comprehensive approach for understanding the main mechanisms that are significant in the di□erent laser cleaning regimes, while the optimum cleaning methodologies for the studied materials are being established.(Wolfgang Kautek,2006).

Blasting techniques in shipbuilding and ship repair have been developed for surface preparation of steel to a standard equivalent to SA2.5 as defined by ISO Standard 8501. The usage of consumables, such as abrasive materials, air and water, constitutes a recurring cost in these processes. When blasting work is carried out in the open space, such as during a dry docking, abrasive blasting generates a lot of dusts which in turn pollutes the environment with consequential social and economical costs. Laser blasting or laser cleaning, which has not been introduced commercially in shipbuilding and ship repair, offers an alternative for green manufacturing and green repairs. Laser cleaning has significant advantages on these issues over the conventional blasting techniques. It is a well controlled process with unique properties, such as precise treatment, high selectivity, and high flexibility. A cleaning technique using a high-power fiber laser is developed for the surface preparation of steel. Fiber laser has advantages of compact system, automation capability, and low maintenance cost. We report the laser cleaning results using a 500-W pulsed high-power fiber laser. The laser cleaning is able to meet the SA 2.5 requirements of blast cleaning as described in the International Organization for Standardization (ISO) standard 8501. (G. X. Chen, T. J. Kwee, K. P. Tan, Y. S. Choo, and M. H. Hong,2012).

1-5 Research Methodology:

The method comprises the step of focusing a laser beam upon the rust to effect evaporation of rust from the surface of the object. The method preferably further comprises the step of pulsing the laser beam. The present invention relates to removal of scale or rust (hereinafter called rust) from the surfaces of metallic objects, and more particularly to improvements in a method of removing undesirable products of oxidation from surfaces of metallic objects, such as ducts, pipes or sheets made of steel or other oxidizable material.

1-6 Objectives:

The main objectives of this work are:

1- To Clean Rust from Ionic object (flat and curved) using pulsed CO_2 Laser

2- To show the efficiency of laser in cleaning process of rust

1-7 Thesis Layouts:

This dissertation is consist of four chapters, chapter one provides a general information and aim of this study. A brief background on the basis of laser and laser interaction with matter are given in chapter two. Chapter three presents the method and results while, chapter four discusses the results and makes conclusion and final list of references.

Chapter Two

Basic Concepts

Chapter Two

Basic Concepts

2-1 Laser:

Lasers are devices that produce intense beams of light which are monochromatic, coherent, and highly collimated. The wavelength (color) of laser light is extremely pure (monochromatic) when compared to other sources of light, and all of the photons (energy) that make up the laser beam have a fixed phase relationship (coherence) with respect to one another. Light from a laser typically has very low divergence. It can travel over great distances or can be focused to a very small spot with a brightness which exceeds that of the sun. Due to these properties, lasers are used in a wide variety of applications in all walks of life.

The term “laser” is an acronym for (L) Light (A) Amplification by (S) Stimulated (E) Emission of (R) Radiation. To understand the laser, one needs to understand the meaning of the following terms. The term “light” is generally accepted to be electromagnetic radiation ranging from 1 nm to 1000 mm in wavelength. The visible spectrum (what we see) ranges from approximately 400 to 700 nm. The wavelength range from 700 nm to 10 mm is considered the near infrared (NIR), and anything beyond that is the far infrared (FIR). Conversely, 200 to 400 nm is called ultraviolet (UV); below 200 nm is the deep ultraviolet (DUV).(P. Sanjeevan and A. J. Klemm, 2000).

2-1-1 Properties of Laser Radiation:

Light produced from the lasers have several valuable characteristics not shown by light obtained from other conventional light sources, namely monochromaticity, directionality, laser line width, brightness, and coherence. These special characteristics make laser light as one of highly important source for various materials processing and characterization applications. These properties are discussed separately in the following subsections. (P. Sanjeevan and A. J. Klemm, 2000).

A) Monochromaticity:

Theoretically, waves of light with single frequency v of vibration or single wavelength λ are termed as *single color* or *monochromatic* light source. Practically, no source of light including laser is ideally monochromatic. *Monochromaticity* is a relative term. One source of light may be more monochromatic than others. Quantitatively, degree of monochromaticity is characterized by the spread in frequency of a line by v, line width of the light source, or corresponding spread in wavelength λ.(P. Sanjeevan and A. J. Klemm, 2000).

B) Directionality:

One of the most striking properties of laser is its directionality, that it’s output in almost parallel beam. Owing to its directional nature, it can carry energy and data to very long distances for remote diagnosis and communication purposes. In contrast, conventional light sources emit radiation isotropically; therefore, very small amount of energy can be collected using lens. Beam of an ideal laser is perfectly parallel, and its diameter at the exit window should be same to that after traveling very long distances, although in reality, it is impossible to achieve. Deviation in the parallelism of practical laser beam from the ideal is not due to any fault in the laser design, but due to diffraction from the edges of mirrors and windows (P. Sanjeevan and A. J. Klemm, 2000)

C) Coherence:

Coherence is one of the properties of the lasers, over other conventional sources, which makes them useful for several scientific and technological applications. The basic meaning of coherence is that all the waves in the laser beam remain spatially and temporarily in the same phase. Photons generated through stimulated emission are in phase with the stimulating photons. For an ideal laser system, electric field of light waves at every point in the cross section of beam follows the same trend with time. Such a beam is called *spatially coherent*. The length of the beam up to which this statement is true is called coherence length (LC) of the beam. Another type of coherence of the laser beam is temporal coherence, which defines uniformity in the rate of change in the phase of laser light wave at any point on the beam. The length of time frame up to which rate of phase change at any point on the laser beam remains constant is known as *coherence time* (t C).(P. Sanjeevan and A. J. Klemm, 2000)

D) Brightness:

Lasers are more intense and bright compared to other conventional sources such as the sun. Even a 1mW He–Ne laser, which is a highly directional, low divergence laser source, is brighter than the sun, which is emitting radiation isotropically. Brightness is defined as power emitted per unit area per unit solid angle.(P. Sanjeevan and A. J. Klemm, 2000).

2-1-2 Laser construction:

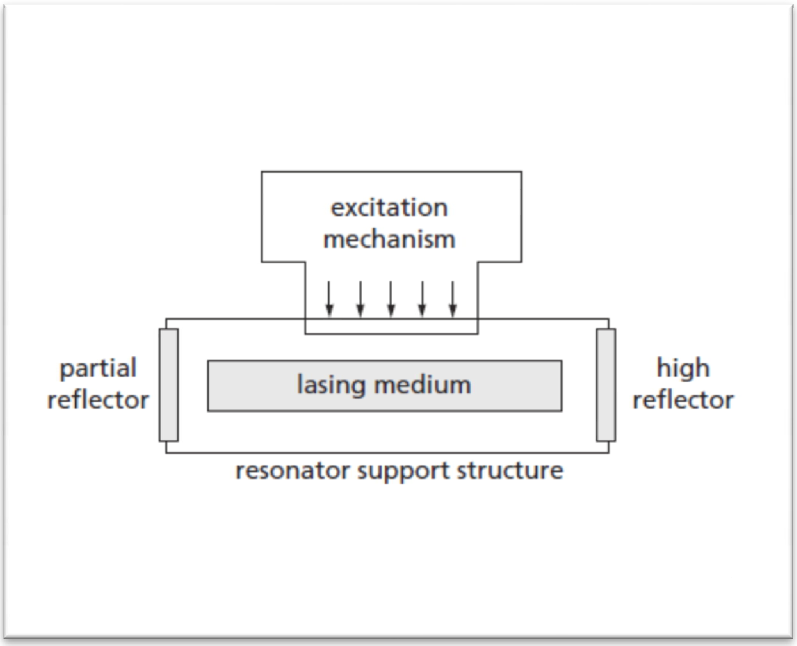

Fig (2-1): Schematic diagram of basic laser elements (William T.Sillivent, 2004).

Figure (2-1) shows parts of laser system. The lasing medium is pumped continuously to create a population inversion at the lasing wavelength. As the excited atoms start to decay, they emit photons spontaneously in all directions. Some of the photons travel along the axis of the lasing medium, but most of the photons are directed outside in other directions. The photons traveling along the axis have an opportunity to stimulate atoms they encounter and therefore photons will be emitted, but the ones radiating in other direction will not. Furthermore, the photons traveling parallel to the axis will be reflected back into the lasing medium and given the opportunity to stimulate more excited atoms. As the on-axis photons are reflected back and forth interacting with more and more atoms, spontaneous emission decreases, stimulated emission along the axis predominates, and we have a laser.

2-1-3 Lasing Action:

Although with a population inversion the ability to amplify a signal via stimulated emission is high, the overall single-pass gain is quite small, and most of the excited atoms in the population emit spontaneously and do not contribute to the overall output. To turn this system into a laser, the positive feedback mechanism is required so that to cause the majority of the atoms in the population to contribute to the coherent output. This is the so called a resonator, a system of mirrors that reflects undesirable (off-axis) photons out of the system and reflects the desirable (on-axis) photons back into the excited population where they can continue to be amplified.

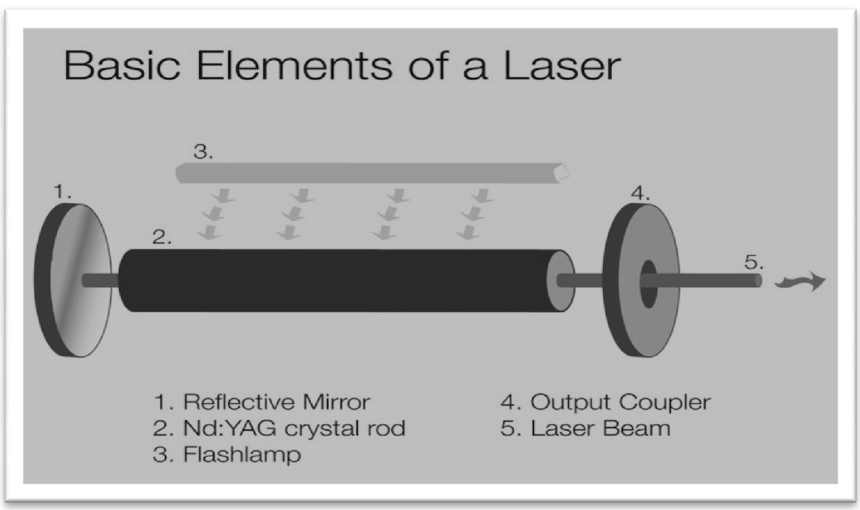

Fig (2-2): Schematic diagram showing basic Elements of laser

(William T.Sillivent, 2004).

2-1-4 Types of Laser:

Depending on the nature of the active media, lasers are classified into three main categories, namely, solid, semiconductor, liquid, and gas. Scientists and researchers have investigated a wide variety of laser materials as active media in each category since 1958, when lasing action was observed in ruby crystal. It is inconvenient to discuss all lasers having these materials as active media. Here, representative of active medium for each of the categories and their operating principle with energy level diagram is discussed. (William T.Sillivent, 2004).

A) Solid Laser:

Solid state lasers have active media obtained by embedding transition metals (Ti^{+3}, Cr^{+3}, V^{+2}, Co^{+2}, Ni^{+2}, Fe^{+2}, etc.), rare earth ions (Ce^{+3}, Pr^{+3}, Nd^{+3}, Pm^{+3}, Sm^{+2}, Eu^{+2},$^{+3}$, Tb^{+3}, Dy^{+3}, Ho^{+3}, Er^{+3}, Yb^{+3}, etc.), and actinides such as U^{+3} into insulating host lattices. Energy levels of active ions are only responsible for lasing actions, while physical properties such as thermal conductivity and thermal expansively of the host material are important in determining the efficiency of the laser operation. Arrangement of host atoms around the doped ion modifies its energy levels by means of crystal field.

Different lasing wavelength in the active media is obtained by doping different host materials with same active ions. The following are some of the important hosts: $Y_3Al_5O_{12}$, $YAlO_3$, $Y_3Ga_5O_{12}$, $Y_3Fe_5O_{12}$, $YLiF_4$, Y_2SiO_5, $Y_3Sc_2Al_3O_{12}$, $Y_3Sc_2Ga_3O_{12}$, $Ti:Al_2O_3$, $MgAl_2O_4$ (spinel), $CaY_4[SiO_4]_3O$, $CaWO_4$ (Scheelite), $Cr:Al_2O_3$, NdP_5O_4, $NdAl_3[BO_3]_4$, $LiNdP_4O_{12}$, $Nd:LaMgAl_{11}O_{19}$, $LaMgAl_{11}O_{19}$, $LiCaAlF_6$, $La_3Ga_5SiO_4$, $Gd_3Sc_2Al_3O_{12}$, $Gd_3Ga_5O_{12}$, $Na_3Ga_2Li_3F_{12}$, Mg_2SiO_4 (Forsterite), CaF_2, Al_2 BeO_4 (Alexandrite), and so on,. Active atom replaces an atom in the crystal host. Nd:YAG is one of the best solid lasing material. (William *T.Sillivent, 2004).*

B) Semiconductor Laser:

Semiconductor lasers also known as quantum well lasers are smallest, cheapest, can be produced in mass, and are easily scalable. They are basically p-n junction diode, which produces light of certain wavelength by recombination of charge carrier when forward biased is applied, very similar to the light-emitting diodes (LEDs). LEDs possess spontaneous emission, while laser diodes emit radiation by stimulated emission. Operational current should be higher than the threshold value in order to attain the condition of population inversion. The active medium in a semiconductor diode laser is in the form of junction region of two-dimensional layers. No external mirror is required for optical feedback in order to sustain laser oscillation. The reflectivity due to the refractive index differences between two layers or total internal reflection to the active media is sufficient for this purpose. The diodes end faces are cleaved, and parallelism of reflecting surfaces is assured. (William T.Sillivent, 2004).

C) Gas Laser:

Gas lasers are widely available in almost all power (milli watts to megawatts) and wavelengths is extended from ultraviolet to near infrared (UV-IR) and can be operated in pulsed and continuous modes. Based on the nature of active media, there are three types of gas lasers, ionic, and molecular. Most of the gas lasers are pumped by electrical discharge where the electrons in the discharge tube are accelerated by electric field between the electrodes. (William T.Sillivent, 2004).

D) Liquid Laser:

Liquids are more homogeneous as compared to solids and have larger density of active atoms as compared to the gasses. In addition to these, they do not offer any fabrication difficulties, offer simple circulation ways for transportation of heat from cavity, and can be easily replaced. Organic dyes such DCM (dicyanomethylene- methy -dimethylaminostyry-H-pyran), rhodamine , styryl, LDS, coumarin, stilbene, and so on, dissolved in appropriate solvents can act as gain media. When the solution of dye molecules is optically excited by a wavelength of radiation with good absorption coefficient, it emits radiation of longer wavelength, known as fluorescence. The energy difference between absorbed and emitted photons is mostly used by non radiative transitions and creates heat in the system. The broader fluorescence band in dye/liquid lasers fascinates them with the unique feature of wavelength tuning. Organic dye lasers, is tunable and coherent light sources, are becoming increasingly important in spectroscopy, holography, and in biomedical applications. (William T.Sillivent, 2004).

2-1-5 Laser Applications:

Industrial applications (Welding, Cutting), Scientific applications(laboratories research),Noncontact measurement, Marking and Scribing, Photolithography, Clinical and medical application, Surgical Applications

2-2 Rust:

Rust is the common name for a very common compound, iron oxide. Iron oxide, the chemical Fe_2O_3, is common because iron combines very readily with oxygen – so readily, in fact, that pure iron is only rarely found in nature. Iron (or steel) rusting is an example of **rust** an electrochemical process involving an anode (a piece of metal that readily gives up electrons), an electrolyte (a liquid that helps electrons move) and a cathode (a piece of metal that readily accepts electrons). When a piece of metal corrodes, the electrolyte helps provide oxygen to the anode. As oxygen combines with the metal, electrons are liberated. When they flow through the electrolyte to the cathode, the metal of the anode disappears, swept away by the electrical flow or converted into metal cations in a form such as rust. (Catherine Oertel,2005).

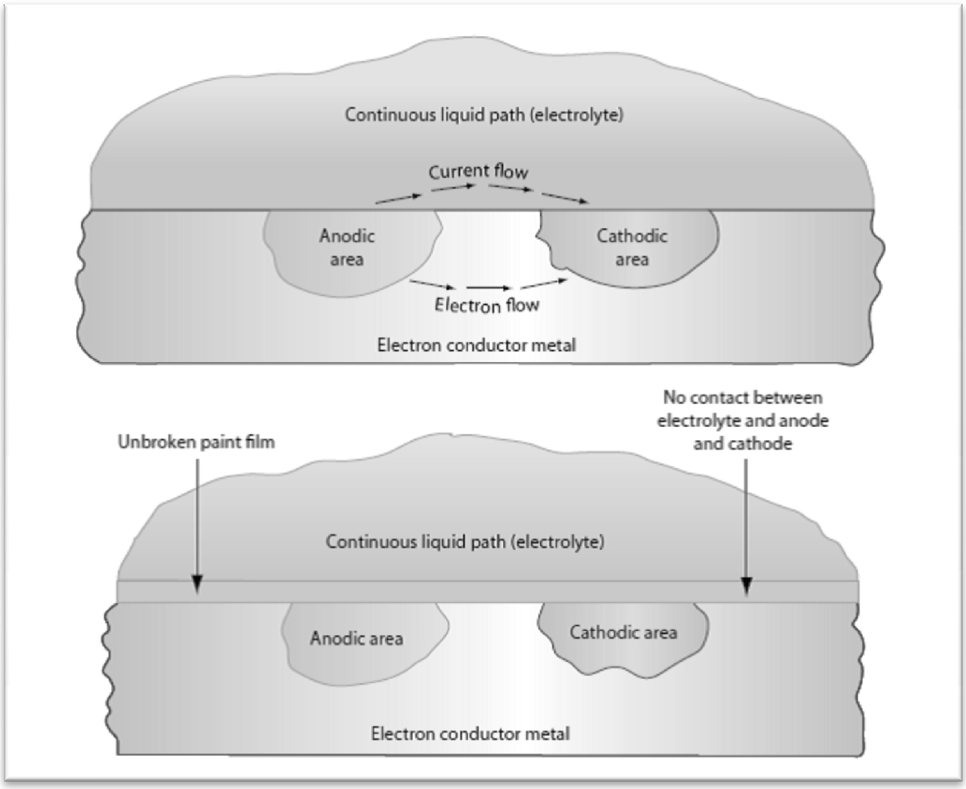

Fig (2-3): Electrochemical attack. (Catherine Oertel,2005).

Rusting of iron consists of the formation of hydrated oxide, $Fe(OH)_3$ or FeO(OH), and is an electrochemical process which requires the presence of water, oxygen and an electrolyte - in the absence of any one of these rusting does not occur to any significant extent. In air, a relative humidity of over 50% provides the necessary amount of water and at 80% corrosion is severe.

The process is complex and will depend in detail on the prevailing conditions, for example, in the presence of a small amount of O_2 the anodic oxidation will be:

$$Fe \rightarrow Fe_{2}+ {}^{+} 2e \qquad (2\text{-}1)$$

and the cathodic reduction:

$$2H_2O + 2e- \rightarrow H_2 + 2OH \qquad (2\text{-}2)$$

Overall:

$$Fe + 2H_2O \rightarrow H_2 + Fe_2+ \ 2OH \qquad (2\text{-}3)$$

$Fe(OH)^2$ and this precipitates to form a coating that slows further corrosion. If both water and air are present, then the corrosion can be severe with oxygen now as the oxidant the anodic oxidations:

$$2Fe \rightarrow 2Fe_2+ 4e \qquad (2\text{-}4)$$

and the cathodic reduction:

$$O_2 + 2H_2O + 4e- \rightarrow 4OH \qquad (2\text{-}5)$$

Overall:

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)^2 \qquad (2\text{-}6)$$

with limited O_2 magnetite is formed (Fe_3O_4), otherwise the familiar red-brown Fe_2O_3 H_2O "rust" is found. The presence of an electrolyte is required to provide a pathway for the current and, in urban areas, this is commonly iron (II) and sulfate formed as a result of attack by atmospheric SO_2 but, in seaside areas, airborne particles of salt are important. The anodic oxidation of the iron is usually localized in surface pits and crevices which allow the formation of adherent rust over the remaining surface area.(Prof. Robert J. Lancashire,2006).

2-2-1 The Metals suffer from Rust:

The term “corrosion” has its origin in Latin. The Latin word corroder means “gnawing,” and corroder means “gnawing to pieces.” Corrosion is a complex form of materials deterioration. It has been defined many ways, some of which are: “Corrosion is the destructive attack of metal by chemical or electrochemical reaction with its environment”. Corrosion may be defined as unintentional attack on a material through reaction with a surrounding medium. “Eating away” of metals. “Corrosion is the deterioration of a substance or its properties because of a reaction with its environment .There have been recent tendencies to include the destruction of materials other than metals such as glass, plastics, ceramics, leather, and cloths etc., which find usage in modern society.(X. Naixin, L. Zhao, C. Ding, C. Zhang, R. Li and Q. Zhong; Corros. Sci. , 2002).

All metals and alloys are electrically active and have a specific electrical potential in a given chemical environment. This potential is commonly referred to as the metal’s “nobility.”The less noble a metal is, the more easily it can be corroded. The metals chosen for use in aircraft structures are a studied compromise with strength, weight, corrosion resistance, workability, and cost balanced against the structure’s needs.

Table (2-1): The series of metals and alloys suffer from rust.

+ corroded End (anodic or least noble)	Brass
Magnesium	Copper
Magnesium alloy	Bronze
ZnC	Copper-nichel Alloy
Aluminum	Monel nickel-Copper Alloy
Cadmium	Silver
Steel or Iron	Nickel (passive)
Cast Iron	Inconel nickel-chromium alloy
Chromium Iron (active)	Chromium – Iron
Type 304 Stainless (active)	Type 304 Stainless (passive)
Type 316 Stainless (active)	Type 316 Stainless (passive)
Lead-tin solder	Hastelloy Alloy C (passive)
Lead	Silver
Tin	Titanium
Nickel (active)	Graphite
Inconel – chromium alloy (active)	Gold
Hastelloy Alloy C (active)	Platinum
	– protected End (catholic or noble)

2-2-2 Standard methods to removal rust:

Several standard mechanical and chemical methods are available for rust removal. Mechanical methods include hand sanding using abrasive mat, abrasive paper, or metal wool; and powered mechanical sanding, grinding, and buffing, using abrasive mat, grinding wheels, sanding discs, and abrasive rubber mats. The method used depends upon the metal and degree of rust.

The protection of iron and steel against rusting takes many forms, including: simple covering with paint; coating with another metal such as zinc (galvanizing) or tin; treating with "inhibitors" such as chromate(VI) or (in the presence of air) phosphate or hydroxide, all of which produce a coherent protective film of $Fe2O3$. Another method uses sacrificial anodes, most usually Mg or Zn which, being higher than Fe in the electrochemical series, are attacked preferentially. In fact, the Zn coating on galvanized iron is actually a sacrificial anode. .(Prof. Robert J. Lancashire,2006).

2-3 Laser interaction with metal:

Shortly after the advent of the first ruby laser in 1960, experimental investigations of laser effects on materials began to appear. The first lasers developed were too weak and too unstable for any industrial use, but since the early 60's the field of lasers and photonics has evolved and expanded at such a rate that modern lasers are capable of cleaning, marking, cutting, welding, drilling and surface treating diverse forms of materials with remarkable precision.(David Bergström,2008)

As higher powers, better beam qualities and an expanded number of wavelengths have become available, more and more applications are being invented, investigated and brought into practical use. For a laser metal processing application to be possible, the electromagnetic energy of the laser light needs to be transformed into thermal energy inside the metal. The amount of transformed energy is determined by the light absorption mechanisms in the metal. It is this "secondary" type of energy, the absorbed energy, rather than the laser beam itself, that is available for heating the metal and producing the effect that we want, whether it be cutting, welding, drilling or so on. (David Bergström,2008)

Laser absorption in a metal depends on a number of different parameters, involving both the laser and the metal. The laser parameters of importance are the wavelength (or colour) of the light, the angle with which the beam impinges on the metal surface and the polarization of the beam, which is related to how the electric field in the light wave is oriented. Laser can also, in some circumstances, be dependent on the intensity, which is a combination of the power and focal spot size of the laser beam. (David Bergström,2008)

Metals also naturally have a layer (or several layers) of oxides on the surface and the chemical and optical properties of the oxides can often be very different from the properties of the metal or alloy underneath. then, for instance get the situation depicted in where the light is “caught” by the oxide layer which may further increase the absorption. (David Bergström,2008)

Basically, the laser is bright enough and focused enough that anything that absorbs the light strongly will get heated to plasma. A CO_2 laser can put out ~1000 watts of power in the infrared (10 µm) that can be focused to a strip or spot smaller than a millimeter. A material that absorbs at that wavelength will be heated very quickly. At lower powers you can use this for laser engraving. But for rust removal you can dump enough heat into the rust to heat it to plasma.

Metals reflect light very well, especially in the infrared. So once the rust burns off, the laser reflects off the iron rather than heating it up. Edit I talked about CO_2 lasers as an example, but many rust removal systems actually use diode pumped YAG lasers (1.06 µm wavelength). The mechanism is still the same (laser ablation). A YAG laser will be less damaging to skin (since water absorbs less), but would be more nervous about eye damage (it is harder to filter out 1.06 µm light from visible light compared to 10 µm) When a metal interacts with light the electric field of the light is screened by free electrons.

In general the better the conductor the metal is the easier electrons can move. Since light is an oscillating electromagnet field, the more easy an electron moves the higher oscillation (lower wavelength light) it can screen. So iron is a poor conductor and aluminum is better, so aluminum can screen a lot higher frequencies than iron. Absorption depth is the depth at which light is absorbed. You'll notice that as the wavelength of the light becomes longer so does the absorption depth. This is analogous to the skin effect in which current in a conductor only flows a certain depth on the surface at AC frequencies. The higher the AC frequency (lower the wavelength) the thinner the layer .

Now even though the depth is increasing it doesn't mean more is absorbed, it just means the field that hasn't been reflected penetrated by this amount. I regularly evaporate gold in my line of work and even at ~ 30nm you can just about see though it. It's still highly reflective but some light can pass through as well as not all is absorbed. The stuff that isn't absorbed however is still subject to high reflectivity; it's not just going from air to metal that is highly reflective; the opposite is also true generally ablation is the mechanism. Ablation is achieved by laser pulsing, which result in high peak powers and low (hundreds of Watts) average powers. The high intensity and short period of the laser pulse combine to result in extreme heating rates. In the duration of the pulse, either the surface oxidation is directly heated and vaporized (typical for 10µm wavelength CO_2 lasers) -the metal beneath it is heated and vaporized resulting in high pressure, mechanically removing the oxide (typical for 1µm wavelength fiber, disk, and diode lasers) The difference in mechanism is a result of the transmission characteristics of the oxide. The oxide is predominately transmits the 1µm wavelength, with high absorption in the metal. For 10µm however, the oxide predominately absorbs the laser.(William T.Walter ,1982).

The harnessing of laser irradiation for surface treatment has been practically made at once as the first lasers were developed. Both the gas discharge IR lasers on CO2 molecule transitions and solid-state Nd:YAG lasers have gained major application in this field'. CO_2-based laser with high efficiency and specific output parameters has a comparatively big wavelength and limited gas mixture lifetime. The Nd:YAG laser also has a high efficiency and it provides operation both in continuous and pulsed repetition modes (up to 100 kHz).(Victor F. Tarasenko,2001)

2-4 Advantages of using laser in cleaning rust:

Abrasive free (non contact)

Chemical free

Cleaning of sensitive surfaces

Removal rates controllable

Manual / automated technique

2-5 Applications of using laser in cleaning rust:

Local pre-treatment of coated parts

Removal of oil and grease [*as pre-treatment for welding*]

scale removal of weld seams

Preparation of bonding surfaces by removal of scales and grease

Removal of paint on zinc coated metal sheets

Chapter Three

Experimental Part

Chapter Three

Experimental Part

3-1 Introduction:

This object describes the review of laser cleaning methods for construction materials. The effects of laser radiation on substrate and the factors affecting the efficiency of rust removal are discussed. The laser cleaning (more precisely a degree of removability) depends on a large number of factors including surface roughness, porosity, cavity, moisture content, chemical/physical properties and thickness of rust, laser parameters such as energy, wavelength, duration and number of pulses, scanning speed and others. The most notable lasers already in use for laser cleaning are CO_2 laser, Nd:YAG laser, high power diode laser and a number of excimer laser systems. They have different properties and offer different advantages in practical applications. For example, excimer lasers can be used to remove varnish and unwanted paint layers successfully.

3-2 Material and equipment:

3-2-1 Equipment:

Fig (3-1) illustrates a portion of an apparatus for the practice of the method which embodies the present invention. More specially, Fig (3-1) shows schematically a gas laser (e.g., a CO_2 gas laser) which directs a beam into a beam guide including several 90-degree elbows and pipes. The elbows contain reflecting mirrors. The reference characters denote couplings (e.g., threaded connections) between the pipes and the respective elbows. The radiation emitting output of the laser is connected to the inlet of the guide, and the outlet of that portion of the guide which is shown in Fig (3-2) is connected with a further portion or mouthpiece of the guide.

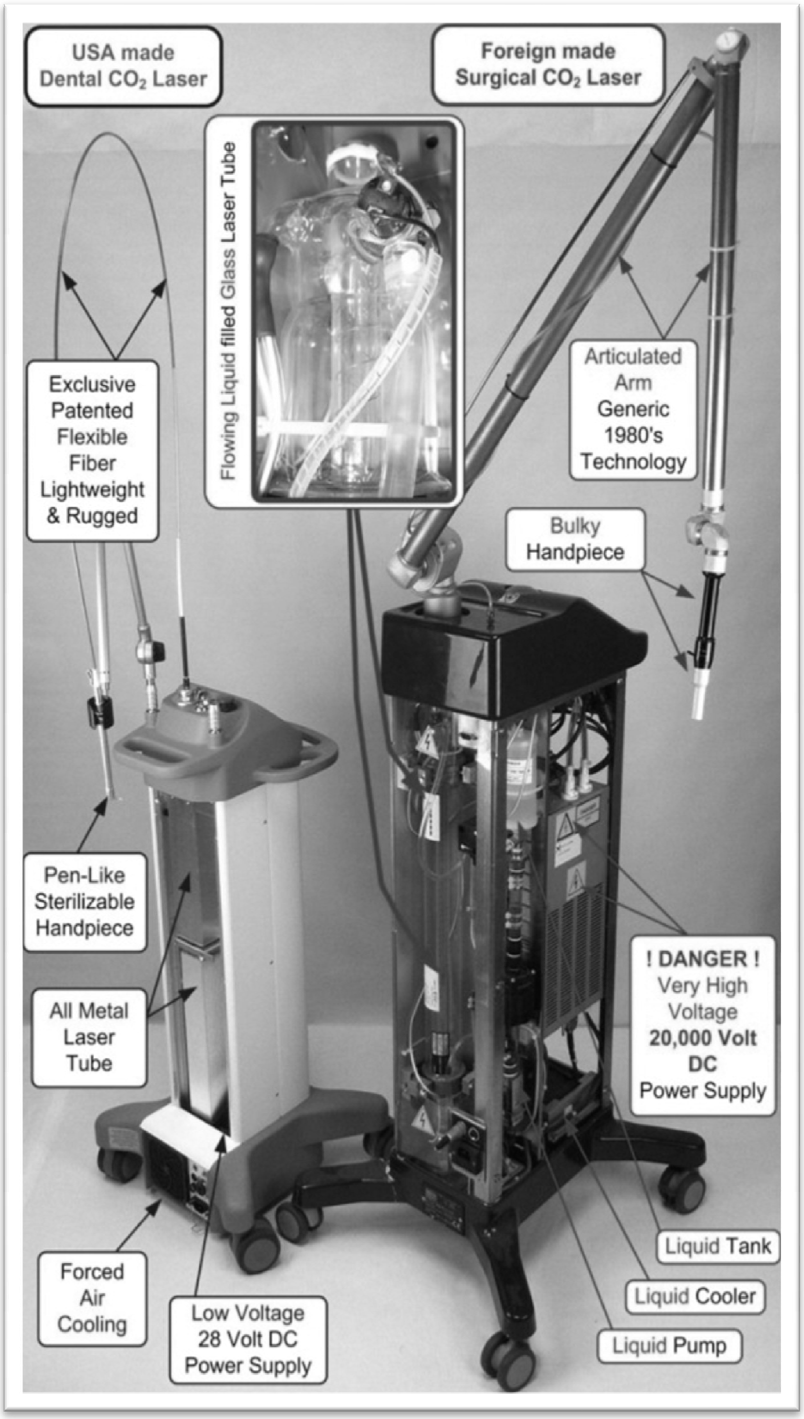

Fig (3-1): CO_2 laser system

Table (3-1): Laser parameters used to removal the rust

Laser type used	CO_2 gas laser (pulsed) with wavelength 10.6 µm
Output power	1 – 30 W
Pulse duration	1 – 500 HZ
Pulse frequency	1 – 1000 HZ
Spot size area	0.3 – 2 mm^2

3-2-2 Samples:

Two objects was used from metal by different shape , sample (a) it flat piece with high concentration from rust .(4cm length, 1.2 cm width)

Fig (3-2): sample (a) iron with rust

Sample (b) from iron it carved and with low concentration from rust to simulated a difficult parts that cannot processing by common method

(3.7 cm length, 1.5 cm width)

Fig (3-3): Sample (b) from iron with carved shape

3-3 The method:

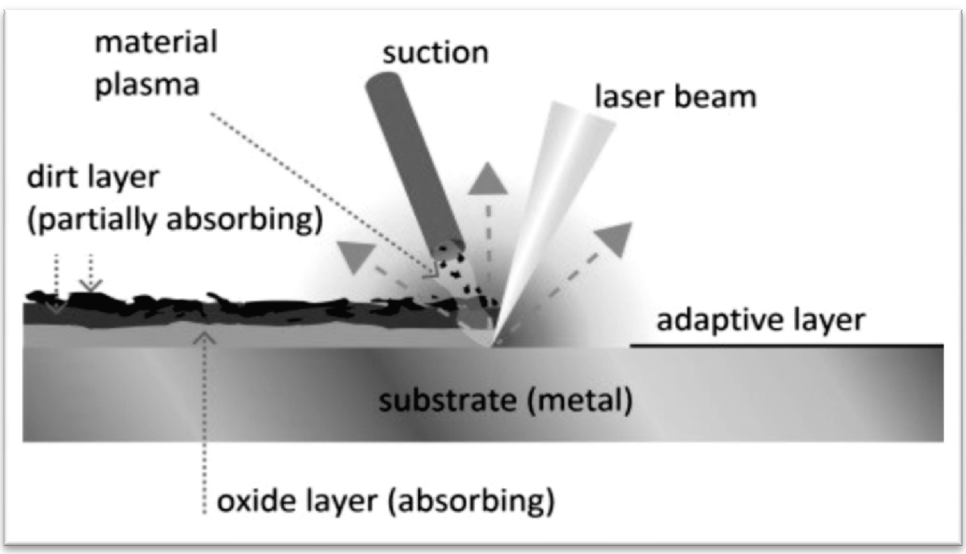

Fig (3-4): Treated surface by laser (United States Patent, 27Oct1980).

The oxide-coated surface of a metallic object to be treated was exposed to a beam issuing from a transversely excited atmospheric-pressure CO_2 laser with a wavelength of 10.6 µm. Under such circum stances, the area of 1 mm^2 has been found to be particularly satisfactory. It has been found that output density should not be too high in order to avoid excessive power losses as a result of pronounced ionization of air at higher energy densities. The metallic objects which were treated constituted scrap of the type found in a scrap metal yard. The objects included **(a)** smooth steel with a rectangular shape outline, **(b)** strongly erode cast steel slit; The laser beam was capable of completely removing the oxide layer from all of the objects **(a)** and **(b).**The rate of rust removal (namely, the number of pulses needed for complete removal of rust from an area of 1 mm^2) was practically independent of the nature of metallic material; it depended primarily on the degree of corrosion of the test object. One to three pulses were needed for removal of rust from slightly corroded surfaces; number of pulses was between two and for removal of oxide layers from surfaces with a reasonably pronounced oxide layer; and the number of pulses had to be increased between 300 and 400 for removal of rust from strongly corroded metallic surfaces. Subsequent metallographic examination of the texture of treated metallic objects failed to reveal any undesirable, dangerous and/or damaging changes as a result of exposure to laser beams.

The results of the discussed experiments indicate that, for practical application of the improved method, resort should be had to a laser with an average power output of or in the range of 1 - 30 W. The pulse energy should be in the range of 0.3 J and the pulse frequency in the range of approximately 400 hertz. In the case of a metallic object exhibiting a medium oxide layer, four pulses per square millimeter of the metallic surface were needed to remove the layer.

Chapter Four

Results and Discussion

Chapter Four

Results and Discussion

4-1 Introduction:

Nowadays lasers are used widely in analysis, monitoring, and conservation of cultural heritage objects. The unique properties of laser are being responsible for high control, selectivity, minimal contact, and versatility attributes that are essential for any conservation intervention on such valuable objects.

In metal conservation, there have been plenty of studies aiming to use lasers to remove different corrosion layers encrustations and coatings from various metal surfaces with mixed results still many issues are not yet resolved and thus the application of lasers in metal conservation is not universally accepted.

Such issues include the preservation of the original surface, the understanding of the formation of unwanted laser-induced alteration layers, the final morphology of the irradiated surfaces, and the establishment of a methodology for the everyday.

4-2 Results and Discussion:

The goal of this work is to find the best method for cleaning iron, objects, which often require controlled cleaning of the surface from corrosion products without a□ecting the metal substrate.

Next figures shows a series of cross-sections on artificially corroded iron figure (4-1, 2, 3,4,5,6,7) shows the formation of corrosion spots both inwards and out wards the original surface.

The next figures (4-1, 2, 3,4,5,6,7) show the result of two sample (a), (b) steel with rust layer before and after interaction with laser:

Fig (4-1): Sample (a) before interaction with laser

Fig (4-2): Sample (a) after interaction with laser

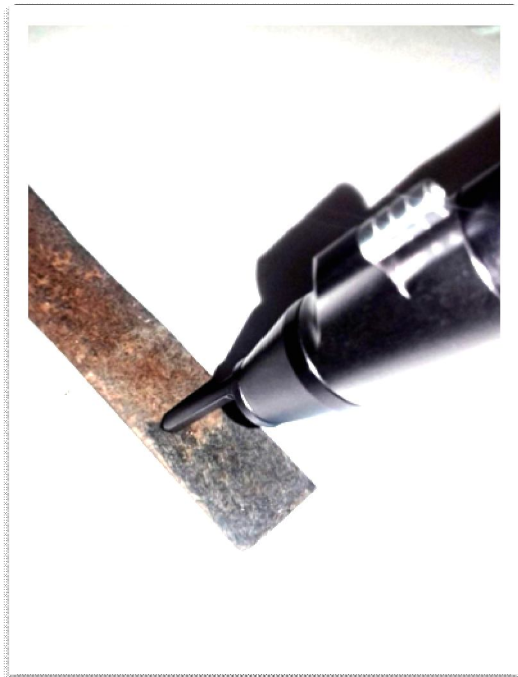

Fig (4-3): Sample (a) during interaction with laser

Fig (4-4): Sample (a) after finished particular cleaning

Result of sample (a) after cleaning by Laser show the rust layer is removing partly to show the different between interactions with Laser. The scan speed it will medium to prove well result to removing rust layer. The spot size of Laser beam should be greater to cover large area from the object

Fig (4-5): Sample (b) before interaction with laser

Fig (4-6): Sample (b) after interaction with laser

Fig (4-7): Sample (b) after cleaning by laser

Result of sample (b) after cleaning by Laser show the rust layer is removing partly to show the different between interactions with Laser. The scan speed it will medium to prove well result to removing rust layer. The spot size of Laser beam should be greater to cover large area from the object. This sample it's carved the Laser system it cleaning well and fast comparing to common methods

4-2 Conclusions:

A method comprising the step of focusing a laser beam upon the rust to heat the rust to evaporation temperature and to thereby effect evaporation of rust from the surface, the parameters of laser, pulse duration between 400 ns. power output 0.3 J, frequency is 500 hertz.

4-3 Recommendations:

- Use morphology imaging to the surface
- Use different types from metal
- Use SEM imaging to the surface
- Use large spot size to cover wide area
- Use different parameters to the laser

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