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Efficient Enhancement of Corrosion Resistance in Steel by Fiber Lasers

Jai Paul Dudeja

Professor and Director, Amity University Haryana, Gurgaon (India)

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***Corresponding Author**

Email: *drjpdudeja[at]gmail.com*

ABSTRACT

Stainless steel is generally considered to be less prone to corrosion as compared to other steel varieties. Even then the corrosion, being a natural process as a result of interaction with the environment, does take place in steel. Annual losses resulting from corrosion in steel in industrialized countries are estimated in the range from 2% to 4% of the gross national product. An estimated 25–30% of the annual cost of corrosion can be avoided if optimum corrosion management practices are employed. One of the most effective methods for protecting the materials against corrosion is the laser treatment. CW and pulsed fiber lasers, as compared to other lasers, have been advantageously used to effectively enhance the corrosion resistance in various grades of steel, details of which are discussed in this paper.

1. Introduction

Corrosion is the deterioration of a material as it reacts with its environment. Corrosion can be defined as a chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties. In other words, "Corrosion is the outcome of the physiochemical interaction between a metal and its environment, which results in the changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment or the technical system of which these form a part" [1]. Corrosion is a natural process. There are various types of environment that are hostile and conducive to corrosion, including fog and humidity, saltwater and alkaline or acidic soils. Therefore, corrosion takes place everywhere and may result in dangerous failures. However, an estimated 25–30% of the annual cost of corrosion can be avoided if optimum corrosion management practices are employed. Just like water flows to the lowest level, all natural processes tend toward the lowest possible energy states. Thus, for example, iron and steel have a natural tendency to combine with other chemical elements to return to their lowest energy states. In order to return to lower energy states, iron and steel frequently combine with oxygen and water, both of which are present in most natural environments, to form hydrated iron oxides (rust), similar in chemical composition to the original iron ore.

According to a Report published in 2014, corrosion is causing a loss of over US $ 5000 billion to global economy every year [2]. Annual losses resulting from corrosion in industrialized countries are estimated in the range from 2% to 4 % of gross national product. Furthermore, the loss of metal, incorporating many of the failed metal structures, products, equipment, is in the range from 10 % to 20 % per year of steel production. The massive costs of corrosion provide many opportunities to users, manufacturers and suppliers. Approximately one-third of these costs could be reduced by broader application of corrosion-resistant materials and the application of best corrosion-related technical practices.

Opportunities exist to reduce corrosion costs and the risks of failure, and to develop new, expanded markets. In order to achieve anti-corrosion characteristics in materials, generally the coatings and paints that protect against the ever-present threat of corrosion are used in industries that use steel. Unfortunately, many of these traditional coatings and paints carry health and safety risks for the industrial workers who come in contact with them [2]. The three most common health and safety concerns of traditional coatings for the people working in such industries, are: (i) volatile organic compounds and hazardous air pollutants, (ii) Many traditional anti-corrosion paints use organic compounds that serve as fuel to a fire in the workplace., and (iii) The danger of microbes, bacteria and other germs on surfaces and substrates, particularly where moisture is present [3].

1.1 Need for the use of lasers for enhancement of corrosion resistance in metals

Laser materials processing is a bourgeoning field of materials research. The power from a laser is used to heat, melt or ablate materials to change their character or topography. For the past several years, there has been a tendency to find new ways to change surface properties of metals to increase corrosion resistance. One of the breakthrough methods for protecting the materials against corrosion is laser treatment.

Application of lasers to improve the **corrosion performance** of many types of metallic alloy and some composites can be broken down into four basic categories [4]:

i. **Laser melting**, where the surface of the alloy is melted, which in turn changes the microstructure and in many cases improves corrosion.
ii. **Laser surface alloying,** where a new material is introduced to surface during the laser melting process, which changes the microstructure and in many cases the corrosion performance.

iii. **Laser cladding,** where a new more corrosion resistant material is added to the surface to improve the corrosion resistance.
iv. **Laser heating,** where a solid state phase transformation is induced to change the microstructure to improve corrosion performance.

2. Laser processing techniques for improving surface corrosion performance of alloys

2.1. Laser surface melting

Laser surface melting (LSM) is performed by heating a metallic substrate using a laser with high enough power to create a melt pool. The melt pool travels with laser movement and thus an area of material can be melted. The laser power level required to melt the material is dependent on the thermal diffusivity, conductivity and melting point of the substrate material as well as the rate at which the laser is being traversed. Because only a small portion of the substrate material is being melted the cooling rate is high. This can result in new types of microstructures formed, which are typically more homogeneous and exhibit improved corrosion performance.

2.2. Laser surface alloying

Laser surface alloying (LSA) is where a preplaced powder is melted with the substrate to form a layer with a combined composition. The high cooling rates associated with the process results in the novel microstructures to be formed, which can exhibit improved corrosion performance.

2.3. Laser cladding

Laser cladding (LC) is a process where a new layer is created on the surface of a metal/alloy.

A traversing laser is used to heat the substrate to form a molten pool. Into the pool either a wire or a powder is blown of a desired composition, which then melts and then quickly solidifies when past the laser beam, forming a new layer. The spot size of the laser, the traversing speed, the powder feed rate and power of the laser influences the resulting clad layer. By cladding materials that exhibit good corrosion performance the corrosion performance of a component can be increased.

2.4. Laser heat treatment

Laser heat treatment (LHT) is where the laser heats the substrate without melting the top surface layer. The heating then allows solid-state phase transformation(s) to occur which when coupled with the high cooling rates of laser materials processing, new microstructures can be formed. This is a new field of laser material processing for improved corrosion performance and has the advantage over LSM in that the residual stress after processing is lower.

3. Fiber Laser Advantages

Different laser sources exist, such as Nd:YAG, fiber, CO_2 etc. for enhancing the corrosion resistance in steel. The fiber laser produces a beam of outstanding optical quality. The small focus diameter of fiber laser technology offers enhanced power density, a smaller heat-affected zone, lower cycle time, and lower heat input. Fiber lasers are designed to be maintenance free with ‘fit and forget technology’, making them a reliable, efficient and effective solution to many other technologies. Fiber lasers can work with all of the key metals including aluminium, brass, copper, and various types of steel. CW fiber lasers can enhance corrosion resistance for every type of steel: from thin steel to thick carbon steel and stainless steel. The use of pulsed fiber lasers represents another direction for similar task. The architecture of the fiber laser is scalable, with laser powers available at multi-kilowatt levels. Fiber lasers use power modules that are made up of individual modules ranging from 200 to 2000 watts. For example, a 4 kilowatt (kW) laser is made up of multiple modules, with the option of adding an additional module for redundancy. Fiber lasers are very compact, with power up to 1kW offered in rack-sized formats. They can be air-cooled up to 500 W.

4. Some Case Studies of using Fiber Lasers for Enhancing Corrosion Resistance in Steel

4.1 Szubzda et al [5] analysed the results of the influence of nanosecond-pulsed fiber laser fluence on physical and chemical structure and corrosion resistance of stainless steel surfaces. The study was carried out on three types of stainless steel: AISI 304, AISI 316, and AISI 321, with different chemical compositions. Stainless Steel is a steel alloy with at least 10.5% chromium by mass and is more corrosion, rust and stain-resistant than typical metal. Stainless steel AISI 304 is used commonly due to its anti-corrosion properties. AISI 304 can therefore be used in the atmospheric environment, natural water, alkaline solutions and certain acids. 304 Stainless Steel is the typical steel which is used in most non-marine or hazardous environments whereas the extra cost of 316 Stainless Steel, which is more apt to those environments, isn’t required. To put it simply, 316 is more resistant to environmental corrosion than 304 due to the extra molybdenum content in it, which also increases its price, it actually has less chromium than 304. Despite its numerous advantages and known resistance to many corrosive environments, such as HNO_3, significantly diluted H_2SO_4, many organic acids, alkalis (excluding a concentrated NaOH solution and typical weather conditions), AISI 304 steel is susceptible to the effects of acidic and reducing environments, especially those containing aggressive ions, which are destructive for the passive layer, for example, some oxidizing chlorine solutions ($FeCl_3$, NaCl, and $MgCl_2$), acid solutions containing aggressive ion (HCl, HBr, and HF), and some organic acids (oxalic acid, formic acid, and lactic acid).

Corrosion resistance tests for these types of stainless steel were carried out in a weakly acidic environment (H_2SO_4) and a neutral environment (NaCl). The most popular acid-resistant material is steel AISI 316, which exhibits increased resistance to corrosion in very aggressive chemical environments. Dependent on the environment, 316 Stainless Steel might be preferable as it is more resistant to phosphoric acid while 304 Stainless Steel is more resistant to sulphuric acid though hydrochloric acid will corrode most stainless steel types. This is why the environment in which your material will be located will have a direct bearing on which grade or type of stainless steel we have to use. The third tested type of steel is AISI 321, which shows high resistance to inter-crystalline corrosion and resistance in higher temperatures, that is, between 400°C and 800°C. The main components of these alloys are chromium and nickel. It is the content of chromium that predominantly determines the anti-corrosion steel properties because the oxides of this metal form a passive protection layer, whereas the remaining components stabilize this layer in different situations resulting from the work environment.

Samples for the study were prepared using a Master Oscillator Power Amplifier (MOPA) configuration of Yb:glass fiber laser (at 1062 nm) with an average output power of up to 20 W, beam factor $M^2 \leq 1.5$, a constant pulse duration of 230 ns, and a prf within the range of 20–80 kHz. The laser system was equipped with a galvanometer-based optical scanner allowing the beam to be deflected within an area of the irradiated substrate. The laser beam was focused on the target through a 160-mm focal length lens. The beam diameter at the focal point was approximately 38 µm. For the purpose of this experiment, sixteen values of accumulated fluence were chosen, which ranged between 10 and 400 J/cm^2. The average laser power was constant and was 4.4 W and a change in fluence values was achieved by changing laser scanning rates of sample surfaces. The obtained results showed very high corrosion resistance for samples made by fluency of values lower than 100 J/cm^2.

Corrosion resistance tests were performed by a potentio-dynamic method in which the electrolytic environment of measurements was chosen in such a way that it could reflect the most frequent risks in the conditions of a potential application of layers. The tests were carried out in a diluted solution of sulphuric acid. Changes in potentials and the measurement of intensities caused by the currents were measured.

4.2 Ruzankina and Vasiliev [6] reported the study of the improvement of corrosion resistance of metals using laser-induced oxide surface structure. Besides titanium, the other material under study in this work was ST20 steel by using ytterbium fiber laser (1064 nm). Defocusing of the laser beam was done to allow the surface treatment of a wide beam for covering the maximum region of the metal. Increase of corrosion resistance in ST20 steel was carried out with the formation on the surface oxide films, as well as by reducing surface roughness. For the study of the irradiated surface on the corrosion resistance, the processed metal oxide was tested in a mixture of copper sulphate and hydrochloric acid. It was observed that steel displayed enhancement in its corrosion resistance by this method.

4.3 Ruzankina et el [7] studied the effect of a CW fiber laser with the wavelength of 1064 nm and a power up to 18.4 W on the enhancement of corrosion resistance of steel. The power density of laser radiation was varied in the range 7×10^4 W/cm^2 and 9×10^4 W/cm^2. Experimental samples (of steel plates) were irradiated for 20-35 seconds by this laser. Surface treatment of metal was held at a room temperature of 23 ˚ C and a relative humidity of air of 55%. Analysis of results obtained showed that the laser irradiation of steel surface resulted in forming the thin film protecting steel from corrosion processes. The impact of laser radiation on the surface of the steel contributed to a small change in its chemical composition, including the presence of such chemical elements as Al, F and O. The presence of F originally in the studied steel grade increased its concentration in the metal is from 0.01 atom% to 5.24 atom%. This should be a matter for further study.

4.4 Sze Ney Chan et al [8] used a fiber laser for modifying the surface properties of cold-rolled low carbon steel via a pulse laser ablation technique in water. The effect on the corrosion behaviour of the fiber laser-treated metal surface was investigated in NaCl and HCl environments. Electrochemical tests showed significant improvement in the corrosion resistance of the laser-treated sample in NaCl, with an increase in open-circuit potential (OCP) from − 0.65 to − 0.60 V and an inhibition efficiency of 89.22%, as obtained from the impedance study. The analysis indicated a passive film built by spherical grains of regular size on the metal surface after laser treatment. The corrosion inhibition effects in NaCl were evident by the nonexistence of the common corrosion products of lepidocrocite and crystalline structures that were seen on the samples; only polyhedral crystals with micrograins grown on them were seen covering the laser-treated surface. Therefore, the laser treatment using a fiber laser source improved the corrosion resistance of cold-rolled low carbon steel.

4.5 Uroš Trdana et al [9] investigated the evolution from super hydrophilic to super hydrophobic surface state on corrosion behaviour of SS316L produced by nanosecond direct laser texturing (DLT). Results confirmed perfect correlation among wettability and corrosion, hence superhydrophobic surface with a contact angle of 168 ± 3.0° reflected in enhanced passivity, lower anodic dissolution and corrosion current reduction. Characterization of the corrosion attack by 3D microscopy revealed high sensitivity of superhydrophilic surfaces on corrosion propagation direction in regard to the laser beam passage (90. However, this trend completely diminished with superhydrophobic development.

It had also been demonstrated that superhydrophobic surfaces on SS304 with steady contact angle of 154° and contact angle hysteresis of 4° can be fabricated via direct laser texturing (DLT) with cost-effective, compact nanosecond fiber laser system.

So in this study the direct laser texturing (DLT) using a nanosecond laser was confirmed as an effective method for fabrication of superhydrophobic surfaces on 316L stainless steel. It was shown that the transition from superhydrophilic ($\theta = 0°$) through hydrophobic ($\theta = 109 \pm 6.7°$) to superhydrophobic ($\theta = 168 \pm 3.0°$) state occurs due to exposure of the textured surface to ambient conditions, which enables examination of the isolated influence of wettability on corrosion behaviour. Further, the 3D topography of superhydrophilic surface after corrosion test revealed a strong preferential direction of corrosion propagation along µ channels that are oriented along the last texturing passage (0°). However, this effect was significantly reduced by development of water repellency, resulting in non-oriented pitting attack. More importantly, presented results indicated that laser texturing completely inhibited the initiation of inter-granular corrosion as a consequence of more homogeneous microstructure with smaller amount of galvanic cells, i.e. Cr-depleted grain boundaries/M(Fe,Cr)23C6 carbides.

4.6 Xiaohui et al [10] have reported a unique approach to grow graphene on carbon steel and explore its anti-corrosion application. By introducing Ni element into carbon steel through a laser alloying process to form a Ni/Fe alloy catalyst, they made it feasible to grow graphene on carbon steel. The corrosion rate of graphene covered carbon steel was only 0.05 mm/year, much lesser than that of the stainless steel (0.09 mm/year). The corrosion resistance was up to ≈ 1900 Ω cm2, which is almost 7 times that of original steel (270.7 Ω cm2). These results indicate that the in situ grown graphene coatings perform very well in resisting harsh environments, much better than stainless steel itself.

In this work, the most common carbon steel, 45# steel (GB, equals to 1045# in ASTM), was used as the substrate. High-purity (99.99%) Ni powders of uniform size, about 75 μm, were assembled into a side shaft powder feeding apparatus. The melting point of Ni powder is 14550 C, the density is 1.8–4.8 g/cm3 and the flowability is ≈ 30 s/50 g. Second, a high power density continuous wave (CW) fiber laser with wavelength of 1.07 μm and maximum power of 2000 W, was employed to synthesize the catalyst. Before impinging on the surface, the beam is focused to be 0.3 mm in diameter. The power density used was 2.15 X 104 W/cm2 with a scan rate of 4 mm/s. With the assistance of airflow, the powders were delivered into the laser irradiating area. Almost at the same time, the powders and the substrate were heated and melted by laser irradiation. Then the molten powders and substrate merged together. When the laser moved forward, a Ni/Fe band was formed on the surface. Graphene growth on Ni/Fe catalyst was done by laser irradiation. The authors found an excellent anti-corrosion performance of in situ grapheme owing to its high impermeability, conductivity, chemical inertness and good adhesion with the substrate.

5. Conclusion

Any metal will be corroded due to its interaction with the environment. Even steel is no exception to it. A significant percentage of steel is getting degraded every year due to corrosion, resulting into a great loss to the economy of the industrialized nations. Therefore we have to devise methods to slow down this corrosion process. Laser-based treatment to these metals has been found to be an effective method for enhancing the corrosion in them. Out of all the lasers, CW and pulsed fiber lasers have proven to outdo other lasers in their performance. In this paper these lasers have been shown to effectively enhance the corrosion resistance in various grades of steels.

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