Chapter 1

Laser Materials Processing for Improved Corrosion Performance

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Additional information is available at the end of the chapter

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1. Introduction

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. Their application to improve the corrosion performance of many types of metallic alloy and some composites can be broken down into four basic categories:

- laser melting, where the surface of the alloy is melted, which in turn changes the microstructure and in many cases improves corrosion,
- 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.
- laser cladding, where a new more corrosion resistant material is added to the surface to improve the corrosion resistance,
- laser heating, where a solid state phase transformation is induced to change the microstructure to improve corrosion performance.

The field has been around for almost as long as laser material processing itself and it is the purpose of this chapter to discuss the development in these four areas, to give the reader an overview of the applications of laser material processing for improved corrosion performance.

2. Lasers and their operation

Laser as an acronym stands for 'Light Amplification by Stimulated Emission of Radiation'. Essentially laser are light amplifiers. The physics of how the light is amplified involves quantum mechanics, it is relatively complex and is comprehensively dealt with in [1]. The main difference between the different types of high powdered lasers is the medium used to generate the stimulate emission. These differences for the main types of high powered lasers will be dealt with below.

2.1. Main types of high powered lasers

2.1.1. CO2 lasers

Carbon dioxide laser were the first generation in industrially used high powered lasers, Figure 1. The amplification of the light is achieved through molecular vibration rather than electronic translations as in other lasers. The efficiency of CO2 lasers is around 10% which is quite low by today's standards and is the main reason for why this type laser are being used less and less. The wave length of CO2 lasers varies between 9.4 and 10.6μm which is quite large and because of this the light cannot be transferred by optical fibre and is typically achieved by mirrors, which has implications for applications. The cost of these lasers is relatively low and there are applications which they are suited and will continue to find application.

2.1.2. Neodynium – YAG lasers

This type of laser is finding less and less application but there are still many of them in use in research and industrial sectors. Abbreviated to Nd:YAG laser the amplification of light is achieved by triply ionised Nd as the lasant (a material that can be stimulated to produce laser light) and the crystal YAG (yttrium-aluminium-garnet) as the host. YAG is a complicated oxide with the chemical composition Y3Al5O12. The wavelength of this type of laser is 1.06 μm which is near the infrared spectrum. The light can be transport by optical fibre, which makes their application flexible and was responsible for their industrial uptake.

2.1.3. Diode lasers

Diode lasers are commonly used today and can be used in different configurations. Essentially as the name suggests diode lasers are didoes that have the ability to amplify light. Diodes are semiconductor materials for which there are many types and the wavelength produced range from 0.33 to 40μm. Of the known diode materials there are 20 that will lase. The most common ones are GaAs and AlxGa1-x. A variation on the diode laser principal is 'diode-pumped solid-state (DPSS) lasers '. This type of laser works by pumping a solid gain medium, like a ruby or a neodymium-doped YAG crystal, with a laser diode. This configuration of laser is compact and very efficient and is finding wide spread industrial use. The industrially used version of theses lasers can have the light transported by optical fibre which is important to their application.

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Figure 1. POM DMD (direct metal deposition machine) featuring 6-axis rotating, CAD-CNC control using a 5kW CO2 Trumpf laser.

2.1.4. Fibre lasers

Fibre lasers are the latest technology in high powered lasers and can be banked together to produce powers in the range of 20-30kW. Fibre lasers use a doped optical fibre to amplify the light. The doping agents range from erbium, ytterbium, neodymium, dysprosium, praseodymium, and thulium. The high powers that can be generated with this technology are opening up new application for laser materials processing in the manufacturing sector and are currently the future of high powered lasers.

2.2. Laser optics

Apart from the CO2 laser, which use mirrors, the major types of high power lasers use optical fibre to deliver the light. Once near the region where the laser material processing is to occur, the light from the fibre needs to be collimated and then focused. Depending on the application the focal distance the distance can be varied by the choice of lenses for collimating and focusing. The profile of the light/beam is also dictated by the lens and can take the form of a Gaussian, top hat, bimodal (donut) or a line beam profile, Figure 2. For most applications a Gaussian beam is used, but top hat profile gives a sharp thermal profile in the material, which has advantages. Typically for laser materials processing applications the focal point is about 1mm in diameter and has a top hat profile. Above focus the beam profile changes from top hat to bimodal, which increasing radius and below focus the beam is Gaussian with increasing diameter, Figure 2.

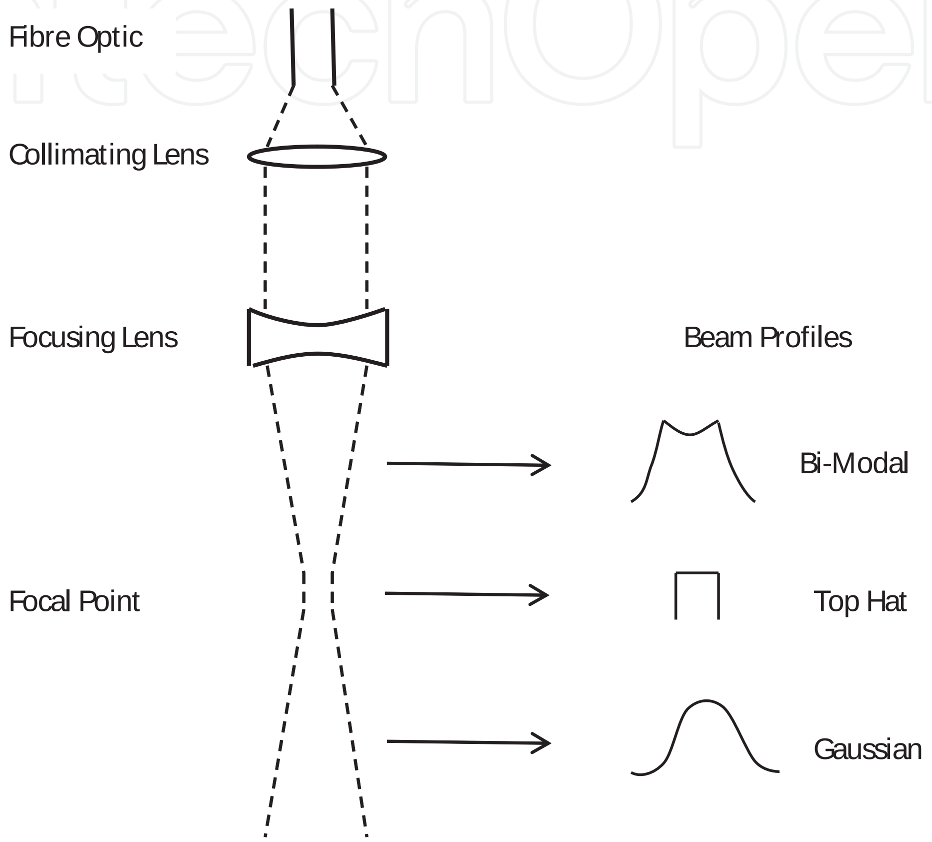

Figure 2. Laser optical configuration and resulting beam profile.

2.3. Controlling the movement of the laser

In the early days of laser materials processing the laser and optics were fixed to a CNC table and basic movement in X,Y and Z direction were possible. Nowadays robots are readily available and affordable, laser can be couple to the head of a robot allowing five-axis movement. Also computer programs and CAD drawings can be used to develop paths for laser movement, which can allow complex geometries to be processed. This development has been crucial to the application of laser materials processing technology and has applications for treating manufactured component that required improved corrosion resistance. A sixth degree of movement can also be obtained through the use of a rotating chuck that can grip the component to be processed and is common on many commercial laser cladding systems.

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2.4. Materials preparation

Not all of the energy of the laser is transferred into heat in the substrate material. In fact the condition of the substrate plays a big role in how much energy is absorbed. In the as machined state metallic materials are highly reflective and between 0.1 - 0.3 of the energy is absorbed by the laser. The range is because some metals absorb the laser energy better than others. Coatings can be applied to the substrate to improve the absorption and in many cases the absorption can be as high as 0.9 of the energy of the beam. Sand or grit blasting reduces the reflectiveness of metallic materials and the rough surface also improves absorption and absorption values as high as 0.5 can be achieved. It should also be noted that the angle of incidence also affects the absorption of the laser. This is known as the Brewster effect and needs to be considered when processing complex geometries.

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

3.1. 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, which when coupled with a raster pattern, 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 and ranges from 103 – 106 °C/s depending on the thermo-physical properties of the substrate material and the traversing rate of the laser. This can result in new types of microstructures formed, which are typically more homogeneous and exhibit improved corrosion performance. The geometry of the melt pool during LSM is dependent on the power density and hence laser traversing speed. With increasing laser traversing speed the melt pool geometry changes from hemispherical to flat-bottomed with increase of traversing speed as thermal diffusion becomes limited. The flat-bottomed shape is the most desired for LSM.

3.1.1. Improving the pitting potential of alloys

By far most of the research into LSM for improved corrosion performance has been conducted on improving the pitting potential of commercial alloys. The general tendency of LSM to increase the homogeneity of the surface of a treated alloy is the reason for its application to increase pitting potentials. Low pitting potentials are associated with galvanic couples that can exist between second phase particles and the matrix which lower the potential for corrosion to occur and cause localised corrosion at the interface between the particles and the matrix, forming pits [2]. By dissolving the particles this mechanism is eliminated and the pitting potential is increased. The increase in the pitting potential is dependent of the potential of the galvanic couple of the particle and the matrix and the effect of the dissolved alloying element of the oxide layer formed and its ability to form a passivation film. While for many alloys the pitting potential is improved in some cases the pitting potential can be reduced if the alloying elements are not completely dissolved and the increase in the number of grain boundaries and fine second phase particles increases the pitting potential by increase the number of regions for pitting to occur. An example of pitting potential diagram showing how the pitting potential is determined is shown in Figure 3.

LSM has been trialled on a range of stainless steels to improve the pitting potential. The sensitisation of stainless steels during welding and other thermo processes is an issue for manufacturing stainless steels that will be used in corrosive environments. Essentially the thermal processes cause the formation of carbides with chromium, which locally depletes chromium available to form a passivation film and hence reduces the corrosion performance. LSM has proven to dissolve these carbides and restore the chromium levels to form the passivation film [3]. This can be applied to the welds of stainless steels to restore corrosion performance.

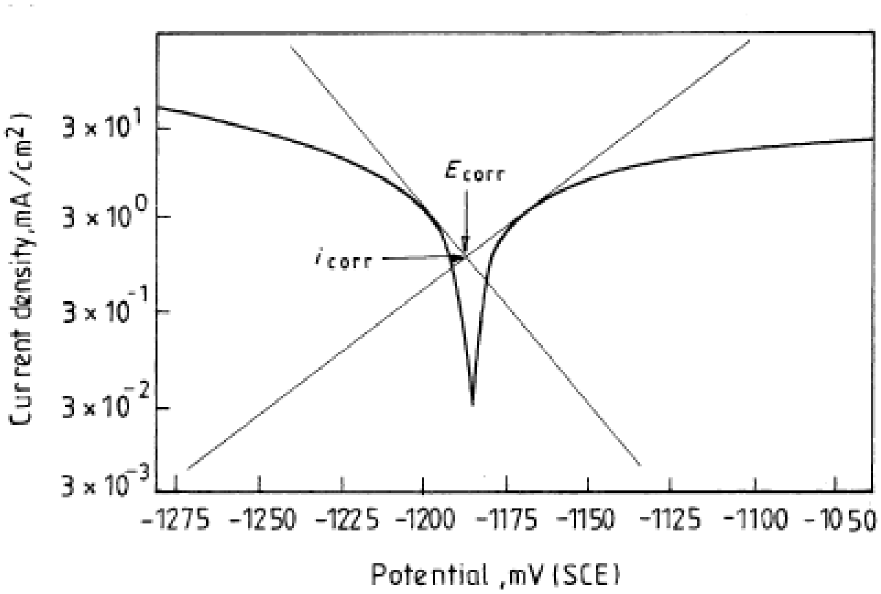

Figure 3. Variation of current density with potential indicating the pitting potential and current, taken from [3].

It has also been shown that LSM can change the surface chemistry of AISI 304 stainless steel to improve the pitting potential [4]. It was found that Cr_2O_3, Fe_2O_3, FeO and MnO_2 were detected on the surface only after LSM and was used to explain the higher pitting potential of the LSM treatment. LSM of 3CR12 stainless steel revealed that pitting potential was also enhanced by redistribution of non-intermetallic inclusions and the formation of a homogenous ferritic microstructure. Kwok et al [5] has performed the most comprehensive investigation into the pitting behaviour of AISI 440C martensitic stainless steels. It was found that larger carbides are more harmful to corrosion resistance than fine carbides due to greater inhomogeneity in the former case. It was also found that the formation of retained austenite was favourable for increasing the pitting potential. The laser scanning speed also influenced the pitting potential and was attributed to the effect of power density. In summary a range of stainless steels show an increase in pitting potential due to LSM and can be attribute to enhanced surface chemistry and an increase in the homogeneity of the microstructure.

Aluminium alloys have shown a mixed response in pitting potential due to LSM. 2xxx aluminium alloys have received the most attention. While 2014 has shown an improvement in pitting potential due to LSM it was found that the most significant result was a change in the morphology of the pits to be shallower due to both the distribution of copper and the refinement of the microstructure [4]. 2024 shows no significant change in the pitting potential due to LSM [5], it was found that the sites for corrosion shifted from the second-phase precipitates to the α-aluminium dendrites and with the elimination of inter-granular corrosion. Al-9wt% Si casting was also subjected to LSM and again the pitting potential was not improved [6]. This was attributed to an increase in the silicon aluminium boundaries caused by the refinement of the microstructure by LSM because these boundaries are more susceptible to the corrosion action. Aluminium alloy 6013 shows improved pitting resistance due to LSM brought about by a more homogeneous microstructure which increased the initial resistance to pitting [7].

The poor corrosion properties of magnesium alloys have resulted in many investigations using LSM to improve the pitting potential. AZ91 has received the most attention [8-10] where it was found that LSM dissolves the β-Mg17Al12 precipitate present in the as cast alloy which was responsible for micro galvanic corrosion and the formation of α solid solution of aluminium of up to 10wt%, which provides passive properties to the melted surface. ACM720 has also been investigated [11]and it was found that the rapid solidification of LSM supressed of the formation of Al2Ca phase which is present in the cast alloy in the grain boundaries. This change coupled with the extended solubility of aluminium in the microstructure increased the pitting potential. Rare earth containing alloy MEZ showed improved corrosion resistance [3]. It was suggested that the decrease in the anode cathode area due to the refinement of the microstructure coupled with the extended solubility of the rare earths increase the pitting corrosion resistance.

Ti-6Al-4V has also been subjected to LSM and it was found that the refinement of the microstructure improved the pitting potential in both Hank's solution and 3%NaCl solution [12, 13]. Alloy 600 also responded well to LSM and due to its high chromium content and forms an excellent passivation film during testing [14]. High speed tools steels M2, ASP23 and ASP30 were subjected to LSM and it was found that the pitting corrosion potential increased. This increase was attributed to the dissociating and refinement of large carbides and the increase of the passivation alloying elements in the ultrafine solid solution of austenite and martensite. Metal matrix composites have also responded well to LSM [15-17]. The corrosion behaviour of metal matrix composites is due to heterogeneity of their structure. LSM increase the homogeneity by dissolving the reinforcement phase.

3.1.2. Cavitation erosion and corrosion

Cavitation erosion corrosion occurs due to the formation and collapse of bubbles in fluid near the metallic surface. When a metal surface is subjected to high speed fluid flow sudden changes of liquid speed cause changes in the local vapour pressure which induces the formation and collapse of bubbles. The collapse of the bubbles generates shockwaves, which impact on the metal surface and leads to fatigue damage. LSM has been used on several types of stainless steels to improve the resistance to this form of corrosion [18-20]. The response of different alloys varies for example S31603 shows improved performance while S32760 and S30400 showed a decrease in the cavitation erosion corrosion performance. The decrease in performance for the two alloys was attributed to increased levels of twining in the two alloys. For martensitic stainless steel S42000 the cavitation erosion corrosion performance was improved through increased levels of retained austenite, which for this alloy is highly transformable. The stresses of the cavitation process are absorbed more readily due to the stress inducing a transformation of the retained austenite, hence increasing the resistance of the material to this form of corrosion.

3.1.3. Stress corrosion cracking

Stress corrosion cracking (SCC) is a form of cracking where an applied stress or residual stress in a component in combination with a corrosive environment acts to accelerate crack growth of the component. LSM has been conducted on AA 7075 in two separate studies [21, 22] to counteract this effect. Both studies found that the homogeneous refined microstructure produced by LSM delayed the onset of SCC when compared to the untreated material. Electrochemical impedance measurements showed that the film resistance was higher than that of the untreated material and provided an effective barrier to corrosion attack. It was also found that a nitrogen atmosphere during processing forms AlN phase which improves the corrosion resistance of the film further.

3.2. 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 novel microstructures are formed, which can exhibit improved corrosion performance. Like for LSM, process parameters are dependent on the thermo-physical properties of the substrate and alloying material as well as the processing speed. The level of dilution plays a big role in the composition of the melted layer, which in turn can have a dramatic effect on the microstructure produced. There are several techniques for preplacing the alloying element(s), the powder can be combined with a polymer to form a paste, which is then smeared onto the surface to be alloyed. Flame spray is another method to preplace the powder as is hot dipping.

One avenue to improve the corrosion performance using LSA is to alloy with an element, which forms a strong passivation film. For example, alloying AA7175 with chromium to improve its crevice corrosion performance [23], the alloying of ductile iron with copper [24] and the alloying of copper with titanium[25]. Another method is to alloy to form an intermetallic with alloying elements that exhibit good corrosion performance such as the alloying of steels with aluminium to form iron aluminides [26]. The area that has received the most attention is alloying to improve the cavitation corrosion properties. LSA is ideal for this application because not only can the corrosion resistance of the surface be improved by alloying but the hardness of the surface can be improved as well, which are both properties required of a cavitation corrosion resistant material. Aluminized steel prepared by LSA showed a 17 fold increase in the cavitation corrosion resistance [27]. The high hardness of the intermetallic layer and the shift in the pitting potential to a more noble level was used to explain the dramatic increase. Ni-Cr-Si-B alloy was LSAed with brass for improved cavitation corrosion[28]. Variations in the power density during processing influence the cavitation corrosion behaviour and it was found that it was a compromise between cavitation erosion performance and corrosion, the harder layers exhibited improve cavitation corrosion and while the corrosion is improved by a more homogeneous microstructure. A substantial investigation into LSA of stainless steel has been conducted by Kwok et al [29]. UNS S31603 was alloyed with Co, Ni, Mn, C, Cr, Mo, Si. As would be expected a vast variety of microstructures were produced and were interpreted with reference to the appropriate phase diagrams. Essentially the layers alloyed with Co, Ni, Mn, C contained austenite as the main phase while alloying with Cr and Mo resulted in ferrite. While the corrosion was improved in some cases, there was no underlying trend between the different alloying elements. This highlights the complexity of the microstructural formation in LSA and its dependence on process parameters.

3.3. 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 and 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.

This field of research has received limited attention. The cladding of stainless steels on mild steel has been investigated and like for laser surface melting the high cooling rates produce a fine microstructure, which coupled with the excellent corrosion properties of stainless steel the corrosion performance of the surface of the mild steel was improved [30]. The effect of La2O3 on ferritic steel was investigated [31] an proved to increase the corrosion resistance of the substrate by increasing the passivation effects of the film during testing. Nickel silicide as a clad layer have also been investigated [32]. This particular type of intermetallic displayed excellent corrosion response, which was attributed to the large amount of silicon which promotes the formation of highly dense and tightly adherent passive thin film when contacting with corrosive media.

3.4. 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.

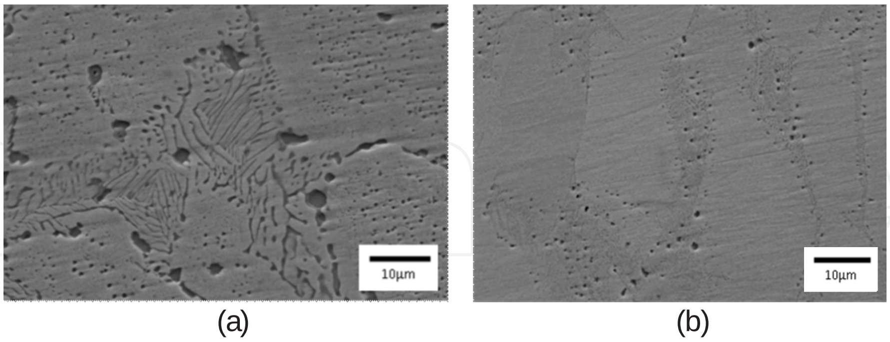

Figure 4. Nickel-aluminium bronze microstructure before and after laser heat treatment processing; a – Cast microstructure showing precipitates and κ_{III} lamella; b – laser heat treated microstructure showing that the κ_{IV} and κ_{III} lamella was dissolved.

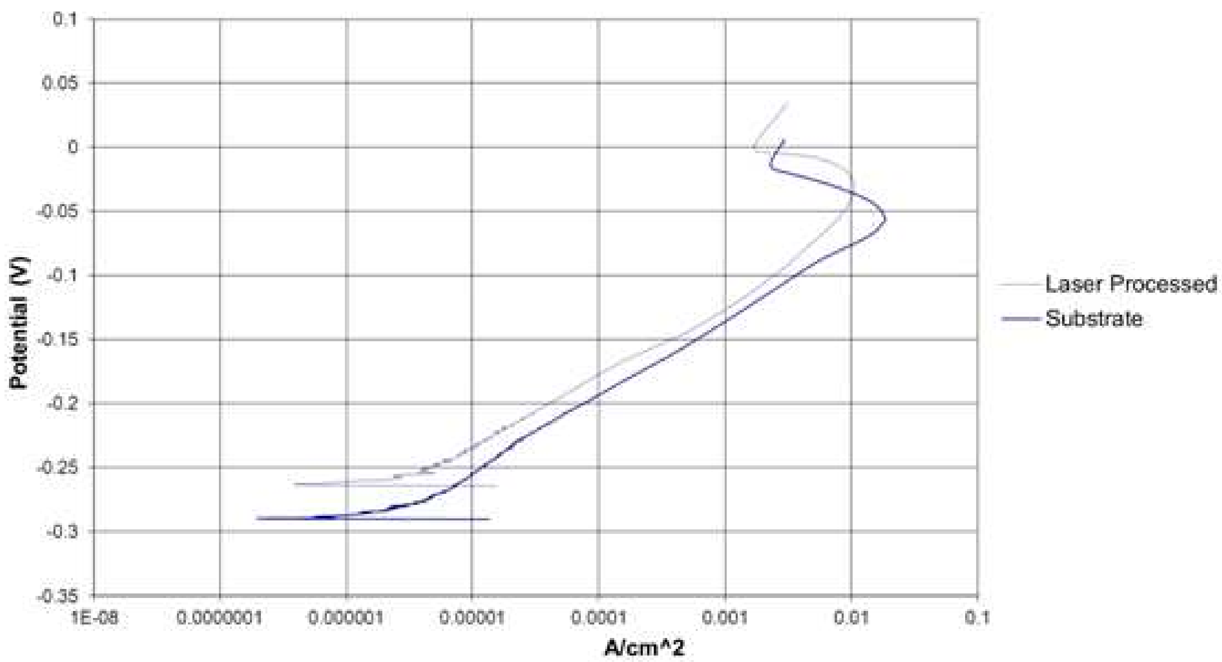

Figure 5. Linear polarisation curves for as cast substrate and laser processed nickel-aluminium bronze.

An example of this is laser transformation hardening of steels. The heat from the laser causes the ferrite and pearlite to transform to austenite and then the rapid cooling provided by conduction to the substrate produces hard martensite. Typically this technique is uses to produce a wear resistant layer, however it has been applied stainless steel for improved cavitation corrosion resistance [20]. It was found that the ratio of austenite to martensite was better than for LSM. Another example of this is the laser heat treatment of nickel-aluminium bronze (NAB). LC of NAB produces the Widmanstatten morphology microstructure, which has poor corrosion properties [33]. Whereas the LHT of NAB produces a microstructure that is free form precipitates, Figure 4, which is responsible for the reduced corrosion performance and is free from the Widmanstatten morphology microstructure [34]. This new type of microstructure exhibited improved corrosion properties as shown by the linear polarisation results, Figure 5.

3.5. Hybrid coatings

Laser melting or heating can also be used in conjunction with other coating techniques. Thermal spray which covers a range of processing techniques applies coatings to metallic substrates by heating a powder and propelling into a substrate. Each individual particle forms a splat on the substrate and the accumulation of many splats result in a coating. While these coating have found many applications including thermal barrier coatings and wear resistant coatings they have flaws. They are that the coatings have poor bond strength between the coating and the substrate, and high porosity. Laser melting offer the opportunity removes these two issues and so hybrid coating applications have been investigated.

In relation to developing coatings for improved corrosion resistance the hybrid thermal spray laser melting have found applications with Ni coated WC coatings [35, 36], thermal barrier coatings [37, 38] super alloy WC coatings [39] Al-SI alloy coatings on AZ91D magnesium alloy [40] and NiCrBSi alloys [41, 42]. For all these applications the laser melting consolidated and homogenised the coating which improved the corrosion performance. In some cases if the wrong laser parameters were used cracking of the coating occurred mitigating the effect of reducing the porosity and should be considered when developing this type of coating.

The second group of hybrid coatings and one that has received less attention is electroplating followed by laser melting. Electroplated coatings like thermal spray coatings have porosity and therefore their corrosion performance is reduced. Laser melting of the coatings consolidates the porosity and improves their performance. Examples of this are Ni-W-P coatings [43] and gold coatings [44].

3.6. Superhydrophobic surfaces produced by femtosecond lasers

Superhydrophobic surface are a biomimetic surface structure where nano scale features on their surface cause a hydrophobic response [45]. These surface can be produced on metallic materials using femtosecond laser technology (pulsed laser ablation) [46]. The ability to repel liquids, which cause the corrosive action and the nano-scale of their structure could combine to enhance corrosion performance including bio-corrosion, where the microbes are responsible for the corrosion process. These surface have successfully produced on stainless steel [47]. While there corrosion performance has not been evaluated, this may be the way of the future for specific areas of corrosion prevention.

4. Conclusion

High powered lasers have found many applications in improving the corrosion performance of metallic materials and some composite materials. The high cooling rates associated with laser processing promotes the formation of more homogeneous microstructures, which in turn improves the corrosion performance. As has been shown a wide range of alloy systems can utilise this technology and potentially there are other systems for which the techniques described could be applied. Laser alloying is an area where more work could occur in the further by carefully selecting alloying elements, with reference to phase diagrams, to optimise the effect of alloying. Superhydrophobic surfaces are also an area that could be explored as well. Laser material processing is a growing field of research and as it grows its application to corrosion science and prevention will also increase.

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