Corrosion inhibitors. A review

A. Kadhim,[1] A.A. Al-Amiery,[2]* R. Alazawi,[1] M.K.S. Al-Ghezi[2] and R.H. Abass[1]

[1]Laser and Optoelectronic Engineering Department, University of Technology, Baghdad, 10001 Iraq
[2]Energy and renewable energies technology center, University of Technology, Baghdad, 10001 Iraq
**E-mail: dr.ahmed1975@gmail.com*

Abstract

This review provides an outline of related literatures in which scientists and researchers used different types and procedure of corrosion inhibitors to reduce corrosion that takes place in various equipment made of alloys or metals. Different chemical inhibitors were used to reduce the rate of corrosion in various alloys. The inhibition rates ranged between 30-80% in acidic environments with different molar concentrations. The second part of this article, the laser was used as a tool to inhibit the corrosion of some alloys and under various conditions without used chemical inhibitors as an auxiliary agent. The effect of the laser pulses on the material leads to an increase in its hardness and thus its corrosion resistance. We found that the rate of inhibition reaches about 80%.

Keywords: *corrosion, inhibitor, review.*

Received: October 16, 2020. Published: January 17, 2021 doi: 10.17675/2305-6894-2021-10-1-3

Introduction

Corrosion is defined as the damage of metals and alloys through chemical or electrochemical interaction with their surrounding environment [1]. In the classification of corrosion reactions according to the nature of corrosive environments, they are divided into wet and dry corrosion [2, 3]. Depending on the morphology of metal damage, the corrosion can be classified into general corrosion, pitting corrosion, crevice corrosion, intergranular corrosion, environmentally induced fracture, de-alloying; galvanic, and erosion-corrosion [4, 5]. There are certain ways to protect the metal from corrosion such as coating, alloying, cathodic protection, anodic protection and recently been using the laser for this purpose by surface treatment of metal is considered as the way to improve the properties of metals like roughness, hardness, the resistance of corrosion, *etc*. [6, 7]. Corrosion inhibitors are of considerable practical importance, as they are extensively employed in reducing metallic waste during production and In reducing the risk of material failure, both of which can lead to the sudden closure of industrial processes, which in turn leads to additional costs. It is also important to use corrosion inhibitors to prevent the dissolution of minerals and reduce acid consumption [8, 9]. There are two types of corrosion reactions according to the nature of the corrosive environments: wet and dry corrosion [10]. These types of corrosion can be classified into general corrosion; pitting corrosion; crevice corrosion; Inter-granular corrosion; environmentally induced fracture; de-alloying; galvanic, and erosion-corrosion; this depends on the morphology of metal's damage [11–13]. Several techniques, such as coating, alloying, cathodic protection, anodic protection, and laser treatment are used to protect metals from corrosion [14]. The use of laser technology in surface treatment of materials represents the main areas in which looks set special features enjoyed by the laser beam, which distinguish it from other energy sources and make it more than traditional technologies are all (even modern ones) in this type of heat treatments [15–17]. The increasing utilization of laser in material processing can be contributed to many unique advantages of laser called, high productivity, automation worthiness, non-contact processing, removal of finishing operation, decreased processing cost, improved product quality, maximum material utilization, and minimum HAZ [18, 19]. The process of laser-material interaction is considered as a very complex thermos-physical process under the interaction between temperature, phase transformation, and stress-strain [20]. The use of laser shock peening (LSP) is a new method used as a surface treatment; it is used to reduce metal corrosion. LSP is defined as residual mechanical stress that is introduced as deep pressure by generating shock waves by laser pulses with a high energy density to the target surface [21]. There are methods to reduce metal wear by using modern alloys, thin films, and coatings deposited on the surface of the metal and recently laser is used for this purpose by surface treatment of metals and is a method for improving mental properties such as roughness, hardness, wear resistance, *etc*. [22]. Herein, we investigate the classification, synthesis, and applications of some synthesized inhibitors for the corrosion inhibition of metals in corrosive solutions [23–42].

Classification of corrosion inhibitors

Organic Corrosion Inhibitors are an attractive area of research because of their usefulness in various industries. The efficiency of the inhibitor depends on the stability of the formed chelate, and the inhibitor molecule must have centers capable of forming bonds with the metal surface by electron transport. Most organic inhibitors are absorbed onto the metal surface by displacing water molecules on the surface and forming a pressurized barrier. The availability of non-bonding electrons (a single pair) and p electrons in the inhibitor molecules facilitate the transfer of the electron from the inhibitor to the metal. The efficiency of the inhibitor depends on the stability of the chelate formed, so it mainly depends on the type and nature of the alternatives present in the inhibitor molecule [43]. I.O. Ogunleye *et al*. in the same year 2011 [44] investigated the effect of grapefruit juice in different concentrations on the corrosion rate of mild steel in different acidic media (HCl and H_2SO_4) with the utilization of the weight-loss method, this research used grapefruit juice in concentrations from 0% to 5% weight for each acidic solution and found the corrosion rates for HCl (0.694×10^{-7} to 0.378×10^{-7}) g/cm^2/sec and for H_2SO_4 (4.782×10^{-7} to 1.157×10^{-7}) g/cm^2/sec. It's observed that the addition of grapefruit juice reduced the corrosion rate of mild steel, the inhibitor efficiency was measured at grapefruit juice concentration of 5% for HCl and H_2SO_4 respectively 94.6%, 75.8% that means grapefruit juice is the better corrosion inhibitor in HCl acidic than H_2SO_4 acid. N.S. Patel *et al*. [45] in 2013 used corrosion inhibitor from leaves of plants to decrease the corrosion rate of mild steel in 0.5 M of H_2SO_4 by using different techniques (weight-loss method and electrochemical polarization) it was showed the extract of leaves plants are excellent corrosion inhibitors. The scanning electron microscope shows the surface of mild steel has become more resistant to corrosion as a result of a protective layer that is formed on the surface due to the adsorption of active molecules. A. Kadhim examined the anti-corrosion activity of mild steel corrosion in hydrochloric acid (1 M) media caused by the Schiff base 3-[(5-phenyl-1,3,4-thiadiazol-2-yl)imino]-2-oxoindoline. Weight-loss measurements and scanning electron microscopy were performed during the investigation. The measurements showed that the inhibition efficiency of the chemical compound increased with its increasing concentration. This inhibitor functioned through adsorption following the Langmuir isotherm and the electronic properties obtained through the Austin Model 1. The semi-empirical method was found to be correlated with the inhibitor's experimental efficiency by the nonlinear regression method. The organic compound was synthesized effectively through a reaction between indoline-2,3-dione and 5-amino-2-phenyl-1,3,4-thiadiazol [46]. Al-Amery and Kadihum have invented a coating composition for inhibiting corrosion named 1,5-dimethyl-4-((2-methyl benzylidene)amino)-2-phenyl-1*H*-pyrazole-3(2*H*)-one (Figure 1), on mild steel metal surface. This inhibitor was synthesized with an excellent yield by refluxing *o*-tolualdehyde, 4-aminoantipyrine, and a polar solvent. This new inhibitor can reduce the corrosion rate on metal surfaces [47]. Figure 2 shows the corrosion rate per year as a function of the time with organic inhibitor.

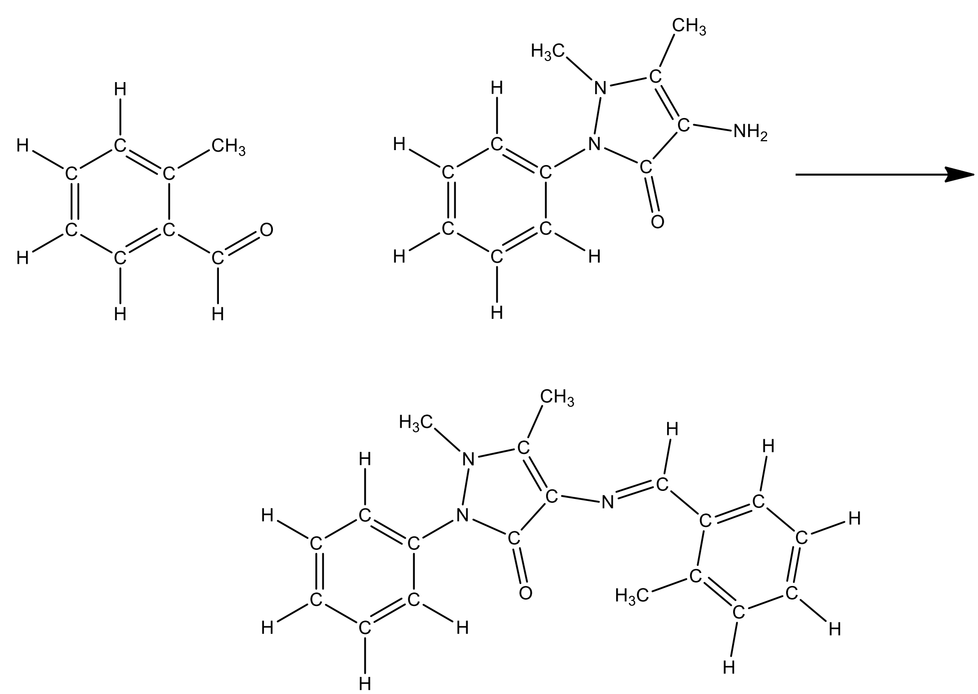

Figure 1. 1,5-Dimethyl-4-((2-methylbenzylidene)amino)-2-phenyl-1*H*-pyrazol-3(2*H*)-one.

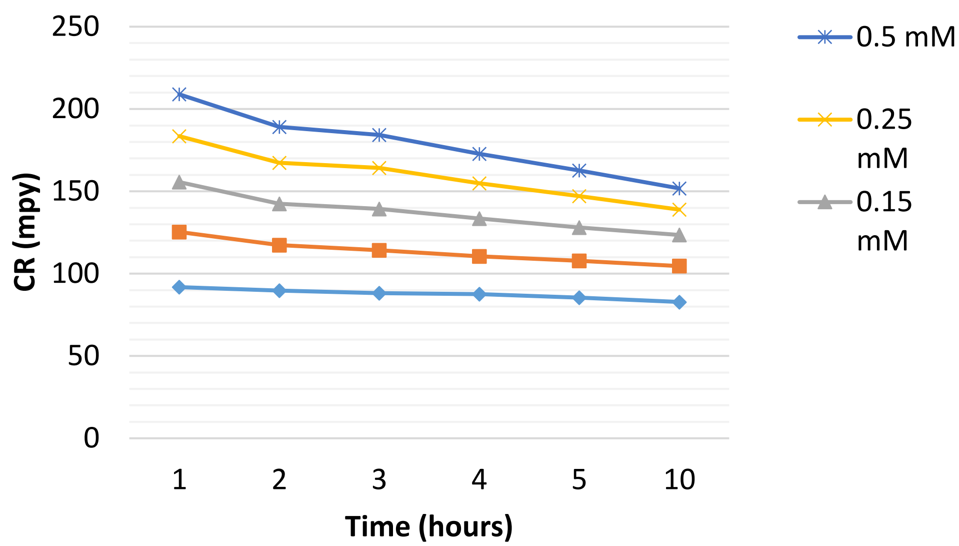

Figure 2. Corrosion rate per year as a function of time period with organic inhibitor for different acid molarity.

The laser is characterized by providing large amounts of energy in the confined areas of the material to reach the required reaction, and this energy will be absorbed by a nearby metal surface and the surface chemistry will be treated [48]. The laser surface processing can be classified according to the change in surface material synthesis into two kinds:

First thermal process: this process doesn't cause any change in the composition of material surface like laser cutting, welding, tempering, annealing, melting, and transformation hardening. And the second kind is the thermo-chemical process: in this process, the metal will have a change in metallic structure by adding another material so the surface composition changes, like laser cladding, alloying. Furthermore, the advantages of these surface treatments include flexibility and the possibility of treating small areas, leaving the other parts unaffected [49]. Laser shock peening represents a modern method used in surface treatment can be defined as a mechanical process based on the introduction of residual pressure of deep pressure by shock waves that are generated by the disposal of laser pulses with a high energy density on the surface target [50, 51]. In 2004, Ocana *et al*. presented a summary providing various experimental results obtained from the latest LSP experiments conducted by the authors along with the conclusions. They rated LSP as a profitable way to extend the life of fatigue in critical components. In particular, an initial display of the frequency power multiplier was obtained [52]. The laser shock peening technique (Figure 3) is a good technique to modify the surface properties and improve the corrosion resistance thus the corrosion rate decreased from 7.7210 mm/y before LSP treatment to 1.0716 mm/y after LSP treatment at the optimum thickness of the confining layer (4 mm). Q-switching Nd:YAG laser is an efficient corrosion inhibitor for an St-37 alloy on immersion in 1 M HCl, the maximum inhibitor efficiency is 85.59%. Polarization curve results show that shifting occurs in the potential to more positive region after applying LSP, while the corrosion current is reduced from 958.02 μA/cm^2 to 138.17 μA/cm^2 after using Nd:Yag laser as a corrosion inhibitor [53].

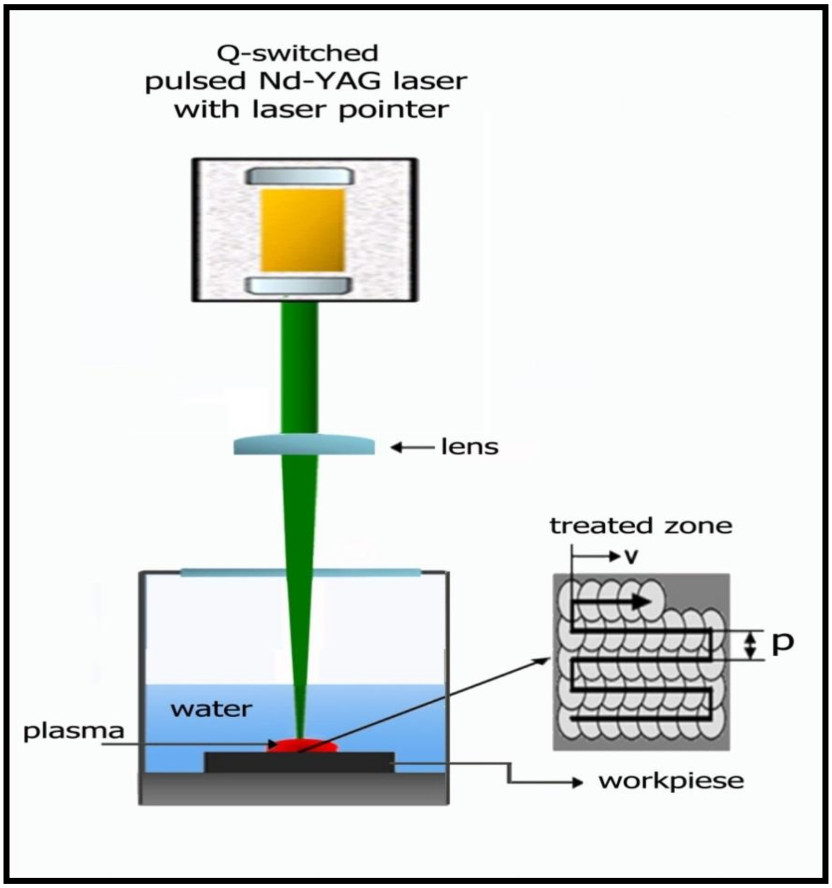

Figure 3. Laser shock peening technique.

Nd:YAG lasers to the remaining residual stresses are stimulated in a highly deformed material such as aluminum. Although there are reasonable doubts about their ability to cause these tensions overextended depths or in less deformed materials (*i.e*. stainless steel).

Janez Grum *et al*. [54] investigated improving corrosion resistance by LSP for aluminum alloys (AlMgSiPb and AlSi1MgMn) in the same year (2010). Nd:YAG laser used (1064 nm) with a pulse duration of 10ns, pulse repetition rate of 10 Hz, and the pulse density was changed. From the polarization tests after increasing the laser pulse density it has been found the potential increased with the increasing of laser pulse density, for AlSi1MgMn the increase occurred in the pitting potential equal to 120 mV and for AlMgSiPb equal to 267 mV so bigger corrosion resistance was obtained with increasing laser pulse density. In 2012, Subhasisa Nath [55] studied laser surface alloying of aluminum with WC+CO+NiCr for improved wear resistance. Laser surface alloying of aluminum with WC+CO+NiCr (in the ratio of 70:15:15) has been conducted using a 5 kW continuous wave (CW) Nd:YAG laser (at a beam diameter of 0.003 m). The output power used was ranging from 3 to 3.5 kW and 0.012 m/s to 0.04 m/s scan speed by simultaneous feeding of precursor powder (at a flow rate of 1×10^{-5} kg/s) and using He shroud at a gas flow rate of 3×10^{-6} m^3/s. Laser surface alloying leads to the development of fine-grained aluminum with the dispersion of WC, W_2C, Al_4C_3, Al_9CO_2, Al_3Ni, $Cr_{23}C_6$, and CO_6W_6C. Figure 4 represents the effect of laser shock on sample surface before and after treatment.

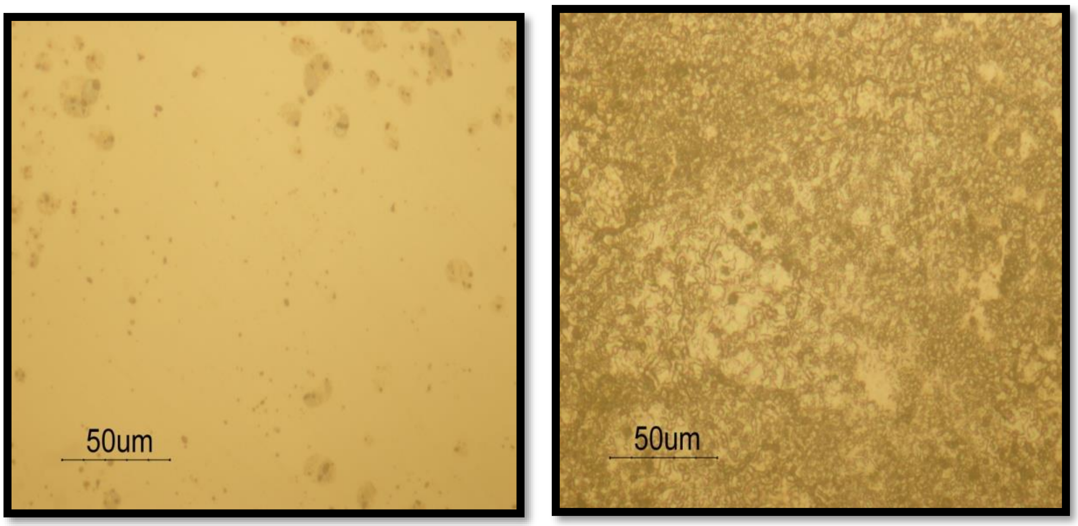

Figure 4. The microstructures of metal's surface before laser treatment and right after laser treatment.

Chemical compounds Added in small quantities to reduce the wear rate. The presence of these compounds delays the corrosion process and keeps its rate to a minimum, thus preventing economic losses caused by mineral corrosion. Chemicals that can act as corrosion inhibitors may be inorganic or organic.

M. Sivaraju and K. Kannan, 2010 [44] studied the effect of *Acalypha Indica* L. alcoholic extract (AIAE) as inhibitor material on mild steel that corrodes in 1 N phosphoric acid by two techniques mass loss and polarization techniques at different temperatures. They found when increasing the concentration of plant extract, the inhibition efficiency increased, also this study showed direct proportionality between the corrosion rate and temperature and reverse proportionality between the concentration of inhibitor and corrosion rate. At 303 K in 1 N phosphoric acid at 5 mg of the inhibitor, the maximum inhibition efficiency from mass loss studies was equal to 95.21% and from polarization measurement it was equal to 90.38%. In 2011 Shylesha B.S. *et al*. [56] used 2-methyl-3-aniline as a corrosion inhibitor for mild steel in different corrosive media (1 M HCl and 0.5 M H_2SO_4) by using mass loss and electrochemical studies. The concentration of inhibitor was changed (0, 0.01, 0.05, 0.10, 0.15, 0.20 M) then the inhibition efficiencies were calculated. The maximum IE was obtained with higher concentration from mass loss measurements, IE=81.7% in H_2SO_4 and IE=84.2% in HCl, and from polarization studies IE=81.9% in H_2SO_4 and IE=82.1% in HCl. An increase in concentrations led to an increase in inhibition efficiency.

Makanjuola Oki *et al*. [57] in 2011 used tannin, tannin:H_3PO_4, and H_3PO_4 as inhibitor materials for mild steel in hydrochloric acid with the use of weight loss measurements that indicated the efficiency of inhibitor was 72% for tannin at a maximum concentration of 140 ppm and with the same concentration of tannin:H_3PO_4 in ratio 1:1 the inhibition efficiency was 61%, while the efficiency of H_3PO_4 was 55%. At inhibitor concentrations of 140 ppm for 6 hour exposure in 1 M HCl solution, the corrosion rate for tannin was 2 mA/cm^2, 2.4 mA/cm^2 for tannin/H_3PO_4, H_3PO_4-inhibited 2.6 mA/cm^2, and 6 mA/cm^2 for uninhibited sample

Sutiana Junaedi *et al*. [58] used 1,5-dimethy1-4-(2-methylbenzylidene)amino-2-phenyl-1*H*-pyrazol-3(2*H*)-one (DMPO) with different concentrations (0 to 0.5×10^{-3} M) to protect mild steel that was immersed in 1 M HCl and the impacting of DMPO into corrosion, from polarization measurement at a higher value of inhibitor concentration, it was found the maximum was IE=87.7% with i_{corr}=39.6 μA cm^{-2} and E_{corr}=–479 mV/sec.

In 2014 S.I. Durowaye *et al*. [69] studied the effect of Methyl red (2,4-dimethylamino-2′-carboxylazobenzene) with different concentrations (1,2,3,4,5 and 6%)as an inhibitor on the corrosion rate of mild steel in 1 M H_2SO_4. The results showed a decrease in corrosion rate as the concentration of the organic compound increased, with the maximum IE=87.3% and with the lowest CR=0.352 mpy. In 2015, AL-Amery, Kadhim, *et al*. [60] used the power of creatinine as an inhibitor. Metals in 1 M corrosive acid solution (hydrochloric acid) were investigated utilizing a weight loss technique. Results demonstrated that the inhibition occurs through adsorption of the creatinine molecules on the surface of the metal and the efficiencies were improved with an increment in creatinine concentration and diminished at higher temperature degrees. SEM was done for the metal surface to examine it. The highest occupied molecular orbital energy, lowest unoccupied molecular orbital energy, and dipole moment were theoretically calculated utilizing Density Function theory.

Anti-corrosion coatings are generally used to prevent average wear and increase the longevity of mild steel. A wide range of organic adsorption inhibitors is currently applied in the area of expensive corrosion. Pairs of electrons and negative ions are transferred from the inhibitors to the metal orbitals d, which leads to the formation of coordination complexes with a specific geometry, such as planar, quadrilateral, or octahedral [61]. Thus, the barrier particles improve the mild steel's resistance to corrosive solutions by absorbing it onto the metal surface and forming a barrier that prevents the active sites of mild steel. Adsorption on slight steel is affected by the nature of mild steel, the type of electrolyte, and the molecular structure of the inhibitor [62].

Nanoparticles coating

The use of nano-coatings is one of the most effective methods for preventing and postponing corrosion. Nano-coatings have a higher thermal expansion coefficient, higher hardness and toughness, and more resistance to corrosion, abrasion, and erosion. The effect of TiO_2 nano-particle coating on the construction of corrosion-resistant blades of centrifugal pumps. Thin layers of titanium dioxide nano-particles were created in two separate steps on GG25 gray cast iron samples with specific dimensions and characteristics using the sol-gel process and immersion method. After each step, heat treatment was performed to stabilize the nano-coating. The thickness of applied coatings was measured by scanning electron microscopy (SEM). To measure the corrosion rate, the samples were exposed to petrochemical wastewater. The corrosion rate was measured by the atomic absorption spectrometry method. The experiments were carried out in a factorial arrangement in a completely randomized design with three temperature levels of 40, 50, and 60°C and four thicknesses. The results showed that the coating of titanium dioxide nano-particles increased the corrosion resistance of GG25 gray cast iron. With an increase in temperature from 40 to 60°C, the corrosion rate of all samples increased by 46.6%. Coated samples with thicknesses of 440–550, 840–970, and 1030–1330 nm reduced the corrosion rates by 39.1%, 67.8% and 73.6%, respectively [63].

In some circumstances, the nano-coating may not act as protective surfaces. Nano coating is an effective physical barrier in high-temperature applications, as its high grain density provides fast diffusion paths for passive ions and better adhesion to the protective oxide layer on the substrate surface [64]. However, the higher boundary portion of the grain provides more anode locations, making the surface more vulnerable to corrosion attack. Moreover, the nano-coating forms a defensive structure by including them in vacant positions, dislocation, and grain- interpolation limits. These features have the advantage of forming a more effective passivation layer, as the inert ions spread will be faster. On the other hand, the agglomeration of these nanomaterials may occur due to the accelerated proliferation of aggressive ions, causing non-uniform surfaces. It increases the ability to form active sites, thereby reducing wear resistance as shown in Figure 5 [65].

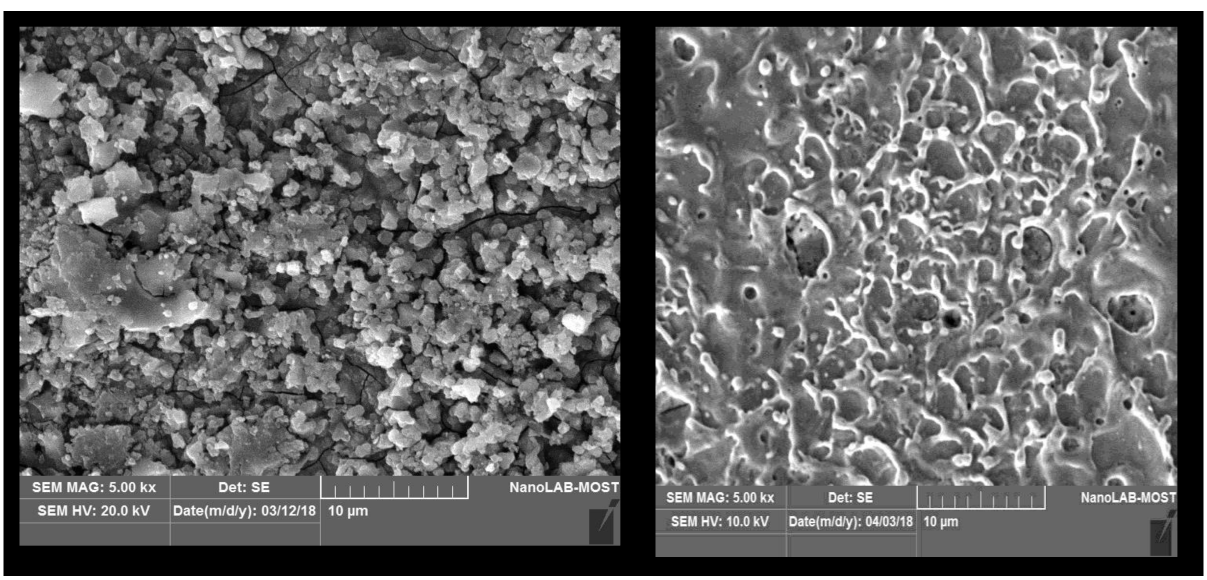

Figure 5. SEM graphs of corrosion samples (left: without nanocoating) & with nanocoating.

Such a discrepancy urges the need to study the corrosion behavior of each nanoparticle, taking into account all the surrounding conditions involved [66].

Zinc oxide nanopowder was studied as an agent to achieve anti-corrosion properties of a coating. The research project discusses the corrosion behavior of epoxy zinc oxide in various media by measuring the wear rate. Mild carbon steel was used as a substrate for epoxy and zinc oxide coating. The corrosion behavior of mild steel has been examined in various modes, freshwater, NaCl solution, HCl solution, and NaOH solution. The immersion test was done and studied for 60 days, with daily and weekly weight and immersion [67].

Conclusions

All types of inhibitors which were used lead to reduced the rate of corrosion, but in varying degrees. When using the organic compound, we observed an improvement in corrosion resistance of up to 80 percent. Laser treatment leads to a reduction in the corrosion rate by a lot of times after applying laser shock processing than without laser treatment. When using a nanocoating layer the corrosion rate was reduced more than upon laser treatment and an organic compound.

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