

REPUBLIC OF TURKEY  
YILDIZ TECHNICAL UNIVERSITY  
GRADUATE SCHOOL OF SCIENCE AND ENGINEERING

INVESTIGATION OF THE EFFECTS OF LASER SURFACE  
TREATMENT ON BRONZE PROPELLERS

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TREATMENT ON BRONZE PROPELLERS**

A thesis submitted by İbrahim ÇINAR in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE** is approved by the committee on 29.07.2021 in Department of Naval Architecture and Marine Engineering, Program of Naval Architecture and Marine Engineering.

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İbrahim INAR

Signature

*Dedicated to my primary school teacher Suna Baran  
meeting her was the luckiest moment ever*



## ACKNOWLEDGEMENTS

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Improving corrosion resistance, hardness and hydrophobic properties of bronze marine propellers by means of laser surface treatment is objective of the present study.

I would like to thank Laser Technologies and Application Center of Kocaeli University where I did experiments of the current study and personnel of the center.

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## LIST OF SYMBOLS

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Al	Aluminium
$i_{aM}$	Anodic partial electric current density
$^{\circ}\text{C}$	Celsius Degree
Cr	Chrome
$R_c$	Corrosion resistance
C	Coulomb
n	Dimensionless charge number
$i_{corr}$	Electric current of corrosion
$V_{corr}$	Electric potential of corrosion
E	Electrode potential
F	Faraday constant
$\rho$	Gravitational density
z	Height above a predetermined level
HCl	Hydrochloric acid
Fe	Iron
Pb	Lead
Mo	Molybdenum
Ni	Nickel
N	Nitrogen
$K_2Cr_2O_7$	Potassium dichromate
P	Pressure
a	Relative activity of ions
$R_e$	Resistance to cavitation erosion

$E^\circ$	Standard electrode potential
$H_2SO_4$	Sulphuric acid
T	Temperature
Sn	Tin
R	Universal gas constant
V	Velocity
Zn	Zinc



## LIST OF ABBREVIATIONS

---

ASTM	American Society for Testing and Materials
CCT	Critical crevice temperature
CPT	Critical pitting temperature
EDS	Energy dispersive X-Ray
EMF	Electro-motor force
FHWA	Department of Transportation Federal Highway Administration
GDP	Gross Domestic Product
HAZ	Heat affected zone
LSA	Laser surface alloying
LC	Laser cladding
LD	Laser dispersion
LSM	Laser surface melting
LST	Laser surface treatment
LTH	Laser transformation hardening
MMCs	Surface metal matrix composites
PREN	Pitting resistance equivalent number
SCC	Stress corrosion cracking

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# Investigation of the Effects of Laser Surface Treatment on Bronze Propellers

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Department of Naval Architecture and Marine Engineering

Master of Science Thesis

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Marine propellers are mostly exposed to corrosive and erosive environments due to working conditions. Propellers are designed to endure under hard conditions. Material selection and design of the propeller must ensure enough strength and flexibility. On the other hand requirements of surface properties to endure under working conditions may conflict with bulk metal properties. Laser surface treatment is very effective method to differ surface properties while bulk metal remains intact. In the present study effects of laser surface treatment to corrosion resistance, hardness and hydrophobicity properties of bronze marine propellers are investigated. Hardness tests are applied in accordance with Standard Test Methods for Vickers Hardness and Knoop Hardness of Metallic Materials before and after laser surface treatment processes. To expose the materials to corrosive environment by following Standard Practice for Modified Salt Spray (Fog) Testing, salt spray test is applied. After the salt spray test, by means of optical microscope the results are observed and evaluated. To examine changes in micro structure and evaluate the results Standard Practice for Microetching Metals and Alloys is followed and etching methods are applied. Corrosion resistance is improved with a significant rate. Some of the laser surface treatment parameters are very succesful to improve corrosion resistance. On the other hand hardness did not increase sufficiently. Laser surface treatment methods with added material may be beneficial to achieve improvement in hardness. Contact angle measurements demonstrates that approximately superhydrophobic and hydrophilic surfaces are obtained. Hydrophilic surfaces may be beneficial for chemical coating applications with more adhesive behaviour.

**Keywords:** Laser surface treatment, corrosion, ship propellers



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# Lazerle Yüzey İşlemenin Bronz Pervaneler Üzerindeki Etkilerinin Araştırılması

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Çalışma şartları nedeniyle gemi pervaneleri genellikle korozif ve aşındırıcı ortamlara maruz kalır. Pervaneler zor koşullara dayanacak şekilde tasarlanmıştır. Pervanenin malzeme seçimi ve tasarımı; yeterli mukavemeti ve esnekliği sağlamalıdır. Öte yandan, çalışma koşullarına dayanacak yüzey özelliği gereksinimleri, ana metal özellikleri ile çelişebilir. Lazerle yüzey iyileştirme, ana metal olduğu gibi kalırken yüzey özelliklerini farklılaştırmak için çok etkili bir yöntemdir. Bu çalışmada bronz gemi pervanelerinin korozyon direnci, sertlik ve hidrofobiklik özelliklerine lazerle yüzey işlemenin etkileri incelenmiştir. Sertlik testleri, lazerle yüzey işleme uygulamalarından önce ve sonra "Standard Test Methods for Vickers Hardness and Knoop Hardness of Metallic Materials" dokümanına uygun şekilde gerçekleştirildi. Numuneleri korozyona maruz bırakmak için "Standard Practice for Modified Salt Spray (Fog) Testing" dokümanı takip edilerek tuz püskürtme testi uygulandı. Testten sonra sonuçları incelemek ve değerlendirmek için optik mikroskop kullanıldı. Mikro yapıda meydana gelen değişiklikleri gözlemlemek için "Standard Practice for Microetching Metals and Alloys" dokümanı takip edilerek dağlama işlemleri gerçekleştirildi ve sonuçlar değerlendirildi. Korozyon direnci önemli ölçüde geliştirildi. Bazı lazer parametrelerinin korozyon direncini geliştirmede çok başarılı olduğu görüldü. Diğer yandan sertlik değerlerinde kayda değer bir gelişme gerçekleşmedi. Ekstra materyal kullanılan lazerle yüzey işleme yöntemleri sertliği geliştirmeyi başarmak için faydalı olabilir. Kontak açısı ölçümleri süper hidrofobik özelliklere yakın ve hidrofilik yüzeyler elde edildiğini gösterdi. Hidrofilik yüzeyler tutucu özellikleri ile kimyasal kaplama uygulamalarında faydalı olabilirler.

**Anahtar Kelimeler:** Lazerle yüzey iyileştirme, korozyon, gemi pervaneleri



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**YILDIZ TEKNİK ÜNİVERSİTESİ  
FEN BİLİMLERİ ENSTİTÜSÜ**

# 1

## INTRODUCTION

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Corrosion is a huge problem which causes to decrease in operating life and efficiency of industrial devices and materials. Corrosion is also risky factor for safety and health. Especially food industry must control corrosion to avoid harmful or poisonous contamination. On the other hand while invisible corrosion damage can take very long time but after the damage advanced unexpected cracking can be matter of time. Fighting against corrosion requires highly experienced designers and operators for industrial production. Surely, corrosion awareness of the end products' consumers also has an important role to prevent corrosion. Consumers should have enough awareness as well as producers.

Significant part of national incomes of countries wasted by corrosion. According to Department of Transportation Federal Highway Administration (FHWA) and National Association of Corrosion Engineers NACE International (The Corrosion Society) the sum of direct loss in U.S. because of corrosion is calculated at \$276 billion each year. This is equal to 3.1% of the U.S. gross domestic product (GDP) in 1998. This report is prepared according to analysis of 26 corrosion related sector. After that by extrapolation, countrywide amount is evaluated. Indirect loss because of corrosion is estimated roughly equal to direct costs, i.e. total of indirect and direct loss is 6% [1].

Maritime industry is one of the worst effected businesses by corrosion. Because of the salt rate of ionized and conductive sea water; sea atmosphere with high relative humidity and chloride ions; cavitation on propeller which has synergistic effect with corrosion [2]; chemical goods with aggressive corrosive characters which transported by ships are some important reasons make corrosion prolonging and dangerous for marine industry. There must be enough precautions against to corrosion to avoid the risks.

Corrosion and its side effects are evaluated as the greatest influence on the time-related structural deterioration of ships and metals used in marine industry [3]. Corrosion can lead to hazardous results like fatigue crack, reduction in thickness,

brittle fracture. These consequences have potential to cause loss of life and property. If the ship carries dangerous chemicals there may be an environmental disaster risk. At the ships' design step, increasing the least thickness value to tolerate corrosion loss to provide ships enough strength to endure for expected life time or until planned replacement.

## **1.1 Literature Review**

### **1.1.1 Marine Environment**

The aggressive corrosive environment of sea atmosphere and seawater is related to very high concentration of chloride ions. This is very tiny ion which can diffuse fast and make medium highly conductive. It can produce local acidity when it is fall under hydrolysis reactions which counteract to passivation on the surface of metals. Dissolved solid concentration in seawater changes with geography but there is not enough data convincing to say corrosion rate changes with geography. On the other hand there is enough investigation to persuade many corrosion experts to say high oxygen rate (dissolved) in seawater leads to high corrosion rate [4].

When any kind of design required in a corrosive environment some factors must be considered to determine the material of structure. Important points for material selection listed as follows:

- Mechanical strength
- Corrosion resistance
- Cost
- Accessibility
- Hot workability and machinability
- Ease of maintenance

Corrosion has never been the only factor to consider. Of course there are many other factors though sometimes corrosion is the most important one. Design is already complex process. Moreover corrosion makes it even harder. The factors like corrosion resistance ( $R_c$ ), mechanical strength, hot workability, machinability are related to chemical composition and micro structure of material. On the other hand cost, accessibility and ease of maintenance are related to local factors, economical

situation, geography, transportation, equipment and qualified operator too. According to production steps and operating conditions preponderate factors change.

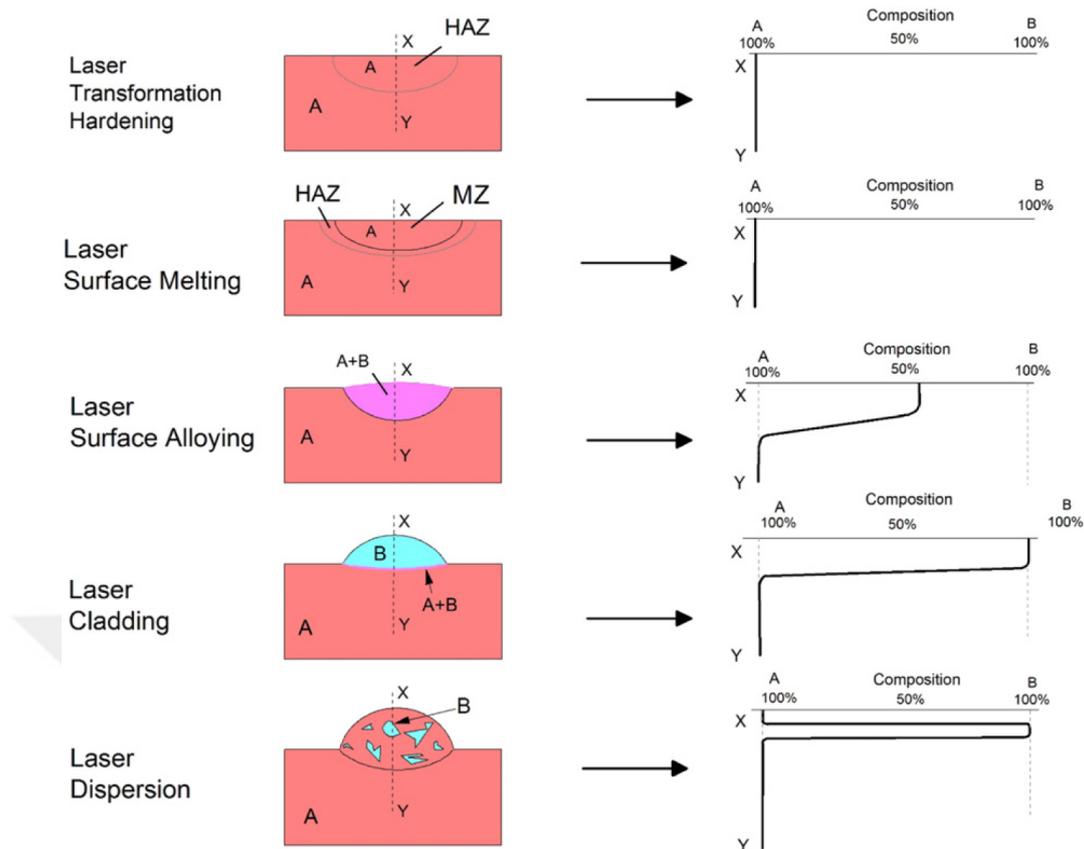
Propeller is the most attacked part of ship by corrosion because of the high relative velocity between seawater and propeller which can lead to synergistic effect of corrosion with cavitation. Also absence of protective coating on propeller is another reason makes it target of corrosion.

### **1.1.2 Importance of Lasers For Material Surface Properties**

Fighting against corrosion and cavitation without changing working conditions is mostly related to surface and surface coating. If the surface is not strong enough, changes in surface properties are required. On the other hand mechanical properties of substrate is supposed to be stable. This can be provided by laser surface treatment (LST). Laser beam hits surface with extremely concentrate energy and very fine layer of metal absorbs it. Immediately rising and decreasing temperature affect only surface and substrate behaves as heat sink. This process may lead to phase changes in micro structure, melting and immediate solidification. If there is added material; process can result with alloying, dispersion and cladding. Choosing the right process can provide with treatment in surface properties. Fig. 1.1 illustrates types of LST with and without added materials [5].

LST can create many surface and bulk material couples which the surfaces have different character from the substrate and consist of very thin layer. This is an enormous flexibility for designers. Also the added material (mostly costly compared to bulk metal) may spent in very small amounts. Without using costly material in substrate, very qualified surfaced end products can be produced. Laser is very effective method compared to conventional coating or heat treatment methods. To sum up advantages of LST:

- Clean and environmentalist technology.
- There is not complicated heat treatment process and LST can be applied in very short time.
- After first investment it is very economical and consumes energy efficiently.
- The methods with added material laser surface alloying (LSA), laser cladding (LC), laser dispersion (LD) creates very strong bond between processed surface and bulk metal.



**Figure 1.1** Types of laser surface treatment [5]

- With very tiny heat affected zone (HAZ) LST does not change bulk metal properties while modifying surface.
- Final surface does not need chemical process or quenching. It is free of dirt.
- It is suitable for automation.

On the other hand LST has some limitations. To sum up limitations of LST:

- Beam diameter is small that prevents applying LST to large surfaces efficiently. On the other hand large surfaces can be processed by rectangular spotted (edges can be approximately 1 inch) diode lasers.
- Reflective surfaces do not absorb most of laser energy.
- Complex structures with invisible surfaces are not suitable for LST. Although LST is very feasible for automation, if the surface has parts out of sight laser beam may not reach there.

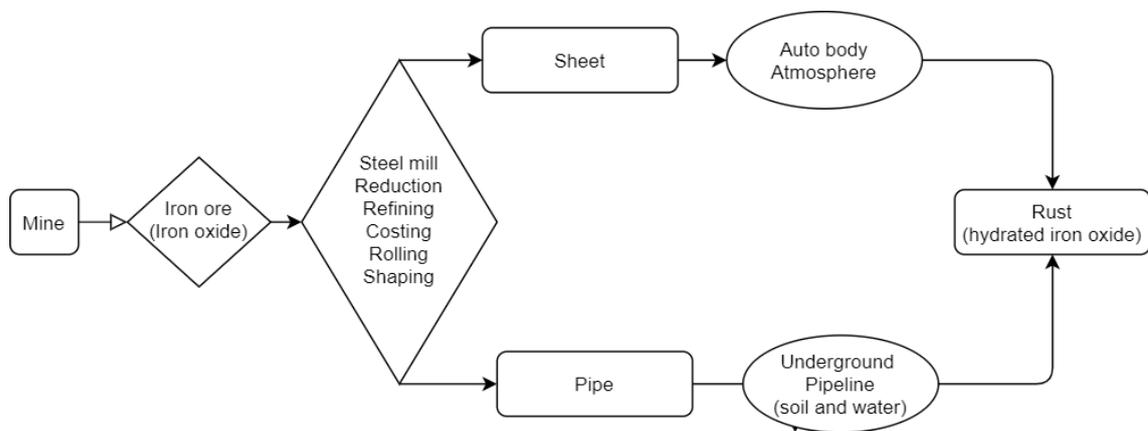
### 1.1.3 Corrosion

#### 1.1.3.1 Definition of Corrosion

Corrosion is defined in similar ways by various references, but there are few slight differences in explanations. To understand corrosion simply, two important documents are sufficiently directive.

According to the definition of the American Society for Testing and Materials (ASTM), corrosion is either a chemical or electrochemical reaction between a material, generally metal, and the medium around it which causes the material to deteriorate [6]. Although some other references claim that corrosion definition should include only metals, to get sufficient results from engineering processes we may examine both metals and nonmetals.

According to Fontana, corrosion is a reversal extractive metallurgy process. In Fig. 1.2 the extractive metallurgy process is illustrated [7]. This process starts from mining ore and ends with refined and alloyed metals. Metal ores have stable compounds of metal elements like iron oxide. Metal alloys are less stable compared to those compounds. So corrosion is a natural and unpreventable process because of thermodynamic laws. Unless the atmosphere or medium is inert or vacuumed, corrosion exists, but it is possible to slow down the corrosion. The aim of fighting corrosion is having an economical solution by an environmentalist way.



**Figure 1.2** Extractive metallurgy

The Iron Pillar of Delhi is a riveting example for resistance to corrosion. It endures corrosion for the last 16 centuries. Fig. 1.3 demonstrates the outlook of the Iron Pillar of Delhi [8]. The Iron Pillar of Delhi by itself demonstrates skills and technology of ancient Indians in producing qualified iron objects. Some claim that the achievement against corrosion is related to the climate of Delhi. Because the relative humidity in Delhi does not reach 70% for most of the year [9].



**Figure 1.3** Outlook of Iron Pillar of Delhi [8]

Some researchers consider material structure as main factor about the  $R_c$  of Iron Pillar of Delhi. The allegations stated in this regard that the purity of the iron, existence of phosphorus and not contaminated by S/Mn, grain form of metal which enveloped by slag, passive layer formation thanks to existence of slag material and the generation of phosphate film are the reasons to achieve this strong durability [9].

### 1.1.3.2 Mechanism of Corrosion

Most of the known metals are not stable. They are produced by artificial extractive metallurgical procedures. Although platinum and gold exist in nature as metallic state, these two elements are only exceptions. All materials have tendency to form the most stable thermodynamic state. Corrosion is the mechanism which extracted metals form more stable compounds, generally oxides or sulfides. These compounds are natural forms of corroded elements. Although corrosion reactions can be chemical or electro-chemical, usually most of corrosion reactions which occur in nature are electro-chemical [10].

Simultaneous anode and cathode reactions result in corrosion. According to ASTM anodic reaction rate and cathodic reaction rate are equal and represents corrosion rate [6]. The corrosion rate is related to anodic and cathodic reaction kinetics. When each anodic and cathodic electro-chemical parameters are explicit, in theory the corrosion rate may be foresaw. Faraday's law states: At each potential  $V_m$ , there is a linear relationship among the dissolution rate of metals and the anodic partial electric current density  $i_{aM}$ :

$$V_M = \frac{i_{aM}}{nF} \quad (1.1)$$

where dimensionless charge number represented by n means amount of the electrons exchanged while metal dissolves, Faraday constant symbolized by F (F=96,485 C/mol). When external polarization does not exist, the metals which touch to oxidizing electrolytic medium create a certain potential (corrosion potential) which is symbolized by  $E_{corr}$ . Current density of partial anodic reaction is equal to corrosion current density ( $i_{corr}$ ). Therefore following equation is obtained:

$$V_{corr} = \frac{i_{corr}}{nF} \quad (1.2)$$

Anodic partial reaction means oxidation of metals and cathodic partial reaction means reducing oxidization agent. Following reaction demonstrates zinc corrosion in acidic

solution:



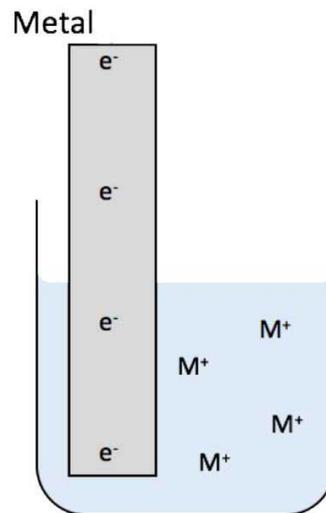
It can be divided into partial reaction of anode:



and partial reaction of cathode:



If a metal rod is immersed to a solution which contains its own ions, metal atoms are ionized and pass to solution. This process results in positive charged solution and negative charged rod. Fig. 1.4 demonstrates the charge distribution of a metal in its own ionic solution. A potential difference arises on the interface between the metal and solution. In time the reactions reach to equilibrium stated in the following equation between metal ions and metal atoms.



**Figure 1.4** Charge distribution of the metal rod and its own solution



After ionization and its reverse reactions are stabilized on equilibrium the potential

difference between the electrolyte and the metal will be stable too. This potential is called electrode potential.

However if the electrons which are cumulated in the metal rod are conducted away from the rod, then equilibrium will be broken. The metal rod continue to ionize and produce electrons. On the other hand if electrons flow to the rod from an out source vice versa the metal ions will be neutralized on the interface.

### 1.1.3.3 Electro-chemical Cells

Different metals have various electrode potentials. If two different metal rods are immersed to same electrolyte solution with a metallic path for conduction of current, a galvanic cell (electro-chemical cell) appears. The lower potential electrode will behave as anode and higher potential electrode will behave as cathode. The electrons cumulated on anode will flow to cathode by metallic path. Also they can conduct each other directly instead of metallic path. Therefore anode will dissolve continuously. On the other hand cathode must use the flowing electrons.

Electrolyte is usually ionic solution. Electric current is carried by ions in electrolyte instead of electrons like in metallic path. So Fig. 1.5 can be considered as electro-chemical battery [11]. As long as enough potential difference exists between anode and cathode, this battery can produce electric current. Electro-chemical corrosion cells works with same principles.

Electro-chemical corrosion reaction must contain at least 2 electrode reactions [10]. Anodic partial reactions and cathodic partial reactions are two essential parts of corrosion. To connect these two partial reactions a conductor, electrolyte, anode and cathode is needed. Fig. 1.5 demonstrates 4 essential components for corrosion. Anodic metal, cathodic metal, electrolyte which allow ions to move and a conductor (metallic path) moves electrons so electrical circle of corrosion is complete [12].

There are common cathodic partial reactions up to the medium. Most common cathodic reactions are listed as follows:

- In acidic solutions, reduction of hydrogen ions which result in extraction of hydrogen:



- In acidic solutions, reduction of oxygen (dissolved oxygen) and production of water:

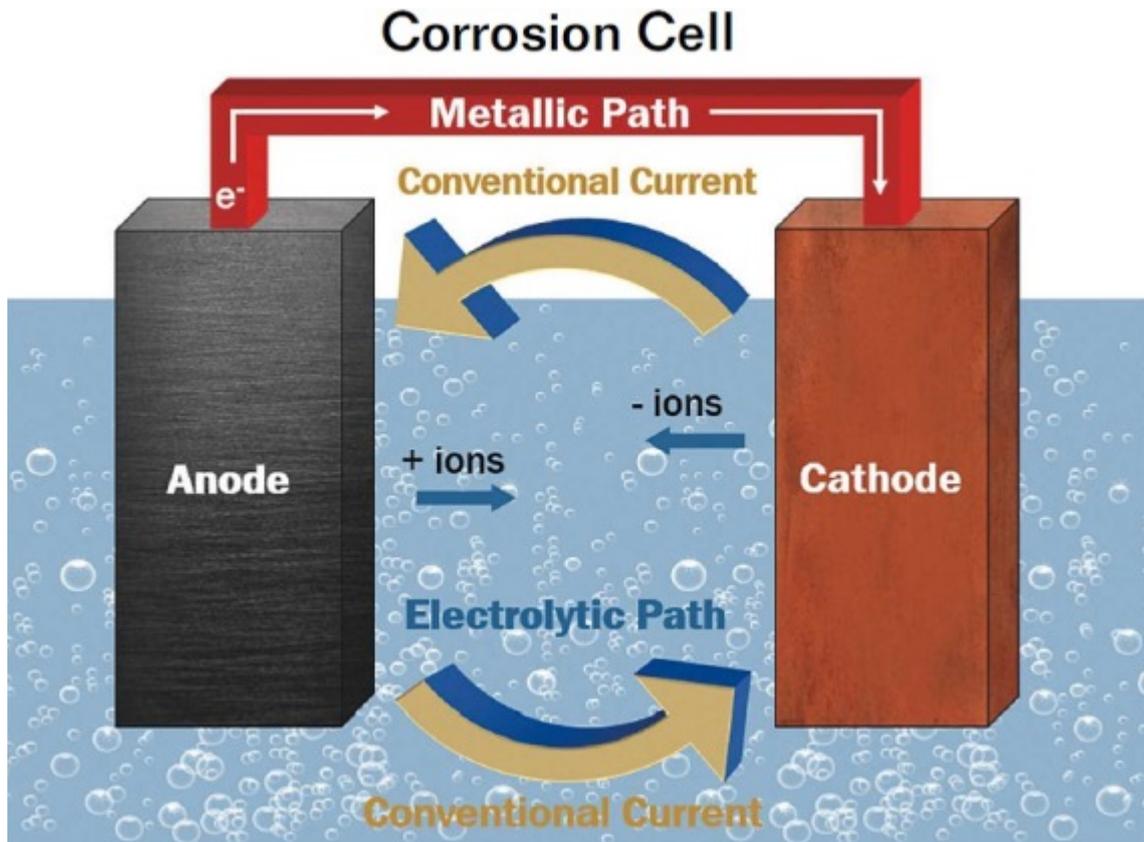
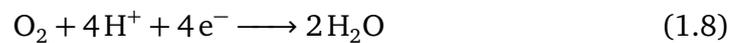


Figure 1.5 Electro-chemical cell components [11]



- In alkaline or neutral medium the cathodic reactions which result in hydrogen extraction:



- Oxygen reduction in alkaline or neutral medium which results in producing hydroxide ions:



On the other hand oxidation of metals has various forms up to ion charge. General equation of oxidation of metals is as follows:



where n states number of electrons released to extract the ion.

Electro-chemical reactions are carried out by electron exchange on cathode and anode. When an electron is produced it must be used immediately. The electrons produced on anode flows to cathode and consumed in cathode reaction. These reactions are simultaneous and they produce equivalent electric current. According to Faraday's law when 96500 C (Coulomb) charge flows on circuit at the anode and cathode 1 gram equivalent material involve reactions.

The force which carry out these reactions is that the potential difference between the electrodes which constitute electro-chemical cell. This is so-called electro-motor force (EMF). An electrode's potential depends on its own relative activity in the solution. To calculate electrode potentials Nernst Equation is used. This equation can be written in different forms:

$$E = E^{\circ} - \frac{RT}{nF} \ln a_{Me}^{n+} \quad (1.12)$$

where:

- E: Electrode potential [V]
- $E^{\circ}$ : Standard electrode potential [V]
- R: Universal gas constant (8,314) [J/mol.K]
- T: Temperature [K]
- F: Faraday's constant, 96500 [Coulomb/mol]
- a: Relative activity of ions

In Nernst Equation  $T=298$  K and  $a_{Me}^{n+}=1$  conditions results in  $E=E^{\circ}$ .  $E^{\circ}$  is so-called standard electrode potential. Each metal has constant standard electrode potential and all of them are known. Standard electrode potentials give clues about relative tendency of the metal to corrosion. Standard electrode potential of hydrogen atom is taken as zero and when all the metals are listed from the most active to most noble standard electrode potentials series is obtained. Fig. 1.6 demonstrates standard electrode potentials of common elements [13]. The values shows oxidizing tendency of electrodes, higher values means oxidizing tendency of the element is high. Namely if an element has high oxidizing potential it is hard to oxidize the element. Elements with lower potential behave as anode for the higher ones. The elements which has

lower potential compared to hydrogen can dissolve in acidic solutions by producing hydrogen gas. But it is important to notice that all these potentials are under conditions of 298 K and element's own solution with 1 molar ionic concentration. While concentration is changing, the potential also changes. Therefore the behaviour of an electrode (anode or cathode) can change. On the other hand oxide layer on the metal surface or corrosion products can reduce electrode potential. In practice evaluating the electrode potentials requires to consider these parameters.

	Half Reaction	potential
	<b>F<sub>2</sub></b> + 2e <sup>-</sup> ⇌ 2F <sup>-</sup>	+2.87 V
	<b>Pb<sup>4+</sup></b> + 2e <sup>-</sup> ⇌ Pb <sup>2+</sup>	+1.67 V
	<b>Cl<sub>2</sub></b> + 2e <sup>-</sup> ⇌ 2Cl <sup>-</sup>	+1.36 V
	<b>Ag<sup>+</sup></b> + 1e <sup>-</sup> ⇌ Ag	+0.80 V
	Fe <sup>3+</sup> + 1e <sup>-</sup> ⇌ Fe <sup>2+</sup>	+0.77 V
	Cu <sup>2+</sup> + 2e <sup>-</sup> ⇌ Cu	+0.34 V
	<b>2H<sup>+</sup></b> + <b>2e<sup>-</sup></b> ⇌ <b>H<sub>2</sub></b>	<b>0.00 V</b>
	Fe <sup>3+</sup> + 3e <sup>-</sup> ⇌ Fe	-0.04 V
	Pb <sup>2+</sup> + 2e <sup>-</sup> ⇌ Pb	-0.13 V
	Fe <sup>2+</sup> + 2e <sup>-</sup> ⇌ Fe	-0.44 V
	Zn <sup>2+</sup> + 2e <sup>-</sup> ⇌ <b>Zn</b>	-0.76 V
	Al <sup>3+</sup> + 3e <sup>-</sup> ⇌ <b>Al</b>	-1.66 V
	Mg <sup>2+</sup> + 2e <sup>-</sup> ⇌ <b>Mg</b>	-2.36 V
	Li <sup>+</sup> + 1e <sup>-</sup> ⇌ <b>Li</b>	-3.05 V

Figure 1.6 Standard electrode potentials [13]

On the other hand in practice metals have never been in their own 1 molar ionic solutions. At working conditions, metal ion concentrations are very low. Moreover

metal surface is covered by very thin layer of oxide film. All these reasons lead researchers to use galvanic series instead of standard electrode potentials. Galvanic series are determined after tests of materials against to saturated calomel electrode in sea water (or synthetic sea water) which is natural and very conductive electrolyte. Fig. 1.7 demonstrates galvanic series of common materials [14].

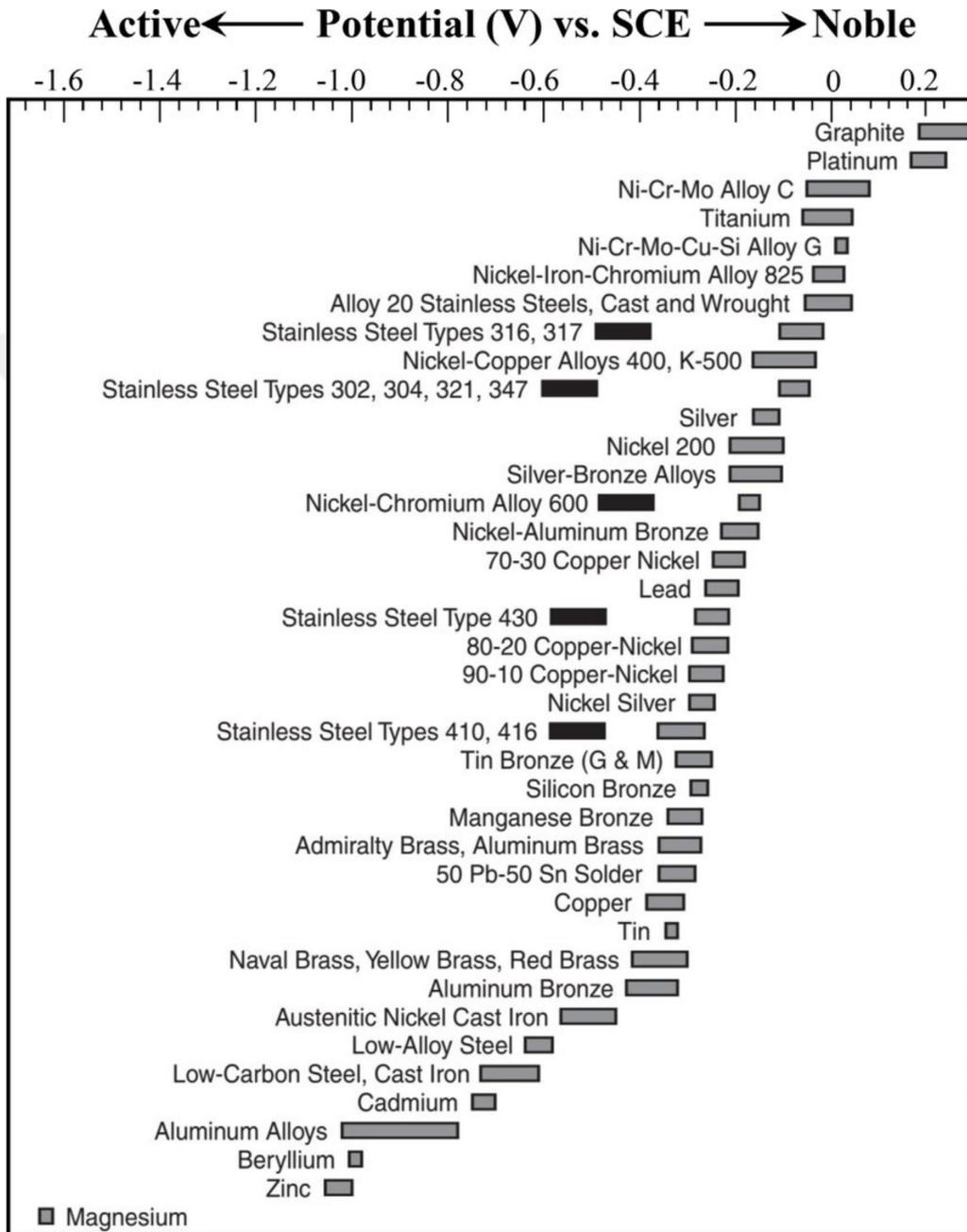


Figure 1.7 Galvanic series [14]

## 1.1.4 Forms of Corrosion

### 1.1.4.1 Uniform Corrosion

Uniform corrosion, in other saying general corrosion, is most common and simplest form of corrosion. Although material loss rate is high, it is not a dangerous form of corrosion. Metal and oxygen compounds flakes off from the surface by the time. The reasons cause to uniform corrosion are usually considered as metal dissolves as ions or chemical attacks on surface. But under high temperature conditions metals compound with another element instead of ionization.

Metals can endure corrosion by means of passive layer which can naturally formed after metals stay in air for enough time. But also there are chemical methods to accelerate formation of passive layer. Formation of film is a corrosion reaction but after passive film come into existence it prevents further growing of degradation. But passive film does not provide with total resistance to corrosion. Strong chemical attacks can break resistance of the passive layer. Chemical composition of the passive layer, aggression level of chemical attack and temperature are aspects of resistance to corrosion.

2 theories exist which defines formation process of passive layer:

**Theorem 1.1.** *Oxide film theory states that the layer is a metal oxide or different reaction compound.*

**Theorem 1.2.** *The other theory claims that oxygen is adsorbed on the metal surface, constitute a chemisorbed layer. In course of time, chemisorbed layers react with the substrate metal to create metal oxides.*

Metal oxide compound films are divided into two classes: Network formers and modifiers (intermediates). This classification is related to thin oxide layers on metals. Both classes are leaning to create protective oxide films. Oxide layers can be formed at room temperature. Although intermediates have tendency to be microcrystalline at low temperatures, the network formers are not crystalline.

Material loss rate is high but uniform corrosion damage is predictable. Depending on the working conditions, the life time of metal pieces can be calculated easily. Fig. 1.8 demonstrates an example of uniform corrosion on a pipe line [15]. Mild steel and low carbon steels are more preferable in a state of uniform corrosion conditions. Because stainless steel has tendency to pitting corrosion. Also, it is open to local attacks. Cheaper materials are serviceable under uniform corrosion attacks.

To avoid uniform corrosion following methods can be applied:



**Figure 1.8** Uniform corrosion on pipe line [15]

- Painting surface
- Organic coatings
- Cathodic protection

#### **1.1.4.2 Galvanic Corrosion**

Galvanic corrosion, in other words dissimilar corrosion occurs when two or more metals touch or close each other and the electrolyte exists. Fig. 1.9 demonstrates an example of galvanic corrosion on stainless steel [16]. One of the most common cases which causes galvanic corrosion is joining carbon steel pipes to copper pipes. Fig. 1.7 demonstrates the way metals behave each other when they are together.

Electrical potential difference appears when two or more metals are in touch and there is conductive electrolyte. This electrical potential will force less noble metal to dissolve while protecting more noble metal. Fig. 1.6 demonstrates some common elements' standard electrode potentials. These principles are the basis for using less noble metals like zinc or magnesium as sacrificial anode. Bronze ship propellers are very common and magnesium alloys are used as sacrificial anode against to bronze corrosion. This is so-called galvanic protection. Fig. 1.10 demonstrates sacrificial anodes used to protect the propeller and ship hull [17].

On the other hand some sacrificial anode metals have tendency to form passive film on the surface while corroding. Passive film makes metal more noble. this situation can even result in polarity change. For example zinc at 60°C combine with oxygen and forms ZnO which is more passive then Fe. So polarity changes and sacrificial anode leads protected cathode to corrode even more.



Figure 1.9 Galvanic corrosion example of stainless steel [16]

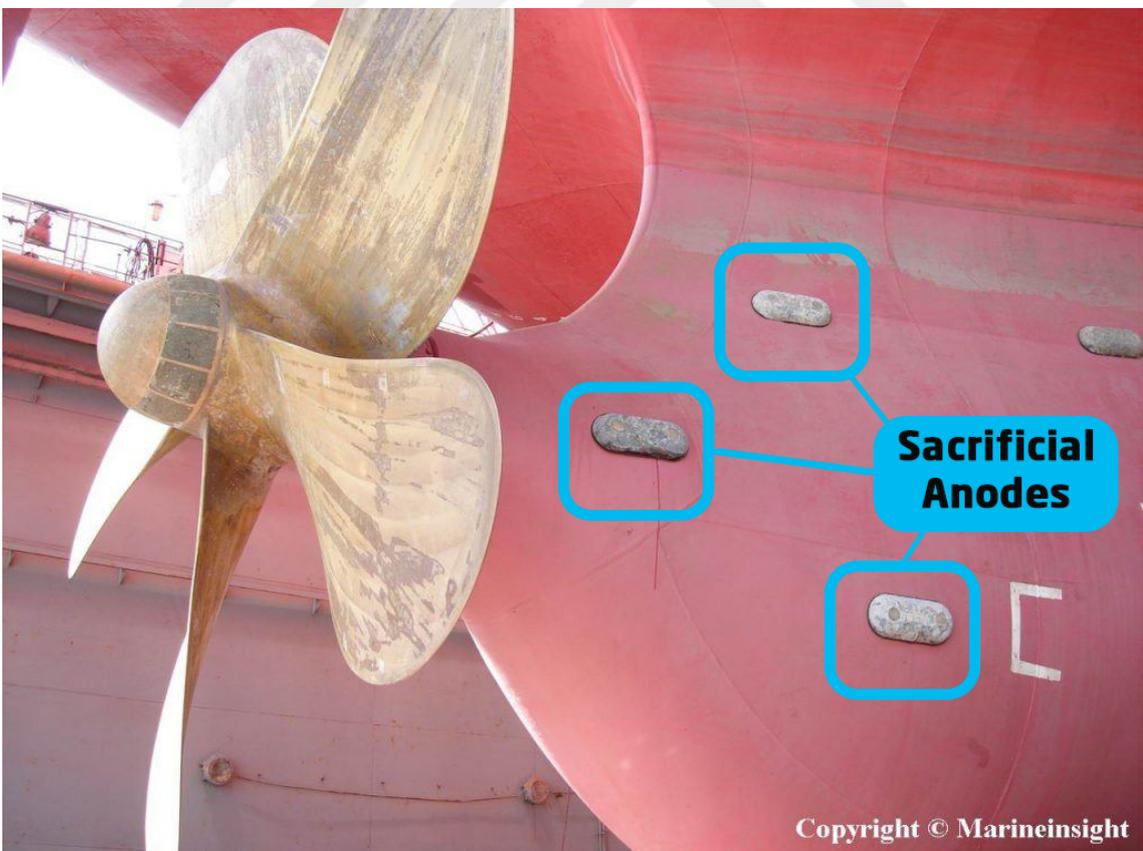


Figure 1.10 Sacrificial anodes used to protect the propeller and ship hull [17]

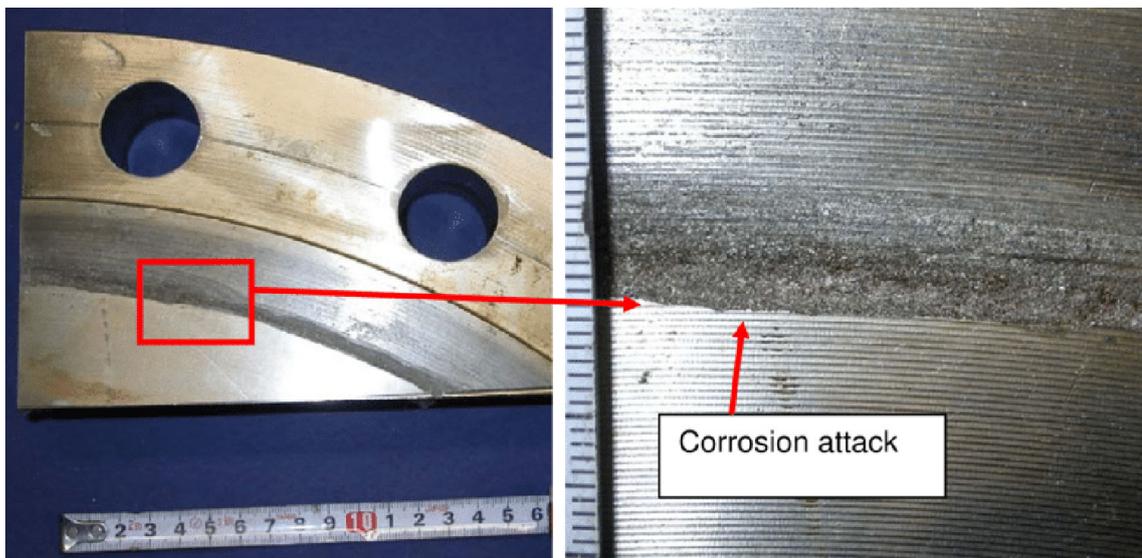
In some cases different metals are needed to use together. To avoid galvanic corrosion, close metals should be chosen from galvanic series. This situation leads to less potential difference and less corrosion as well. Design effects should be considered. For instance in case of corrosive effect of stress, the stressed parts should be more noble compared to the others.

Distance between different metal parts is another significant factor affecting galvanic corrosion rate. The less noble metal's bond to more noble part corrodes more compared to farther parts of it.

Area ratio between metals affects strength of design against to corrosion, it is intuitively apparent. If corroding anode is very small compared to cathode area, anode part tend to diminish quickly. Therefore, it can be said smaller cathodic area is good solution.

#### 1.1.4.3 Crevice Corrosion

Crevice corrosion occurs with localized attacks. It emerges in small gaps which can be between metallic parts or non-metallic and metallic parts like joints which has sealing gaskets. Bolts, rivets, joints etc. can have very small gap which holds leaked liquid stagnant. Local oxygen concentration differences are the main factor to lead crevice corrosion. Fig. 1.11 demonstrates an example of crevice corrosion on flange joint [18].



**Figure 1.11** Example of crevice corrosion on flange joint [18]

Width of the gap should be less than 3.18 mm, wide enough for entrance of liquid but not let to circulation in gap [10].

Each corrosion condition is suitable for crevice. But, metals which produce passive oxide layer that makes the metal corrosion resistant have higher tendency to be affected from crevice corrosion (exclusively in conditions which chloride ions present like sea water). For example stainless steel and aluminium are corrosion resistant thanks to oxide film.

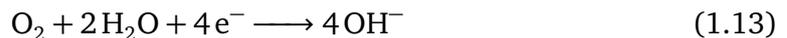
Crevice corrosion can be caused by any type of material. Even living organisms can be responsible for crevice corrosion. When crevice corrosion start, it advances quickly. It is a very dangerous kind of corrosion because it can proceed without any signature.

To avoid from crevice corrosion, design is the key parameter. Designers should avoid from concave corners to prevent stagnancy of liquid. On the other hand threaded or rivet joints should not be preferred; to avoid gaps between metal parts and gasket, butt-welded joints can be preferred instead. If a design with gasket is essential, non-absorbant gaskets should be chosen.

When lap joints are preferred, fillet welding should cover the gap. Therefore the gap will have no contact with liquid or moisture.

In case of crevice corrosion is observed, the gap should be widened. Because, wide gap allows to circulation of liquid and this prevents crevice corrosion.

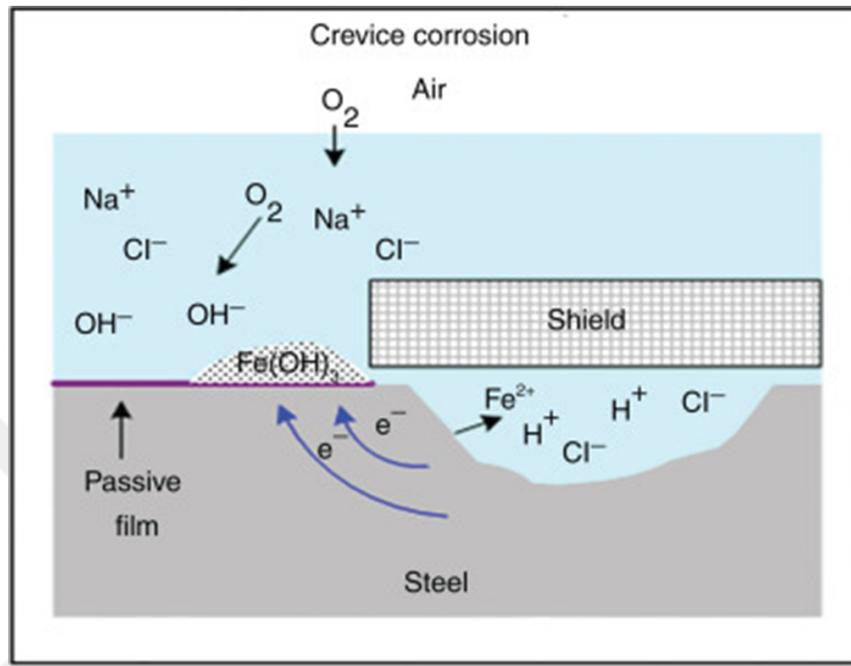
Crevice corrosion reactions advance same to outside of crevice area in neutral chloride solution:



While corrosion reactions keep going, oxygen depletes in crevice area. Nevertheless, lack of oxygen do not stop corrosion reactions. Anodic reactions proceed inside of the crevice and electrons move to out side of the crevice where in touch with oxygen rich electrolyte. This conditions represents an concentration cell between crevice area and the outside.

In case chloride ions exist, the aggression of corrosion goes further. High concentrations of cations in crevice draw negatively charged chloride ions. Fig. 1.12 demonstrates mechanism of crevice corrosion on stainless steel [19]. Hydroxide ions are also capable of moving but they are slow compared to chloride ions. The

metal chloride compounds involve reaction with water to produce hydrochloric acid as following reaction:



**Figure 1.12** Mechanism of crevice corrosion [19]

Passive film can not endure against to hydrochloric acid and corrosion rate goes further. Anodic dissolution reactions accelerate in crevice while cathodic reactions occur outside. To obstruct crevice corrosion damages, following precautions should be considered:

- Design should not contain crevice or parts can cause stagnancy of liquid. Rivet and bolt joints should not be preferred. Butt-welding joints should be preferred.
- Lap joints should be filled by fillet welding or caulking.
- Absorbant and porous gaskets must not be used. Instead of them, impervious materials should be preferred to use as gasket.
- Material selection, as a design parameter, very important. Changing content of alloys can improve resistance to crevice corrosion.
- If control of the corrosion environment is possible, reducing chloride ions' concentration, acidity and temperature helps to prevent crevice corrosion.

- Removing solid depositions from surface is necessary to prevent stagnancy of liquid, namely crevice corrosion.

#### 1.1.4.4 Pitting Corrosion

Pitting corrosion affects very local areas. There is a large similarity between crevice corrosion and pitting corrosion mechanisms. Both mechanisms depend on stagnancy of corrosive liquid. Extreme pitting corrosion damages result in tiny and very deep hole forms while other parts of the surface remain intact. Entrance of pitting corrosion hole can increase but do not excess size of depth. Usually corrosion products cover entrance of the hole. This situation makes detection of pitting corrosion at early stage very complicated, mostly impossible by observing. Fig. 1.13 demonstrates an example of advanced pitting corrosion on steel surface [20].



**Figure 1.13** Pitting corrosion observed on inside surface of steel storage tank [20]

Damages on the protective film leads to initiation of pitting corrosion. With imperceptible amount of material loss and without reduction in material thickness it does not show any signature to identify corrosion. Pitting corrosion on pipe surfaces can lead to perforation of metal. Without mass damage, due to very small holes the pipes can become useless.

Local weakness caused by pitting corrosion can lead to structural failure, although most of the material is undamaged. Fatigue failure, brittle failure, environment-assisted cracking like stress corrosion cracking, and corrosion fatigue due to sites of stress concentration can occur as a result of pitting [10].

Electrical contact to dissimilar metals or sites which have different concentration of oxygen or conductive ions is the major parameter that accelerates pitting corrosion. These situations lead to electrical potential difference. Electrical potential difference is the reason for electrical current flowing from anode to cathode by electrolyte. For active areas (anodes) the cathode can be more noble metal or mill scale. On the other hand, when cathodic area is relatively small, damage is generally imperceptible. Because larger anode spreads the damage to small portions.

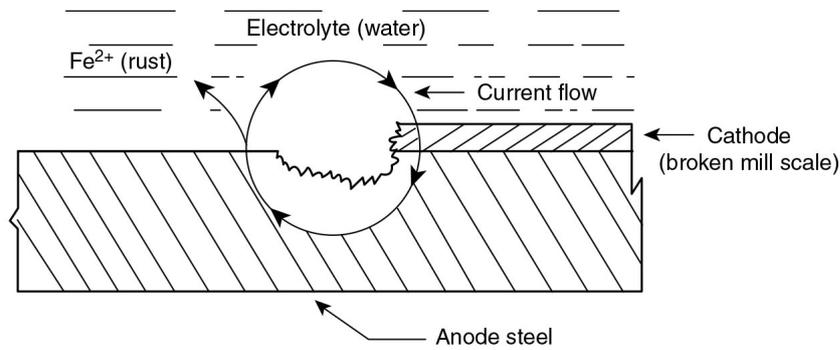
For instance if there is discontinuity while most of the surface is covered by protective layer like coating, depositions or mill scale, pitting supposed to initiate at the areas where the bare metal is not covered. Local dissimilar depositions can also lead pitting. Fig. 1.14 shows the mechanism how the discontinuities lead to pitting corrosion [10].

When surface of the metal is exposed to effectual corrosion attack and anode area is small, the pits are so-called deep. In case that the pit area is comparatively large, they are called shallow. Proportion of deepest penetration to average penetration, which is calculated via weight loss, is pitting factor. If the pitting factor is equal to 1, it is a uniform corrosion attack. Following characteristics describe pitting corrosion:

- Corrosion damages are observed on independent areas. Pits can be accumulated at a specific area or distant points.
- Surface looks rough.
- Pitting corrosion generally starts on top surface of horizontal metals and proceed to gravity direction.
- Detecting pits by observing takes very long time, till pit entrances grow large enough.
- After initiation of pitting, like crevice corrosion, corrosion reaction stimulate itself. Corrosion rate proceed at ever-increasing rate.
- Stagnancy of liquid is a reason for pitting.
- In case of pitting corrosion, carbon steels are preferable compared to stainless steel. Alloys of aluminium and stainless steel have tendency to pitting corrosion. Neutral to acidic chloride solutions are the most corrosive environments to

stainless steel. Alkaline liquids are harmful to aluminium alloys and carbon steel.

- Generally pitings are related to halide ion like chloride. Hypochlorites are even more harmful.



**Figure 1.14** Initiation of pitting corrosion due to discontinuities [10]

Resistance of metals against to crevice or pitting corrosion usually evaluated via critical pitting temperature (CPT), critical crevice temperature (CCT) and pitting resistance equivalent number (PREN). PREN is directly proportional with corrosion resistance. Chromium, molybdenum, and nitrogen contents are the parameters to calculate PREN:

$$PREN = \%Cr + 3.3(\%Mo) + 30(\%N) \quad (1.16)$$

#### 1.1.4.5 Selective Leaching (Dealloying)

Selective leaching, in other words dealloying or dezincification (in case of zinc exist in alloy and dissolved by selective leaching), is the corrosion attack which dissolves one element from the metal alloy while the others do not dissolve. Dezincification of copper alloys is the most common example of selective leaching. After zinc has dissolved the alloy becomes porous but outlook remains intact. It can look like there is not any damage except changes in colour. But, mechanical properties of the alloy are affected. Ductility and tensile strength decreases significantly.

Brass alloys' dezincification can spread uniformly to surface which is so-called layer type or can be localized that is so-called plug type. If percentage of zinc is high, plug type dezincification is supposed to be observed. If zinc percentage is low, layer type is supposed to be seen. The medium of the environment is very effective

to determine corrosion type. Room temperature, acidic (not strongly) and with low salt concentration conditions leads to uniform selective leaching. Higher than room temperature, neutral to alkaline and high salt concentration leads to plug type selective leaching. The factors that lead to crevice condition like scale deposition makes selective leaching process more aggressive.

Following factors promote dealloying:

- Stagnancy of liquids (particularly acidic)
- High temperature
- Deposition of inorganic scale

Tin, arsenic, aluminum and phosphorus additions to alloy can prevent dezincification. The alloys contain less than 15% zinc content, generally resistant to dezincification.

Following precautions should be considered against to selective leaching:

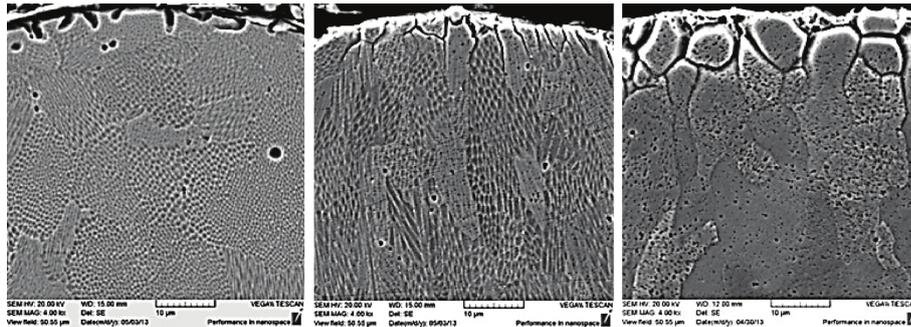
- Cleaning any kind of deposits or scale from surface periodically
- Choosing the alloys has immunity against to dealloying
- Preventing stagnancy
- Cathodic protection

Although its bad effects for mechanical properties, sometimes nano porous surfaces are required. Selective leaching is very beneficial to produce nanoporous surfaces.

#### **1.1.4.6 Intergranular Corrosion**

Intergranular corrosion initiates on the grain boundary phases or very close to them. Grains are not affected from the corrosion attacks or very slightly affected. Although there is not remarkable effects on grain body, intergranular corrosion reduces ductility and strength of metal. Fig. 1.15 demonstrates intergranular corrosion of 316L austenitic stainless steel [21]. Intergranular corrosion generally advances rapidly. Deep penetration characteristic of it leads to failure.

Following factors are effective to lead intergranular corrosion:



**Figure 1.15** Intergranular corrosion of 316L stainless steel [21]

- Some corrosion resistant elements or compounds can segregate, for instance chromium or aluminium.
- Brass has alloying elements which are weaker than copper against to corrosion. On the grain boundary sometimes one of the elements can be enriched. This situation makes grain boundary weaker.
- Grain boundaries can have lack of corrosion resistant constituents. This is another reason to make boundary weaker.

Precipitation of carbides as a result of welding operations can lead stainless steel to intergranular corrosion. Addition of stabilizer elements like niobium or titanium can prevent this by attracting carbon atoms. Also less than 0.03% carbon content is significantly necessary to prevent corrosion attacks.

The reasons related to intergranular attacks have relation with thermal processes which are applied to the material, except percentage of carbon content in the alloys.

#### 1.1.4.7 Erosion Corrosion

Mechanical impacts can lead to deterioration of metals. This situation is so-called erosion. If the erosion attacks feed and accelerate corrosion of metal it is so-called erosion corrosion. Erosion corrosion is usually related to liquid or gas flows on metallic parts. Suspended particles in gas or fluid can hit to surface of metal and lead to erosion corrosion. On the other hand cavitation is another mechanical impact.

Due to the high velocity of propellers, impellers or flow the pressure decreases regarding to Bernoulli Equation:

$$\frac{v^2}{2} + gz + \frac{p}{\rho} = constant \quad (1.17)$$

When pressure decreases to boiling point with constant temperature; by means of pressure drop, water can boil at room temperature. Vapour creates bubbles near to the surface. When pressure rise again, the bubbles collapse with very high velocity and erode surface. Fig. 1.16 demonstrates an example of cavitation erosion which has synergistic effect with corrosion [22]. Fig. 1.17 demonstrates an cavitation tunnel that artificially creates cavitation conditions [23].

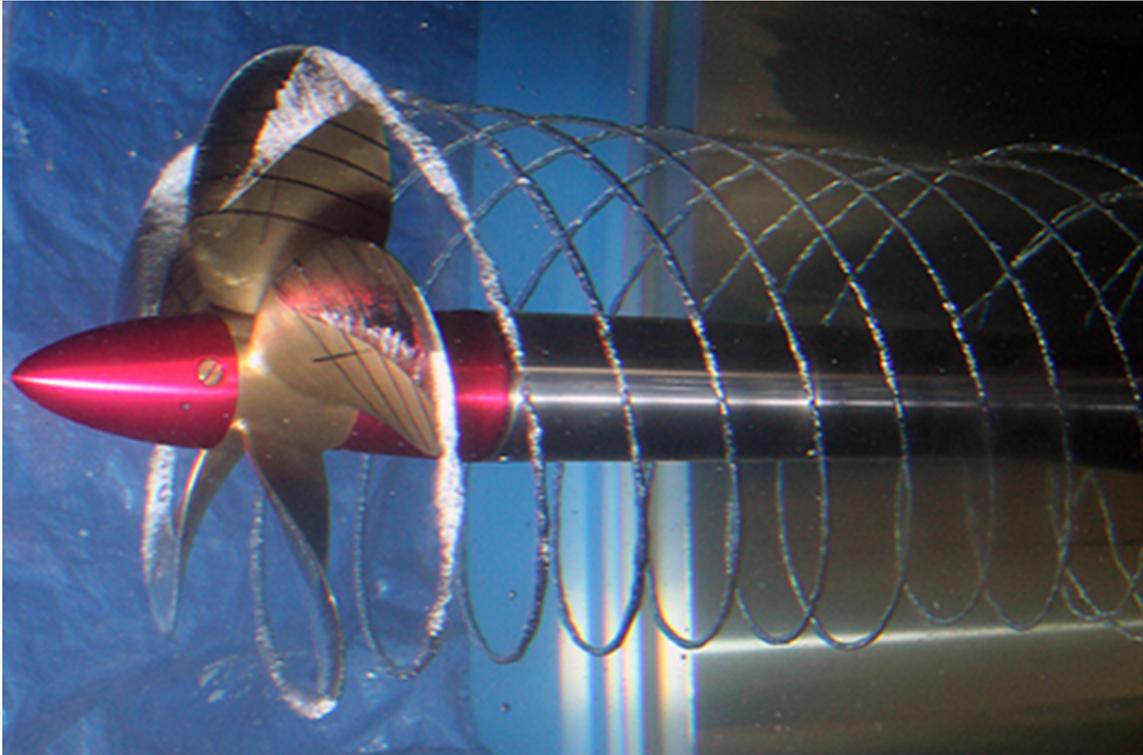


**Figure 1.16** Cavitation erosion of a propeller [22]

Flow related erosion corrosion can shape grooves on metal surface that usually demonstrates flow direction. The area affected from erosion corrosion may have pits. Advanced erosion corrosion can lead to rupture due to reduction in thickness of pipe walls which reduces strength. Therefore pipe wall can not resist to pressure.

Following factors promote erosion corrosion aggravation in flow:

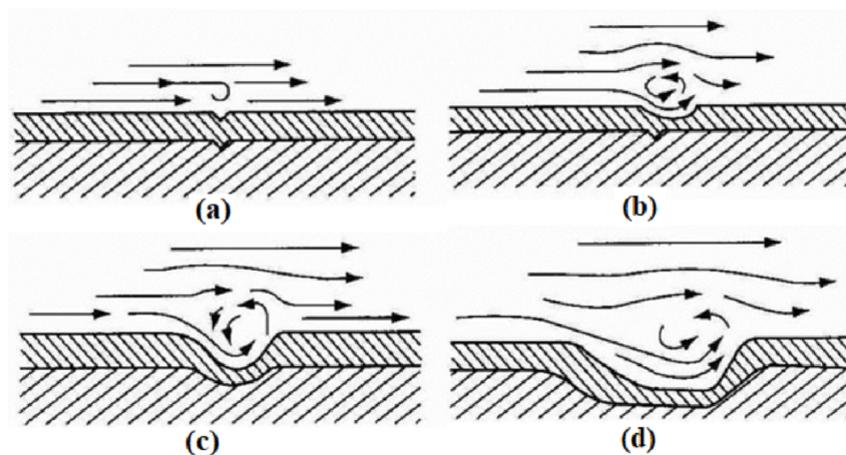
- Temperature of the medium
- Velocity of the flow
- Turbulence
- Impingement of the solid particles suspended in liquid or gas



**Figure 1.17** Cavitation tunnel [23]

- Cavitation

Removal of protective film from the surface of the metal due to the erosion leaves bare metal unprotected in corrosive medium. This situation accelerates corrosion and it is so-called synergistic effect between corrosion and erosion. After surface deformation initiate, turbulence in the flow also increases. Turbulence is a factor that increases erosion. Fig. 1.18 demonstrates increase in turbulent flow due to the pits [24].



**Figure 1.18** Increase in turbulent flow due to the pits [24]

Flow velocity increases rate of corrosion on most of the metals, however the remarkable increase is observed after critical velocity.

Changes in diameter of the pipes, deposits on the surface or any other obstacle for flow increases turbulence. Impingement usually occurs on surfaces of propellers, impellers, turbines and elbows of pipes.

Fretting corrosion is a form of erosion corrosion without liquid flow. In case two metal surfaces touch to each other and have slight relative motion, they damage protective films of themselves and fretting corrosion occurs. Railways are proper examples for fretting corrosion. When a train comes, small amplitude vibration occurs. Oxide layers between fretted surfaces might dislodge. Also there would be debris accumulation which leads to more erosion. Fretting corrosion generally results in pitting.

Soft metals like copper and aluminium have less resistance against erosion corrosion. They have a high tendency to be eroded by cavitation or fretting. Copper is a very common constituent for marine propellers and is used with a high percentage in bronze propellers. Table 1.1 demonstrates rules for chemical compositions of copper based marine propellers according to German Lloyd [25].

**Table 1.1** Chemical composition of copper based marine propellers [25]

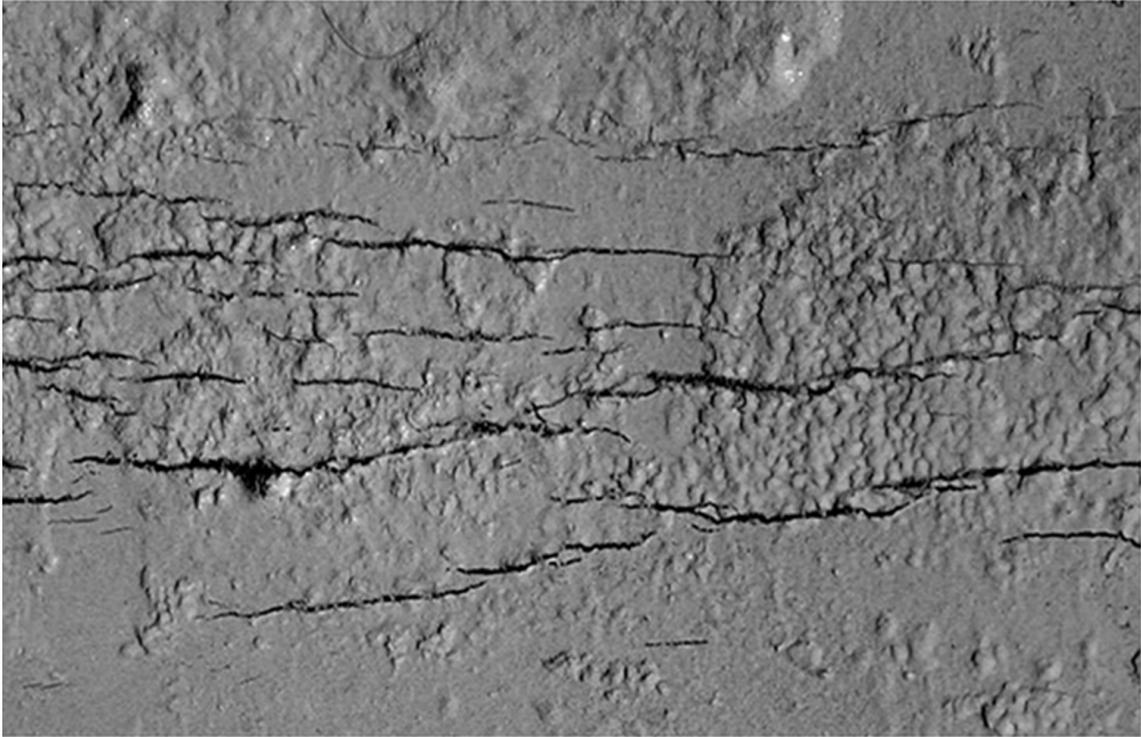
Casting grade	Chemical composition [%]							
	Cu	Al	Mn	Zn	Fe	Ni	Sn	Pb
CU1	52 – 62	0,5 – 3,0	0,5 – 4,0	35 – 40	0,5 – 2,5	max. 1,0	0,1 – 1,5	max. 0,5
CU2	50 – 57	0,5 – 2,0	1,0 – 4,0	33 – 38	0,5 – 2,5	3,0 – 8,0	max. 1,5	max. 0,5
CU3	77 – 82	7,0 – 11,0	0,5 – 4,0	max. 1,0	2,0 – 6,0	3,0 – 6,0	max. 0,1	max. 0,03
CU4	70 – 80	6,5 – 9,0	8,0 – 20,0	max. 6,0	2,0 – 5,0	1,5 – 3,0	max. 1,0	max. 0,05

Following precautions may be considered to prevent erosion corrosion:

- If there is a flow, velocity of the flow can be reduced.
- Controlling or preventing turbulence of fluid will be helpful.
- Selecting proper materials which are harder.
- Design should be proper to control erosion.

#### 1.1.4.8 Stress Corrosion Cracking (SCC)

SCC is a form of corrosion failure which occurs in case static tensile stress and corrosive environment exist. Namely, SCC is a result of synergistic effect between stress and corrosion. The stress level that leads to mechanical failure without corrosion is much more than the stress level that leads to SCC. Without stress, only corrosion attacks do not cause SCC. Fig. 1.19 demonstrates an example of SCC [26].



**Figure 1.19** SCC example [26]

Before SCC the material can seem almost corrosion free. However, slender cracks penetrates to the surface at stress points. Intergranular and transgranular cracking results can be observed. The advancing rate of corrosion has wide range and related to following factors:

- Stress
- Concentration of corrosive medium
- Temperature
- Pits that concentrate stress
- Mistakes in installation of mechanical parts
- Residual stress related to thermal processes
- Bending
- Straightening
- Denting material by mistake

Some corrosive medium and alloy matches can cause extremely aggravate corrosion attacks which result in SCC in hours. However, in most industrial and natural

conditions SCC process is much slower. On the other hand detection of the crack is hard due to its nature.

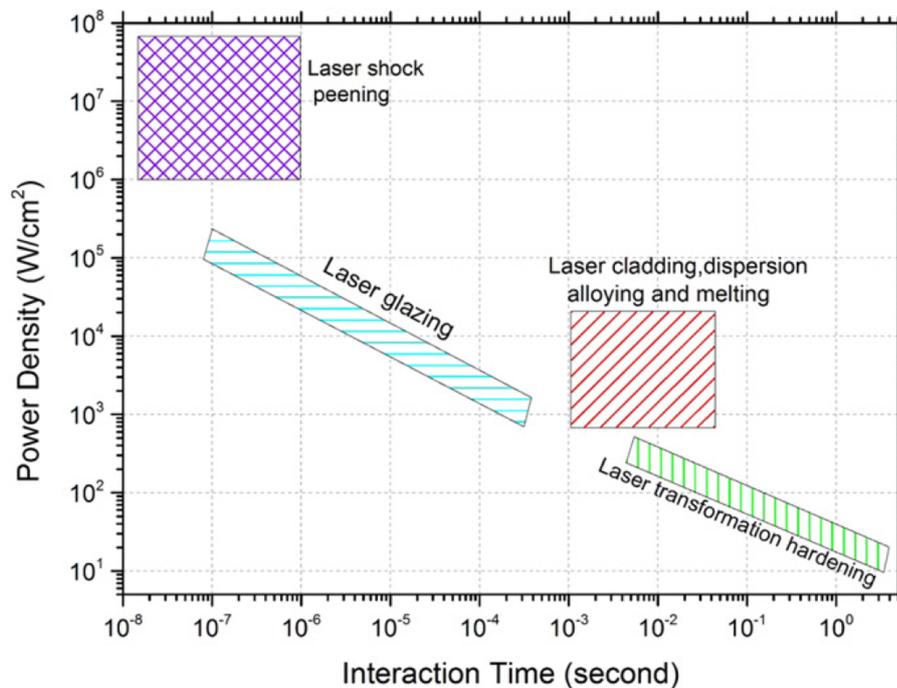
Following precautions should be considered to prevent SCC:

- Stress relief processes should be applied to material if necessary.
- Careful installation process is important to prevent stress.
- Stagnancy of liquids in the system should be prevented to avoid pits that concentrate stress.

### 1.1.5 LST Methods Against to Corrosion and Cavitation

LST methods are illustrated in Fig. 1.1. These methods mainly classified into LST with added material and without added material according to absence or existence of added material. Laser transformation hardening (LTH) and laser surface melting (LSM) are the methods without added material. LSA, LC and LD are the methods with added material.

Results of LST depend on many parameters. But power density and interaction time parameters are resultants of important parameters. Fig. 1.20 demonstrates the graph of power density and interaction time relation.



**Figure 1.20** LST processes as a result of power density and interaction time combinations [27]

### 1.1.5.1 Laser Transformation Hardening (LTH)

LTH progresses without melting surface. Also there is not added material. Transformation happens in solid state. Focused laser beam energy rises surface temperature between solid state transformation and melting points [28]. Relatively huge amount of bulk metal behaves as a perfect heat sink and surface cools rapidly. Fig. 1.21 demonstrates mechanism of LTH process [27].

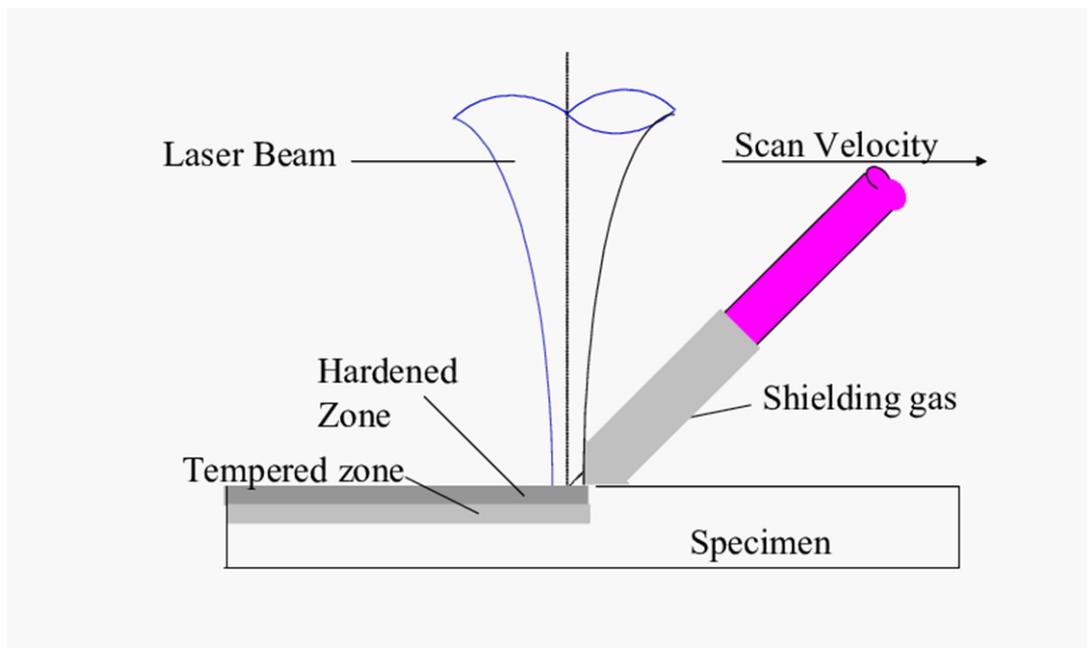


Figure 1.21 LTH mechanism [27]

Reflectivity of material surface has significant role in this process because that is the parameter determines the amount of energy absorbed by material. Ferrous alloys are generally feasible for LTH. If the alloy has a potential for increasing hardness, lower energy concentration and longer interaction period is proper to obtain homogeneous and deeply penetrated transformation. Uniform and very shallow penetration of LTH process results in very little distortion of material. So there is no need to work on surface again.

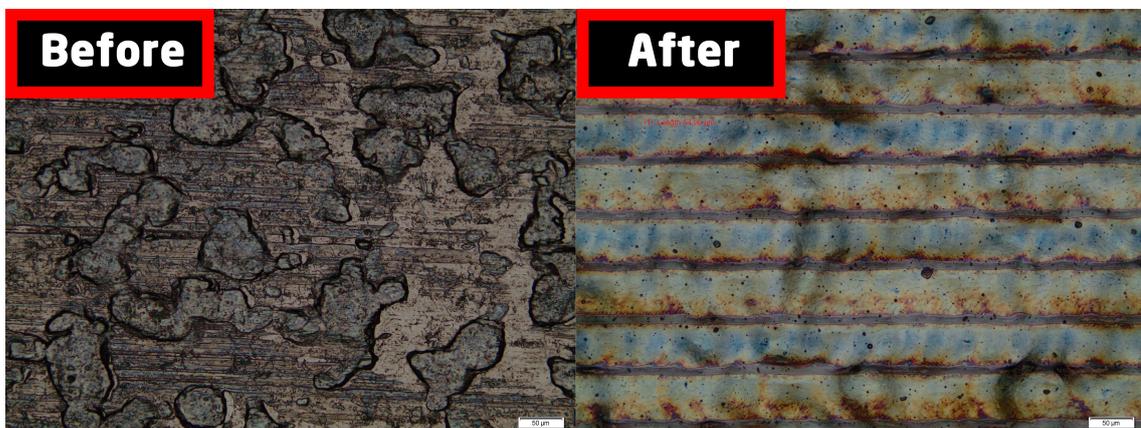
### 1.1.5.2 Laser Surface Melting (LSM)

LTH does not include melting and re-solidification of metal surface and there is not added material. So microstructure is not refined. Therefore effect of LTH is limited. On the other hand LSM requires energy concentration at least as high as to melt surface. Fig. 1.22 demonstrates before and after images of St37 steel surface which is exposed to LSM (20X focusing optic microscope snaps). Microstructure refinement can be observed explicitly. Laser energy focuses on very little part of surface and melt it. Process is very quick. Pulses (if it is pulsed laser) can be stated in picoseconds

depending on laser type. Such a short pulse duration does not give enough time to heat energy for spreading. Laser energy is concentrated in terms of both area and period. Therefore a melting pool can be created on the surface of metal. Melting pool has very high cooling rate which ranges from  $10^3$  to  $10^6$  [ $^{\circ}\text{C}/\text{s}$ ] depending on laser parameters and thermal conductivity properties of the surface. Among the LST methods, LSM is the most known method due to its simplicity relative to other methods and effectiveness to increase resistance to cavitation erosion ( $R_e$ ). Following aspects are effective to achieve increase in  $R_e$ :

- Refinement in grain size which also leads to increase surface hardness
- Fixing faults on the surface like cracks and pores
- Obtaining homogeneous microstructure
- Obtaining monophased hard surface layer

These effects of LSM provide with harder and more homogeneous surface.  $R_e$  is supposed to increase with hardness. Homogeneity comes with improvement in  $R_e$  by forming less sites for initiation of cavitation. Because multiphased surfaces are as strong as the weakest phase [29].



**Figure 1.22** Optic microscope snaps of St37 steel before and after LSM

### 1.1.5.3 Laser Surface Alloying (LSA)

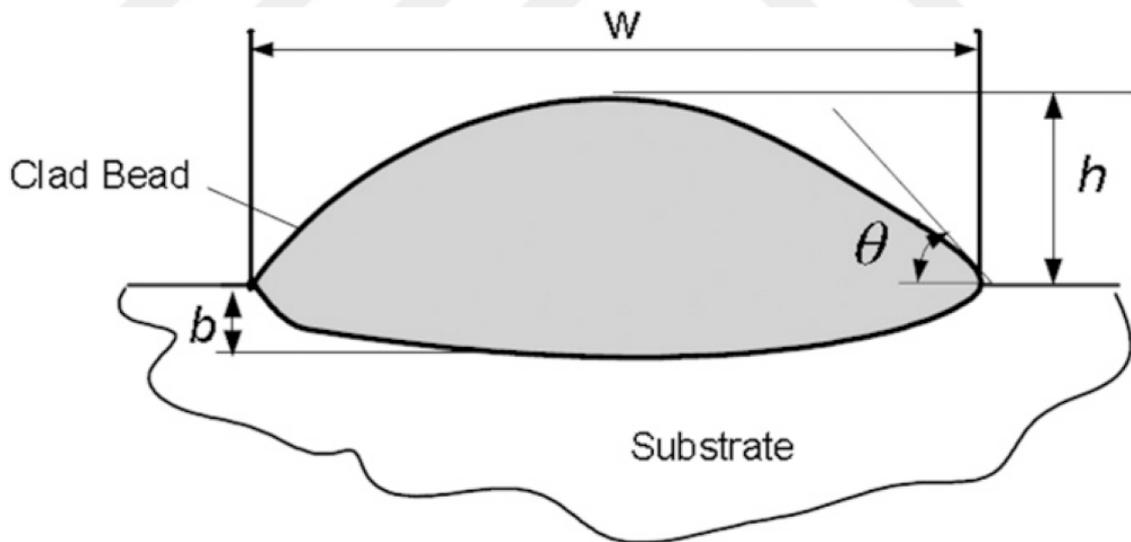
LSA is a process that added material join the surface structure by melting and re-solidification of both substrate and added material. Usually process occurs by melting and alloying within very tiny melting pool which is consist of very fine layer of substrate and the added material that is fed in powder or wire form (simultaneously deposited with laser process) [30]. Alternatively some pre-deposition techniques like

electroplating, chemical or physical deposition, pasting, thermal spraying etc. are used to adjust needed layer thickness of added material for LSA. The melting pool that is created on the surface is very small, so bulk metal is not affected from the LSA and stay cool. Therefore bulk metal behaves as heat sink. Huge temperature difference exists between melted area and solid substrate. Rapid cooling and solidification occurs in each tiny melting pool. Therefore strong metallurgical bond is formed between alloyed surface and substrate. Generally inert shielding gases are proper to prevent oxidation in duration of LSA.

#### 1.1.5.4 Laser Cladding (LC)

LC can be so-called a special form of LSA. Both LSA and LC are processes which result in mixing added material with substrate. Substrate material dilutes added material. Fig. 1.23 demonstrates geometrical shape and dimensions that describes parameters to calculate dilution rate [5]. Dilution rate (d) can be summarised by the following equation:

$$dilution = \frac{h}{h + b} \quad (1.18)$$



**Figure 1.23** Geometrically demonstration of LSA/LC dilution rate [5]

where  $b$  is melted substrate thickness [mm],  $h$  is height of cladding material [mm]. Very fine layer of substrate melts and dilutes added material. Dilution can not be equal to 0% because strong metallurgical bonding is needed. It is commonly accepted that dilution rate should be up to 10% for LC. If dilution occurs with percentage of higher than 20%, process can be classified as LSA which results with a surface that contain substrate metal with non-ignorable rate. So covering of layer can be affected from

properties of substrate.

Dilution rate is important for only LC among LST methods. Because, covering the surface is aimed by only this method. If added material is fed in powder form it is hard to detect the dilution rate. LC produces thicker covering layer compared to LSA. Explicitly LSA and LC are more complicated compared to LTH and LSM. On the other hand they can be more effective with optimized parameters. Fig. 1.24 demonstrates a schematic systems of laser cladding and alloying [31].

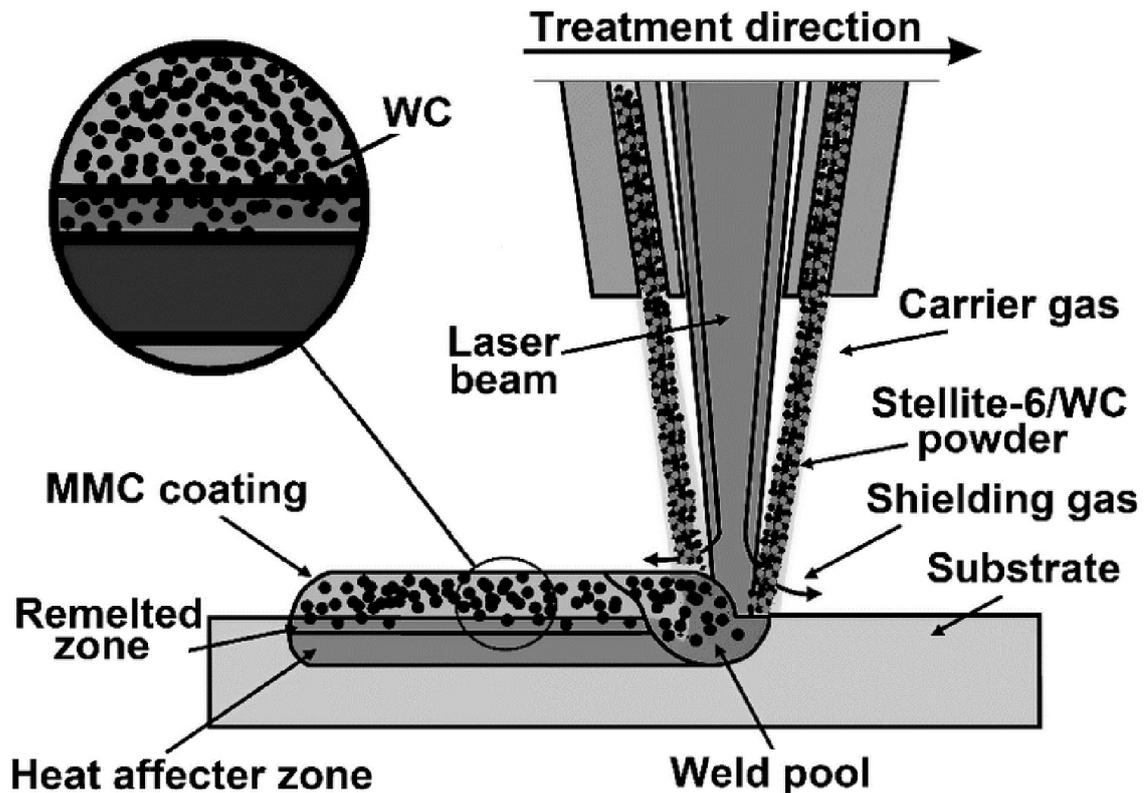


Figure 1.24 Laser cladding/alloying systems [31]

#### 1.1.5.5 Laser Dispersion (LD)

LD is another LST method with added material. Although it looks similar to LSA and LC there is a significant difference that added material never melts in LD. LD aims to place second phase (hard ceramic) into melted surface. To prevent over heating of added material which is not wanted to melt, laser power and interaction time may be reduced. On the other hand process speed can be increased and powder feeding nozzle may follow laser beam with little difference instead of moving concentrically. Therefore dispersed particles remain solid during LD. Surface metal matrix composite (MMCs) can be observed after solidification. Surfaces with MMCs contain secondary phase while bulk metal remains unaffected from this situation [32], [33]. MMCs

surfaces are needed especially under working conditions that require more hard and wear resistant surfaces. There are alternatives to laser for creating MMCs surface like vapour deposition, centrifugal casting, plasma spraying and some other friction assisted mechanical methods.

During LD melting pool temperature must be controlled under melting point of added material. Velocity of laser head can be increased to avoid melting hard phase. But instant cooling can produce residual stress and lead to cracking on surface. Still cracking can be prevented by preheating the surface. To gain strong metallurgical bonding between the second phase particles and substrate, dispersed particles should be wetted by melted substrate but should not dissolve.

### **1.1.6 Hydrophobic Surfaces**

Hydrophobic metal surfaces that can repel liquids are adapted to many engineering application. Wind power stations, medical equipment, automobiles, marine industry, aircrafts etc. Surface structure is the main factor to make a surface super hydrophobic [34].

Lotus leaf is an example for biological hydrophobic surfaces. Imitating surface structure of lotus leaves, which have stable liquid/air interface, can guide to produce structured hydrophobic surfaces [35].

Super hydrophobic surfaces are less adhesive. Because of the air that is trapped to the spaces of the structured surface, liquid can not enter those spaces [36]. Hydrophobic surface structures can be obtained by means of laser ablation [37].

## **1.2 Objective of the Thesis**

Investigating effects of LST on surface properties of bronze marine propellers is the main aim of the present study. LST methods can affect most of surface properties at once. The objectives can be evaluated in three steps. Hydrophobicity, corrosion resistance and hardness are the main properties analyzed after applications of LST methods.

### **1.2.1 Investigation of Hydrophobicity**

Superhydrophobic surfaces have low fricative and adhesive properties that may provide with more efficient propellers. In the present study, gaining superhydrophobic surface properties on bronze marine propeller samples is one of the objectives.

Although hydrophobic surfaces have some advantages compared to hydrophilic surfaces, hydrophilic surfaces give better surface structure to varnish or paint propeller with chemical protecting coating materials. Therefore obtaining hydrophilic surfaces may be useful for propeller endurance improvement.

### **1.2.2 Investigating of Corrosion Resistance**

It is costly to avoid corrosion. However, corrosion of the marine craft parts and equipment causes much more expenses. Especially marine propellers works under very aggravate working conditions. Placing sacrificial anodes close to propellers is a way to protect propeller. However, it is not enough in long term.

Improving corrosion resistance of marine propeller specimens is an important point of the present study.

### **1.2.3 Investigation of Hardness**

Hardness is related to cavitation resistance which has synergistic effect with corrosion. Hardness of marine bronze propeller has significant relation with cavitation resistance.

Hardness of the surface supposed to be affected from LST because of changes in micro structures. Therefore investigating effects of LST to hardness can be another objective of the present study.

## **1.3 Hypothesis**

Bronze marine propellers are the subject to modify surface properties via LST. LST is very effective method to modify surface properties of metals. Changing microstructure via LST can affect corrosion resistance and hardness of the surface. After refinement of microstructure, surfaces become more resistant to corrosion. LST can fix moulding defects on surface and create uniform microstructure.

By laser ablation, texturing nano structure on surface and changing roughness properties can lead to make surface hydrophobic. On the other hand hydrophilic surfaces can be obtained when roughness and surface profile adjusted via LST methods.

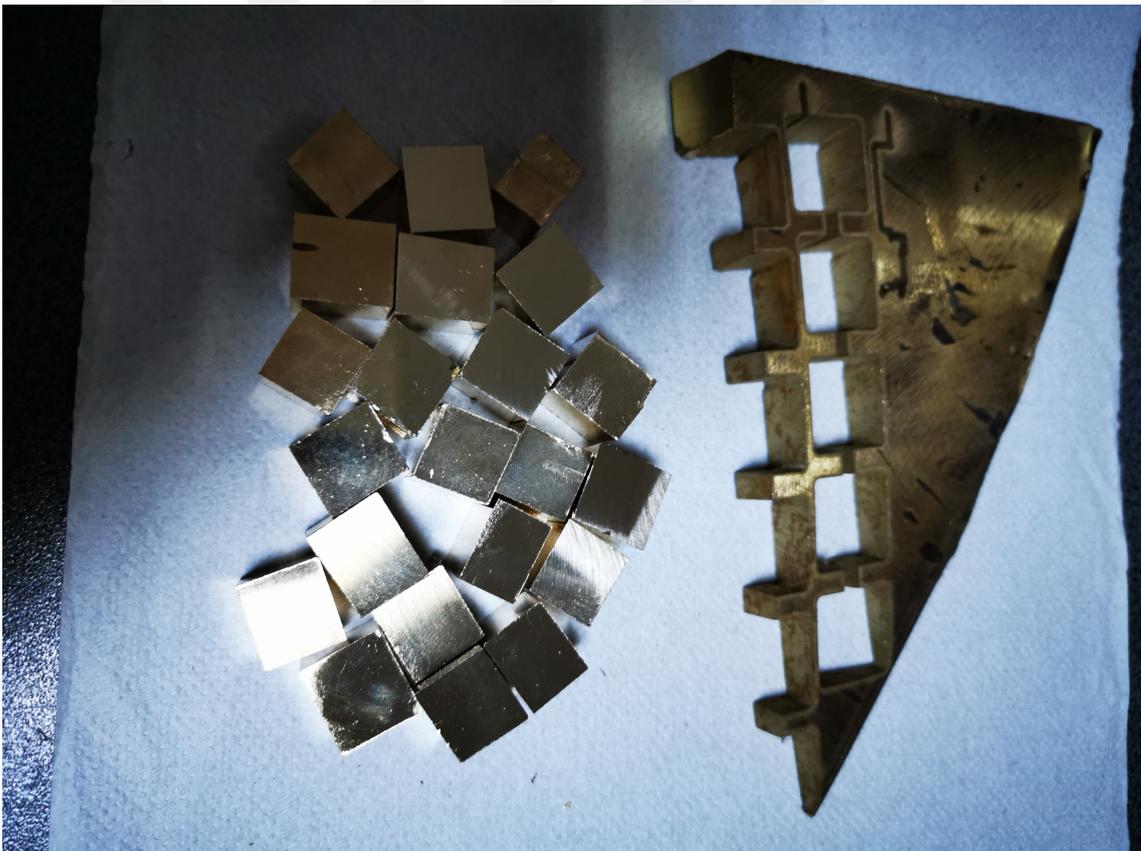
Grain size is very important for hardness of material. Generally, LST is supposed to result in fine grain size which is harder. LST causes to rapid cooling of processed zone and can creates fine grains. Because penetration of LST is very low compared to

thickness of samples. Substrate of samples behaves as heat sink that is very dominant to heat source (LST area). However, sometimes high conductivity of the surface can cause to heat substrate and slow down the cooling rate.



### 2.1 Preparation of Specimens

The specimens of marine bronze propeller is cut by means of water jet to avoid any metallurgic changes. Fig. 2.1 demonstrates the preparation of the specimens for experiments. They are cut from the propeller then they are shaped cubically by milling.



**Figure 2.1** Preparation of specimen by means of water jet

### 2.2 Laser Surface Treatment and Laser Ablation

Laser surface treatment and laser ablation is applied to surface of the specimens by means of 200W fiber laser. Some parameters applied with shielding gas, argon is

preferred on this purpose.

Fig. 2.2 demonstrates the setup of LST system:

- Laser head is above and horizontally positioned.
- Fixed mirror reflects laser beam to vertical direction.
- Optical lens focuses laser beam.
- Shielding gas, argon, is supplied via a nozzle.
- XY linear stage moves the specimen under laser beam to scan its surface.

### **2.3 Contact Angle Measurements**

Hydrophobicity of the specimen surfaces are evaluated according to "Standard Practice for Surface Wettability of Coatings, Substrates and Pigments by Advancing Contact Angle Measurement" of ASTM [38].

Fig. 2.3 demonstrates the contact angle measurement system prepared according to the standard:

- Size of the drop should not exceed 20  $\mu\text{L}$ . To control drop size there is a screw which pushes the syringe.
- The spring on the vertical line provides syringe system with reversing force after leaving drop to surface of the specimen.
- On the other side there is a uniform light source which gives opportunity to create white background for image of drop.
- The focused camera set up monochrome mode to make distinct the boundary of the drop.
- ImageJ software is used to make measurements of the photos. Fig. 2.4 shows screen shot of the software that demonstrates how it works.

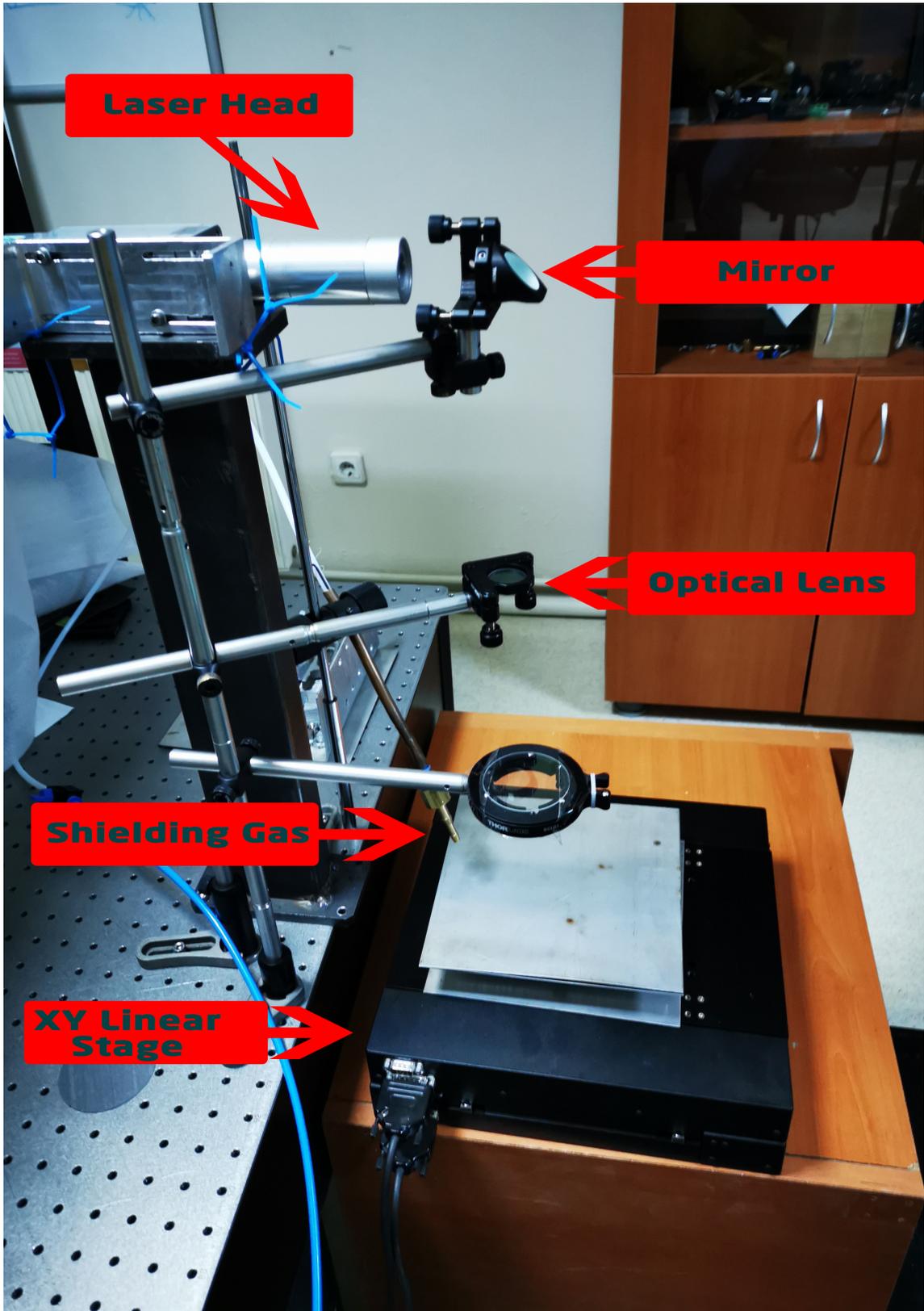


Figure 2.2 LST system

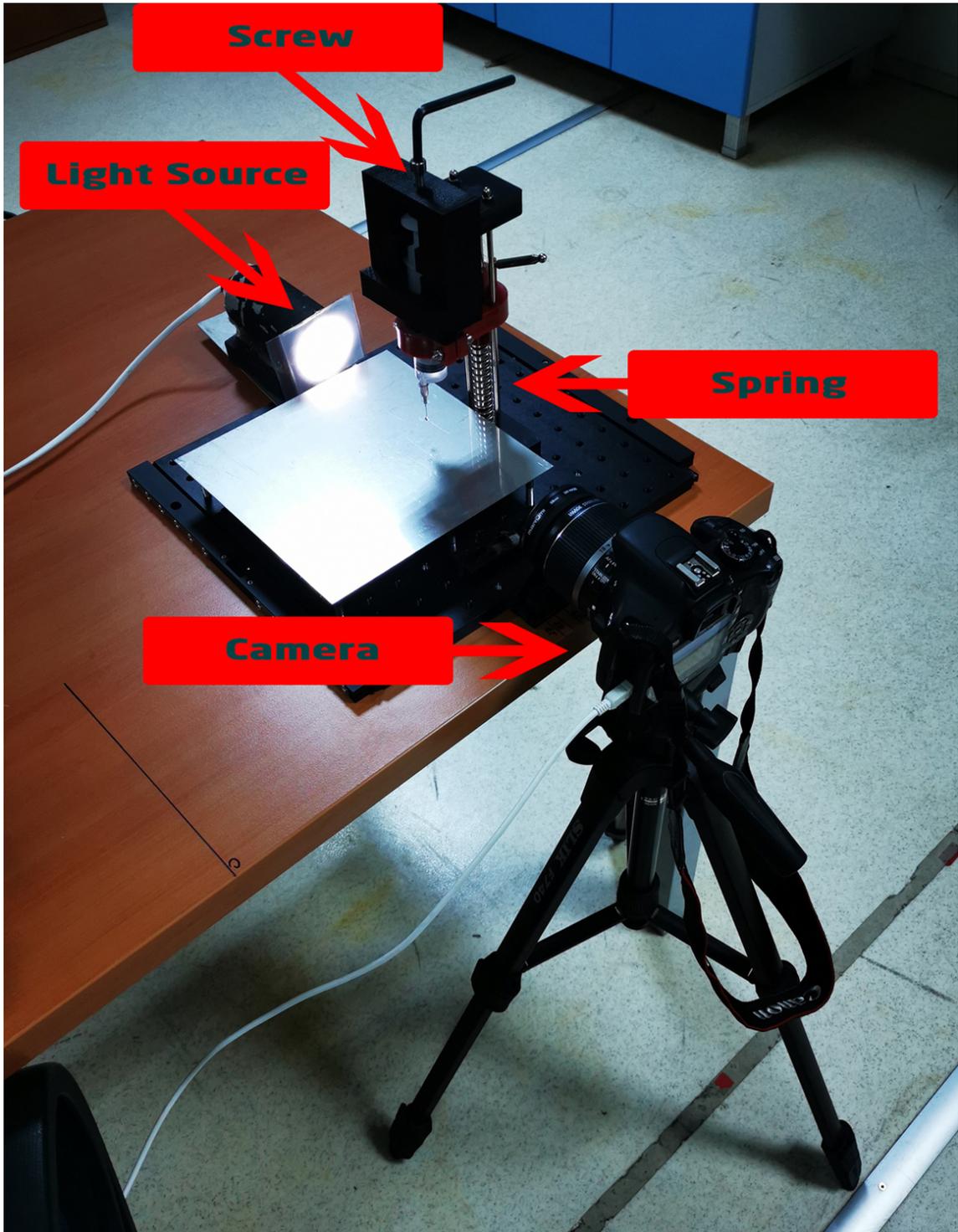


Figure 2.3 Contact angle measurement system

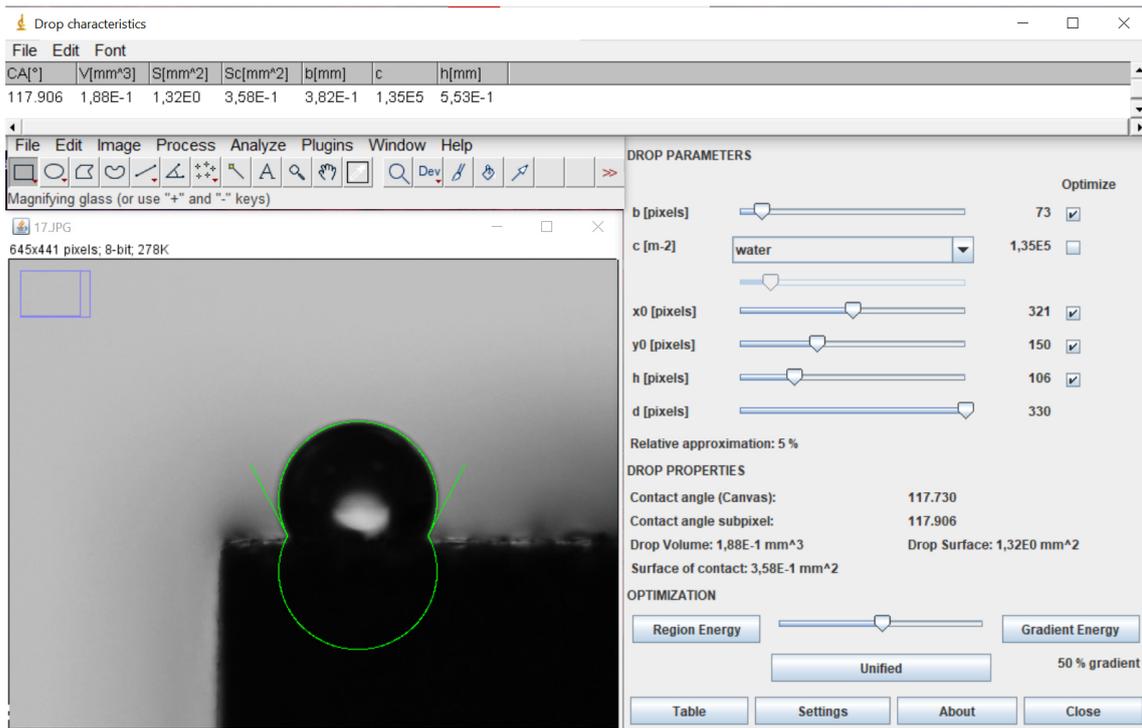


Figure 2.4 ImageJ drop analysis software

## 2.4 Hardness of Vickers Tests

Hardness of Vickers tests applied to evaluate the improvement in hardness. 1 kg and 0.8 s parameters are preferred. The tests are applied according to "Standard Test Methods for Vickers Hardness and Knoop Hardness of Metallic Materials" [39]. Fig. 2.5 demonstrates the Hardness of Vickers testing machine which is used in this study.

## 2.5 Salt Spray Test

Investigating effects of LST to specimens'  $R_c$  is one of the main aims of the present study. To get relative results of  $R_c$  quickly, salt spray test is applied. "Standard Practice for Operating Salt Spray (Fog) Apparatus" is known method for this method [40].

Salt spray tests give results quickly for most metals. However the bronze propeller is resistant to corrosion. Therefore more aggravate corrosion test environment is needed. To meet this need "Standard Practice for Modified Salt Spray (Fog) Testing" method is applied [41]. "Acetic Acid-Salt Spray (Fog) Testing" setup is preferred in accordance with material content.

**Sodium chloride solution is prepared according to following instructions:** Prepare the salt solution by dissolving  $5 \pm 1$  parts by weight of sodium chloride in 95 parts of water conforming to Type IV water in Specification D1193 (except that for this



**Figure 2.5** Hardness of Vickers testing machine

practice, limits for chlorides and sodium may be ignored) containing not more than 200 ppm of total solids. Halides (Bromide, Fluoride, and Iodide) other than Chloride shall constitute less than 0.1 % by mass of the salt content. Copper content shall be less than 0.3 ppm by mass. Sodium chloride that has had anti-caking agents added shall not be used because such agents may act as corrosion inhibitors. Adjust the pH of this solution to range from 3.1 to 3.3 by the addition of acetic acid [41].

Fig. 2.7 demonstrates the salt spray test chamber to apply Standard Practice for Modified Salt Spray (Fog) Test. Working principle of salt spray test is exposing specimens to corrosive environment of test chamber for specified test period at the same time. Corrosive environment is produced by means of heating the chamber to specified temperature in accordance with standards, 35 °C for the present study, and spray the sodium chloride solution into chamber. Spraying is a method that requires air supply. However the supplied air must be clean and oil-free. Fig. 2.6 demonstrates the compressor used to supply oil-free pressurised air. The compressor supplies 8 bar pressure, inlet of salt spray chamber adjust the pressure to 1 bar before arriving spraying nozzle.

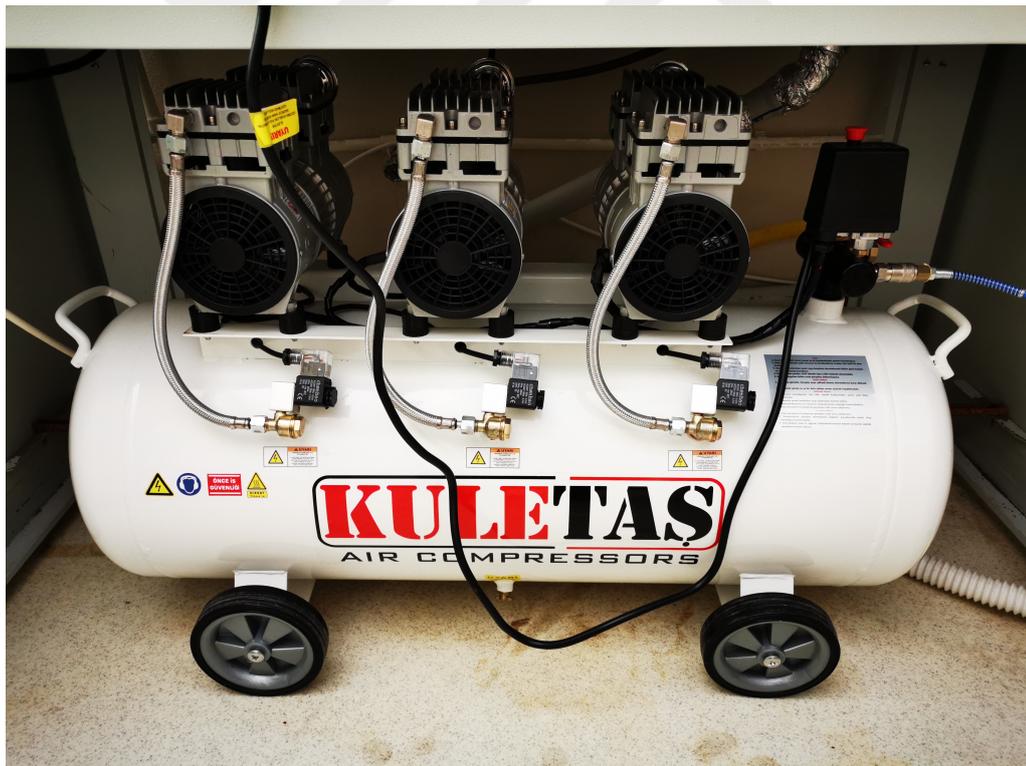


Figure 2.6 Oil-free compressor

pH of the sodium chloride solution is significant factor. Before spraying, pH of the solution is adjusted to 3.00-3.10 range. After spraying solution, the collector of spraying chamber accumulate some solution. pH of the collected solution is supposed to be between 3.10 and 3.30. Fig 2.8 demonstrates pH meter used in the present study.



**Figure 2.7** Salt spray test chamber



Figure 2.8 pH meter with glacial electrode

## 2.6 Preparation for Metallographic Analysis

LST process can change properties of the surface. Effects of LST and salt spray test results should be examined. To understand what happens on surface and substrate, metallographic analysis is needed. Fig. 2.9 shows the grinder and polisher machine used to prepare specimens for analysis.

After grinding and polishing processes, to observe grain boundaries of the cross section of specimens etching process is needed. In accordance with "Standard Practice for Microetching Metals and Alloys", the etching process is applied [42]. Fig. 2.10 demonstrates etching process. After submerging specimens to etching solution for specified periods, to end etching reaction the specimens are submerged to ethanol then rinsed via water. Etching solution consist of following contaminants:

- 2 g of  $K_2Cr_2O_7$
- 8 ml of  $H_2SO_4$
- 4 drops of  $HCl$
- 100 ml water



**Figure 2.9** Grinder and polisher machine

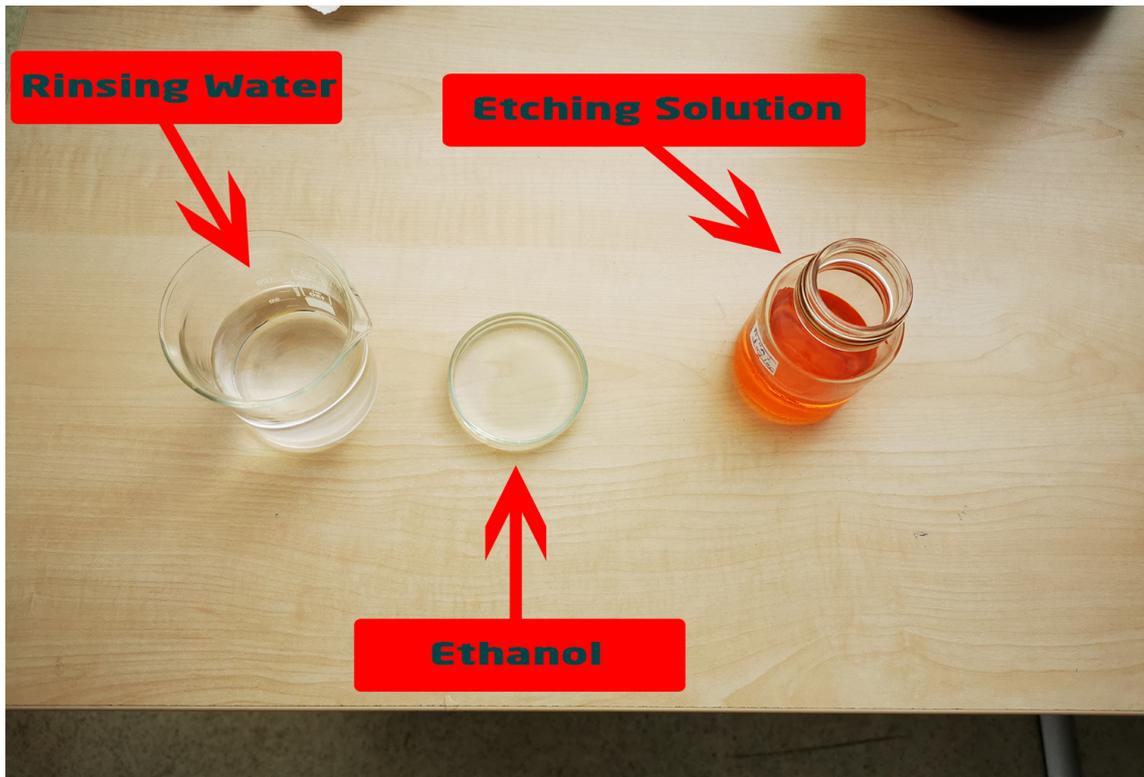


Figure 2.10 Etching process

## 2.7 ENERGY DISPERSIVE X-RAY (EDS)

EDS analysis are made to demonstrate elemental composition of the specimens. Fig. 2.11 shows the results of EDS analysis of specimens.

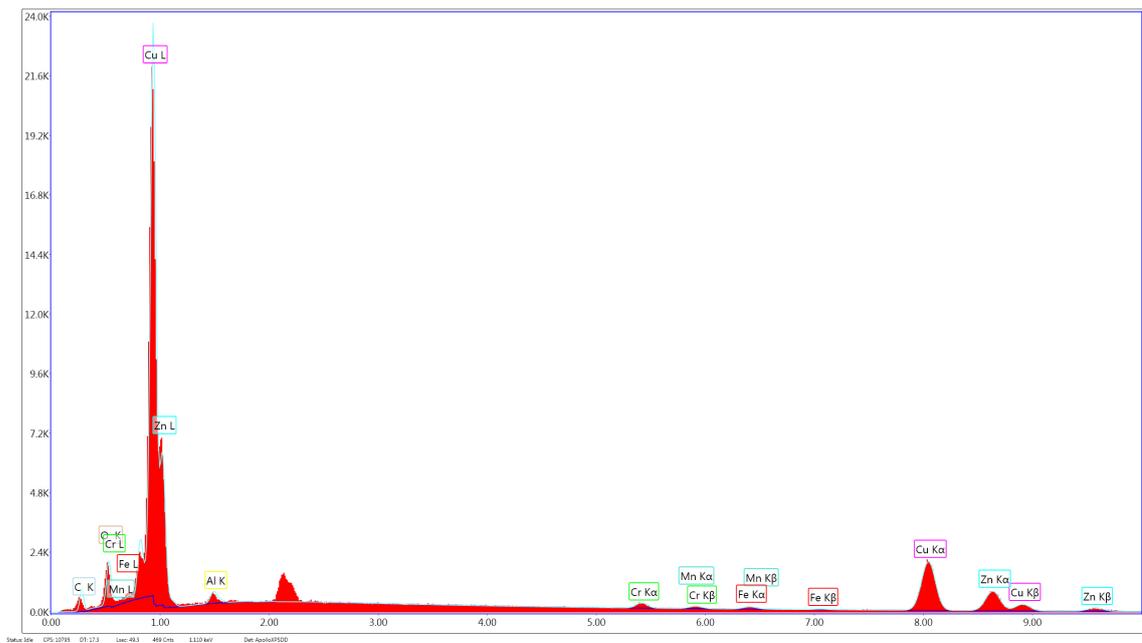


Figure 2.11 EDS analysis of the specimens

## 2.8 Optic Microscope Observations

Optical observations before and after LST are made via Olympus BX51M optical microscope which has 10x, 20x and 50x magnification. Penetration and other effects of LST and salt spray test is observed by means of the microscope.



Figure 2.12 Olympus BX51M optical microscope

## 3.1 Analysis of Hydrophobicity

Contact angle measurements are done in accordance with "Surface Wettability of Coatings, Substrates and Pigments by Advancing Contact Angle Measurement" [38]. Hydrophobicity is related to roughness and surface structure. Hydrophilic and approximately superhydrophobic surfaces obtained. Fig. 3.1 demonstrates a hydrophilic surface with 60° contact angle. Table 3.1 demonstrates some of the parameters used to adjust hydrophobicity and contact angle results. Sample 0 is the reference without any process of laser. "-" signs in "Contact Angle" column means drop is not shaped due to roughness and measurement was not possible. Sample 9 represents approximately superhydrophobic surface with contact angle 146° which is shown in Fig. 3.2.

**Table 3.1** Laser parameters for adjusting hydrophobicity

Sample No.	Power [W]	Duration [ns]	Frequency [Hz]	Speed [mm/s]	Steps [mm]	Shielding Gas	Contact Angle [°]
0	-	-	-	-	-	-	109
1	40	500	100	50	0,2	-	75
2	50	500	100	50	0,2	-	97
3	60	500	100	50	0,2	-	93
4	70	500	100	50	0,2	-	109
5	80	500	100	50	0,2	-	133
6	90	500	100	50	0,2	-	125
7	100	500	100	50	0,2	Argon	100
8	110	500	100	50	0,2	Argon	-
9	120	500	100	50	0,2	Argon	146
10	130	500	100	50	0,2	Argon	-
11	140	500	100	50	0,2	Argon	-
12	150	500	100	50	0,2	Argon	101

Surface structure is the main factor affecting the hydrophobicity. Fig. 3.3 shows cross section of the specimen with 146° contact angle.

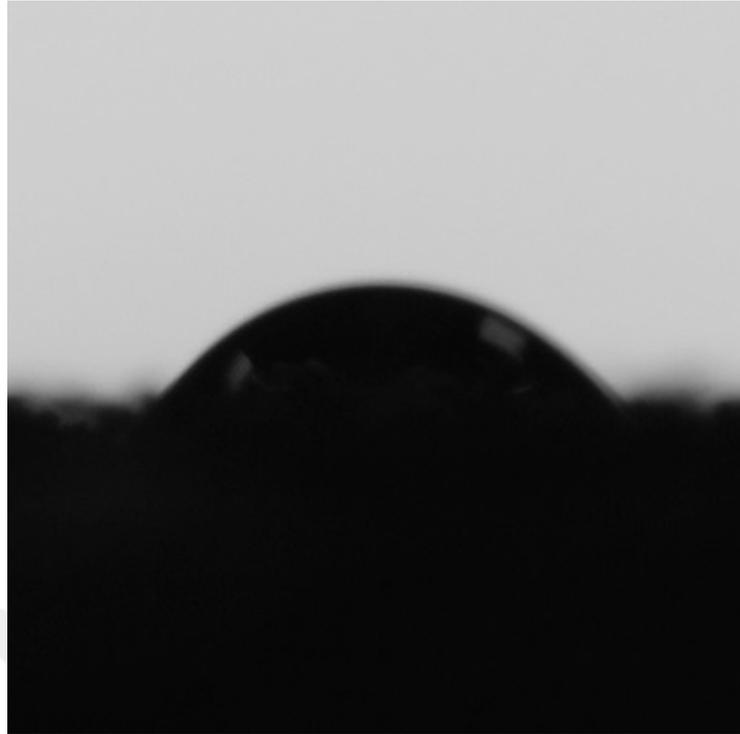


Figure 3.1 Hydrophilic surface with 60° contact angle

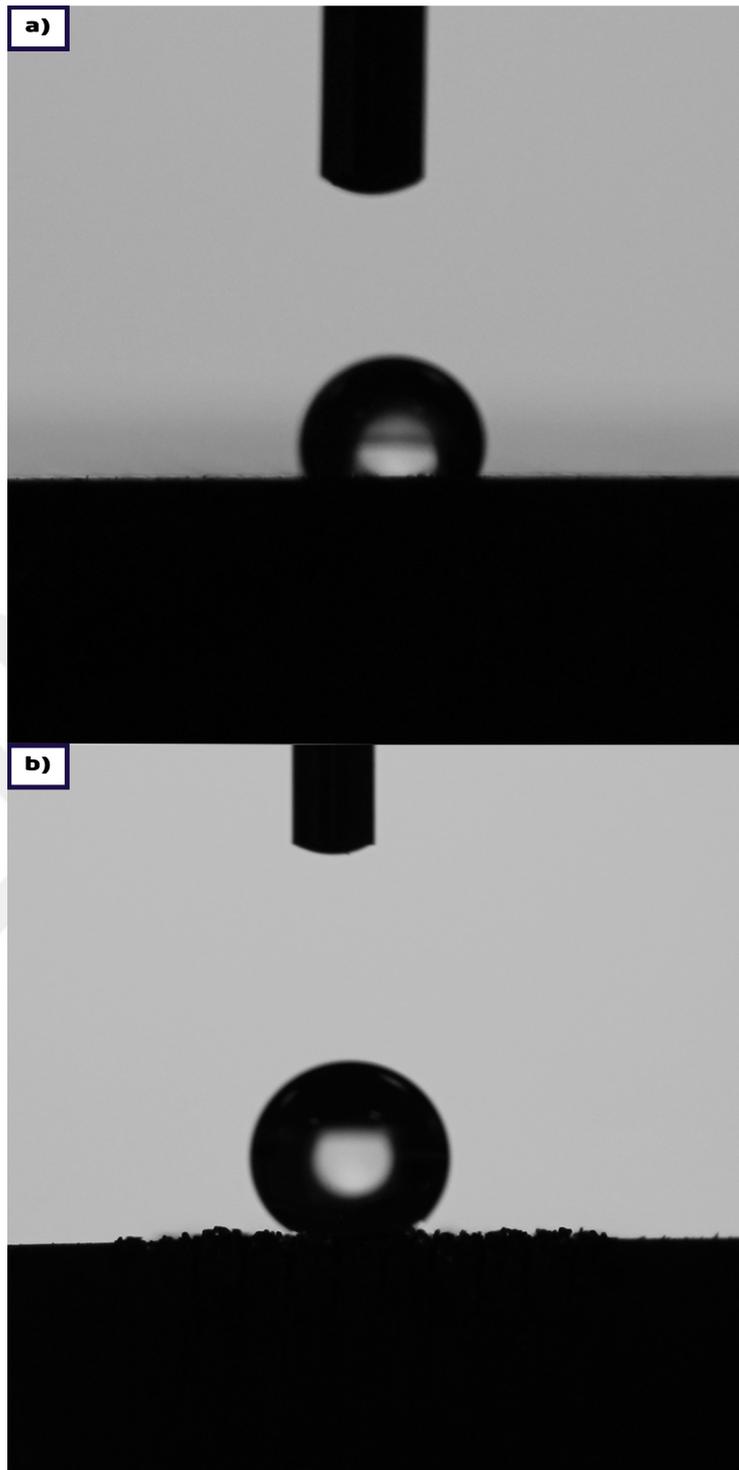
### 3.2 Analysis of Hardness

Grain sizes have significant effect on hardness of the material. Rapid solidification leads to smaller grain sizes and harder surface. Increasing laser power does not mean harder surface everytime. As long as substrate is heated, solidification slows down. Table 3.2 demonstrates some of parameters used to adjust surface hardness and results of them. Sample 0 represents the reference.

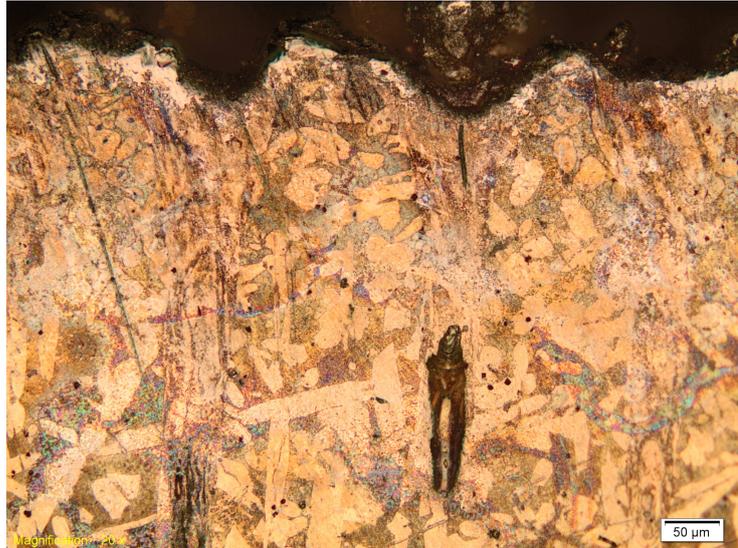
Table 3.2 Laser parameters for adjusting hardness and HV results

Sample No.	Power [W]	Duration [ns]	Frequency [Hz]	Speed [mm/s]	Steps [mm]	Shielding Gas	Hardness [HV]
0	-	-	-	-	-	-	181
1	40	500	100	50	0,2	Argon	188
2	50	500	100	50	0,2	Argon	160
3	60	500	100	50	0,2	Argon	158
4	70	500	100	50	0,2	Argon	139
5	80	500	100	50	0,2	Argon	146

Fig. 3.4 demonstrates the hardest result with 188 HV and reference sample. The distance between steps of the laser is wide compared to HAZ. Therefore rapid solidification occurs and hardening is achieved.



**Figure 3.2** Before LST reference surface with  $109^\circ$  contact angle(a) and approximately super hydrophobic surface with  $146^\circ$  contact angle(b)



**Figure 3.3** Cross section of approximately super hydrophobic surface with  $146^\circ$  contact angle

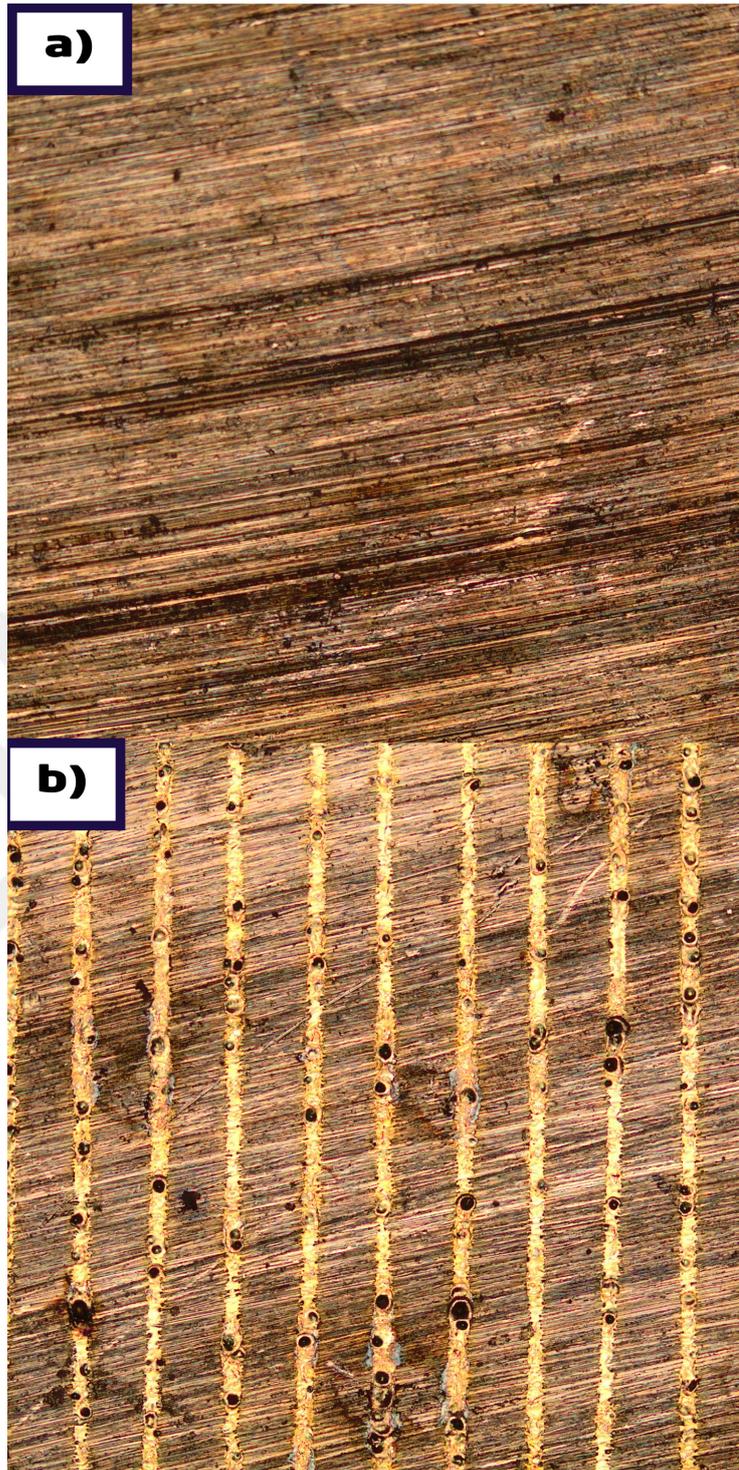
### 3.3 Analysis of Corrosion Resistance

Corrosion has many aspects. Especially corrosion with synergistic effect of cavitation erosion is very complicated. Smooth surfaces are more resistant to corrosion compared to rough surfaces because they hold liquids stagnant. LST process can increase roughness. However uniform micro structure which is obtained via melting and resolidification can contribute to resistance against corrosion. Also polishing surface after LST can be considered to decrease roughness. Fig. 3.5 demonstrates how LST uniforms microstructure and dissolves defects of material.

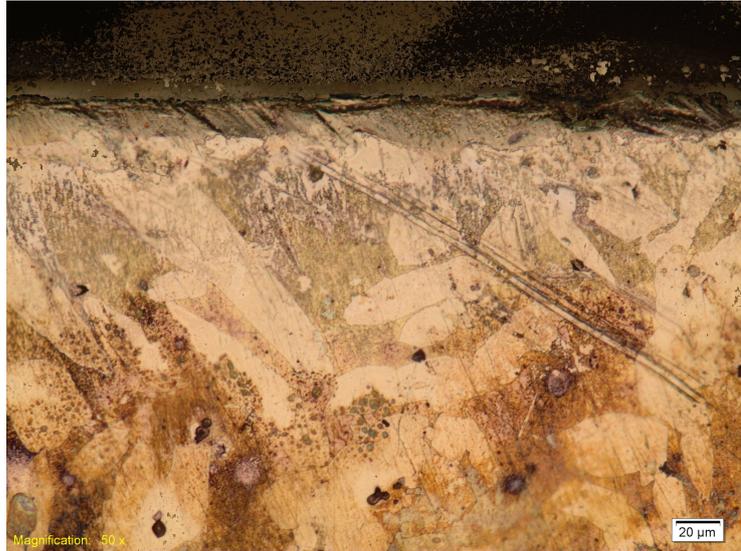
On the other hand laser beam can cause formation of holes randomly on reflective surfaces. Reflective surfaces need more power for LST because they do not absorb most of laser energy. However, once melting start they will lost their reflective properties and absorb laser beam energy much more. After melting, very high energy concentration can lead to evaporate metal and create pits. Surface defects and dirt on the material are the main reasons for logarithmic changes of laser energy absorption. Fig. 3.6 demonstrates the holes and pits formed by laser.

Proper laser parameters to improve  $R_c$  are eliminated by experiments. Table 3.3 demonstrates the selected 5 parameters. 5 samples put to salt spray test with reference sample which has never been exposed to LST. Comparison between processed samples and reference sample is the indicator to evaluate improvement in  $R_c$ .

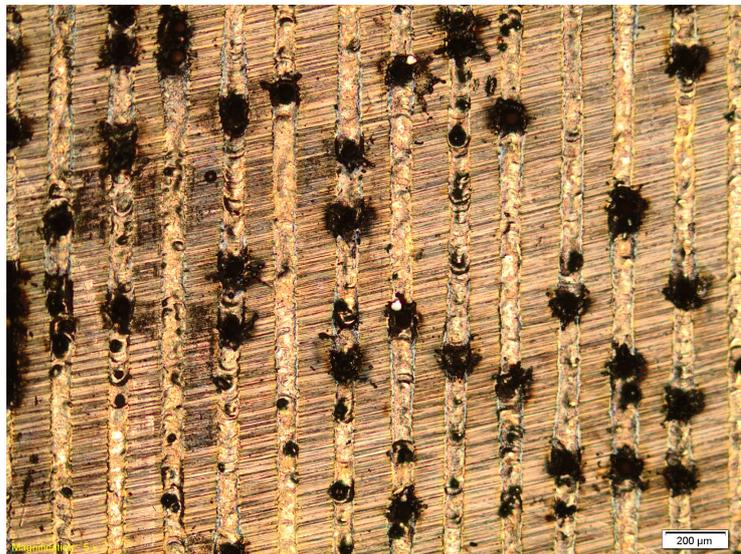
Surface temperature is another aspect that affects results of LST. After long exposition of laser beam with high energy, surface temperature changes. Therefore results of LST and oxidation rate changes. Fig. 3.7 demonstrates effect of surface temperature



**Figure 3.4** 5x magnification microscope images of reference material (a) and hardest result (b)



**Figure 3.5** LST uniforms structure and dissolves defects of the material

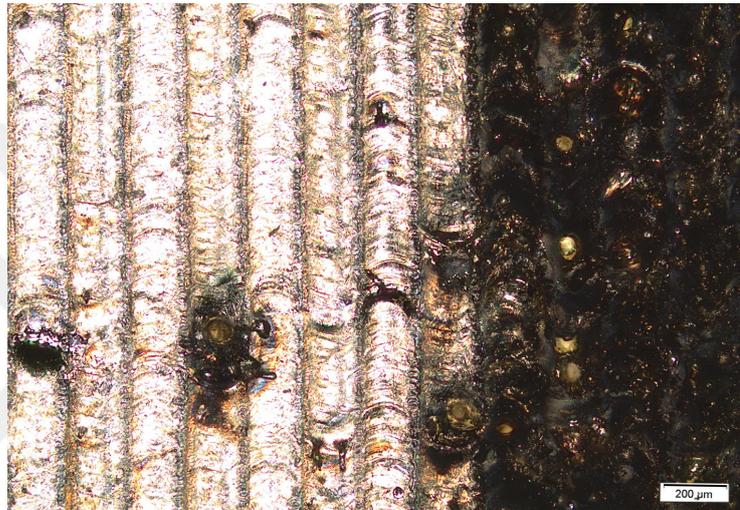


**Figure 3.6** Holes and pits formed by laser

**Table 3.3** Laser parameters for improving  $R_c$

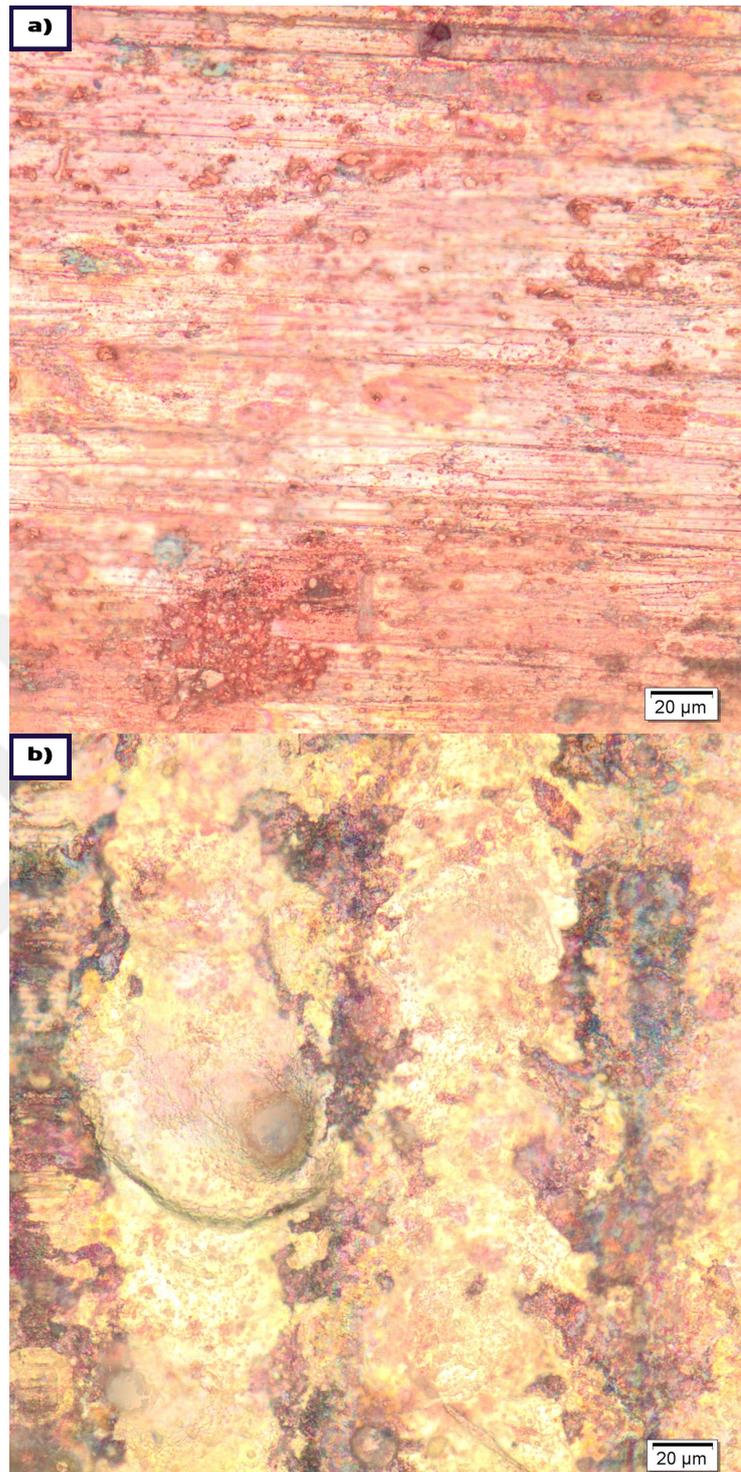
Sample No.	Power [W]	Duration [ns]	Frequency [Hz]	Speed [mm/s]	Steps [mm]	Shielding Gas
0	-	-	-	-	-	-
1	40	500	100	50	0,1	Argon
2	50	500	100	50	0,1	Argon
3	60	500	100	50	0,1	Argon
4	70	500	100	50	0,1	Argon
5	80	500	100	50	0,1	Argon

to results of LST.



**Figure 3.7** Effect of surface temperature on LST (scanning direction is from right to left)

After LST, selected specimens exposed to salt spray test. Comparison is done between successful LST processed sample and reference metal. Fig. 3.8 demonstrates reference metal and Sample 2 after salt spray test. Apparently LST processed specimen is less affected from selective leaching and pitting corrosion. However, LST processed specimen has weaker sites between scanning lines. The reason for this situation may be stagnancy of liquid on the groove shape between scanning lines. Another reason can be weak influence of laser on those sites.



**Figure 3.8** Comparison of salt spray test results between reference metal (a) and LST processed specimen (b)

Creating approximately superhydrophobic bronze marine propeller surfaces by LST is possible. In this study 146° contact angle is achieved (>150° is considered as superhydrophobic). However, the environment that marine propellers work contains too many biological activities and dirt. To approve beneficialness of hydrophobic surface of the propellers, it is required to observe them under working conditions. Salt deposition on the structured surface may spoil hydrophobic property and lead to more corrosion.

Also hydrophilic surfaces are obtained. Hydrophilic surfaces can be beneficial in case the propeller needs to be painted or coated with a chemical. Coating material or paint stick to hydrophilic surfaces much better. There are coating options for bronze marine propellers to avoid corrosion and cavitation. Therefore, LST may be considered as a method to prepare surfaces for coating in aspects of roughness and hydrophilicity.

Surface hardness of propellers is directly related to resistance to cavitation. One of the main purposes of the current study was to improve surface hardness of the specimens. However, sufficient improvement is not observed. Therefore it is possible to state that LST without added material is not proper to increase hardness of marine bronze propellers.

$R_c$  of some specimens increased significantly. Compared to the reference, some LST processed samples has better  $R_c$ . Salt spray test results prove the improvement of  $R_c$ . After salt spray test, much less reddish colour of the resistant LST processed specimen (Sample 2) compared to reference means that LST can increase resistance to selective leaching. Besides, pitting corrosion rate is very high on the reference, compared to the processed specimen. Depth values of the pits are apparently higher on the reference. Therefore it is clear that the resistance against to pitting corrosion is improved.

By applying salt spray test after LST on the bronze marine propeller specimens, the current work constitute to literature unique experiments and analysis. Salt spray test

results constitute to data about effects of LST to  $R_c$  of marine bronze propellers.

However, there are some drawbacks related to LST. LST can increase surface roughness and form some pits and holes. This side effect of LST may be solved by mechanical grinding after LST process. Making the LST processed rough surface smooth again by means of grinding can increase  $R_c$  of the surface significantly. Because roughness is one of the main reasons lead to stagnancy of liquids on surface. Stagnancy leads to dangerous corrosion forms.

To sum up, LST can be beneficial method to improve hydrophobicity and corrosion resistance of bronze marine propellers. However improving surface hardness of the bronze propellers requires LST methods with added material, the results of LST without added material is not sufficient.



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## PUBLICATIONS FROM THE THESIS

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### Conference Papers

1. ınar, İ., Başak, M. E., “Improving Hydrophobicity, Roughness and Hardness Properties of Specimens of Bronze Marine Propeller by Laser Surface Treatment”, 6th INTERNATIONAL MARMARA SCIENCES CONGRESS (IMASCON 2021 SPRING), 21-22 Mayıs 2021, Derince/Kocaeli, TÜRKİYE.

