Characterization and Corrosion Behaviour of Laser Surface Alloyed Ni–Cr–W–Mo–Cu–C–B Coatings

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A microalloyed steel was precoated with three different thicknesses of Ni–Cr–W–Mo–Cu–C–B powder and laser-surface-alloyed in order to achieve a corrosion-resistant surface alloy. In general, laser treated alloys showed good adherence and considerable penetration into the base material, which varied with laser treatment conditions and initial coating thicknesses. Under conditions studied, laser treated alloys presented a dendritic structure. The degree of dilution increased as both laser scanning rate and initial coating thickness decreased. The lowest iron content at the surface was reached for samples with a 1 000 μm initial coating thickness and laser treated at the maximum scanning rate 0.054 ms^{-1} . This low iron content jointed to a high content of chromium and nickel on the surface gave rise to the formation of a protective and stable passive layer that implied a high corrosion resistance in Na_2SO_4 0.1 M. The samples with 250 and 500 μm coating thicknesses presented in most cases a martensitic transformation within the coating due to the high degree of dilution between coating and base material decreasing drastically the corrosion resistance of the melted coating.

KEY WORDS: microstructure; corrosion; Ni-base coating; laser; surface alloying.

1. Introduction

A high power laser beam can be used to modify the microstructure or the chemical composition of a surface if prior to laser treatment the metal substrate is coated with a layer of the alloying elements.^{1–3)} Laser surface alloying (LSA) promotes melting, mixing and alloying of the coating and the base substrate.⁴⁾

Surface alloying by laser improves surface properties, such as hardness, wear and corrosion resistance while preserving at the same time the desired bulk properties.⁵⁾

Several techniques can be used to produce coatings with the desirable alloying elements before laser treatment: electroless plating, electroplating, duplex coating, plasma spraying or sputtered alloy coatings.^{6–11)} Another possible technique to obtain an alloy coating is by blowing powders onto the molten surface during laser melting.^{12,13)} Generally, the powder used for laser-surface-alloying involves the addition of a single substance, either pure metal or pure compounds.^{6–13)} Only limited information is currently available with respect to LSA that involves the use of complex metal/compound powders.

It is well known that alloys containing 8% or more Cr have good corrosion resistance.¹⁴⁾ It has also been reported that in order to improve the corrosion resistance at high temperatures in sulphur environments, chromium, molybdenum and sometimes tungsten are required.^{11,15)} Furthermore, the addition of some non-

metallic elements, to Fe–Cr based amorphous alloys¹⁶⁾ results in an extremely high corrosion resistance.

In this work, nickel-base commercial alloy amorphous powder is predeposited on steel substrates. Powder coatings consisted of a mixture of Ni–Cr–W–Mo–Cu–C–B. The aim of this work is to obtain a laser-surface-alloyed, homogeneous and adherent, Ni–Cr–W–Mo–Cu–C–B coating with a minimal dilution of iron in order to achieve high corrosion resistance over a wide surface area which would prove to be useful in a large range of technological applications. The work includes all of the studies of modifications produced by laser treatment, such as dilution, microstructure, possible defects in the surface alloy and the corrosion resistance of these laser treated coatings.

2. Material and Experimental Procedure

Microalloyed steel sheets of parallelepipedic shape (140 × 35 × 10 mm) were used as base substrate. The chemical composition of the base steel was (wt.%): 0.10% C, 0.34% Si, 1.37% Mn, 0.009% P, 0.002% S, 0.032% Nb, 0.014% Ca, 0.032% Al, 0.06% Cr and 0.15% Cu, balance Fe. The alloyed nickel-base powders were manufactured by atomization from the melt. The particle size of the powder was $-44\ \mu\text{m} + 15\ \mu\text{m}$ and its chemical composition (wt.%) was: 19% Cr, 11% W, 8% Mo, 4% Cu, 1% C and 0.3% B, balance Ni. Alloyed Ni-base powders were mixed with an alquidic melanin

resin used to spread them evenly on the steel surfaces in order to achieve different thickness by means of a recipient of controllable height. Using this method, three different coatings with thicknesses of 250, 500 and 1 000 μm respectively, were obtained.

Coated specimens were exposed to a CO_2 continuous laser beam with an elliptical cross section of $4 \times 6 \text{ mm}$ and a maximum output power of 5 kW. This output power corresponds approximately to 2.6 kW cm^{-2} in the sample.³⁾ The laser beam was scanned in the direction of the major axis. The energy distribution of the beam was uniform and the spot size was adjusted by varying the distance between the sample and the laser lenses. The scanning rate was varied between 0.017 and 0.054 m s^{-1} to obtain different alloying conditions. Single tracks were first obtained to determine the optimal laser operation parameters. After that, a wide surface areas was laser treated by performing successive laser passes with a 50 % overlap between each pass of the laser. The total area of samples processed was about $12 \times 35 \text{ mm}$.

Optical microscopy, scanning electron microscopy (SEM) and electron dispersion analysis X-ray (EDAX) were used to analyse the thickness of the melted layer, the possible presence of defects, and the microstructure and chemical composition of the surface alloys. For optical microscopic observations the samples were etched in concentrated HNO_3 , HCl and methanol to determine the microstructure of laser treated coatings, and in ethanol and concentrated HNO_3 (nital) to reveal the microstructural transformations of the steel substrate.

The corrosion resistance was evaluated by electrochemical tests in 0.1 M Na_2SO_4 solution, $\text{pH}=6.5$ at room temperature in an electrochemical cell. A saturated calomel electrode, as a reference electrode, and a stainless steel wire, as an auxiliary electrode were used. The working electrodes consisted of specimens treated with five overlap tracks exposed at the corrosive medium.

Corrosion resistance was determined by means of two characteristic parameters, *i.e.* the evolution with testing time of the corrosion potential, E_{corr} , and the corrosion current density, i_{corr} . The corrosion current density was calculated by polarization resistance method. The polarization resistance was calculated from the ratio between an applied polarization of $\pm 0.01 \text{ V}$ and the corresponding current response measured after a stabilization time of 30–60 s. Electrochemical impedance spectroscopy (EIS) measurements to characterize the corrosion resistance of the laser treated samples were also carried out. Measurements on the working electrode were performed by applying a sinusoidal potential of 0.01 V in amplitude at a frequency range from 0.001 to $64 \times 10^3 \text{ Hz}$.

At the end of testing time, the pitting corrosion susceptibility was obtained by plotting the anodic polarization curves at a scanning rate of 0.167 mV s^{-1} .

3. Results

3.1. Metallographical Characterization

In order to obtain an adequate laser surface alloying, preliminary experiments for a range of laser output

Fig. 1. Tracks created by laser beam of 4.7 kW over samples with 500 μm initial thickness nickel-base coating on the mild steel:

- single tracks obtained at several output powers and scanning rates from 1.5 to 4.7 kW and 0.006 to 0.054 m s^{-1} , respectively.
- single and multiple overlapping tracks obtained at an output power of 4.7 kW at different scanning rates, 0.017, 0.036 and 0.054 m s^{-1} .

powers and scanning rates were carried out. **Figure 1a)** shows the tracks obtained for 500 μm initial coating thickness samples, laser treated at output powers and scanning rates varying from 1.5 to 4.7 kW and from 0.006 to 0.054 m s^{-1} , respectively. In samples laser treated at the minimum output power, 1.5 kW, the laser treatment leads to accumulation of molten material on local zones of the track (Fig. 1a)). For 3 and 4.7 kW no appreciable differences in the tracks obtained in the samples exist, but, from the cross-section view of the samples it was determined that the best condition was obtained at the maximum output power, 4.7 kW.

Once the optimal laser power was chosen, laser-surface-alloying was carried out at three different scanning rates of 0.017, 0.036 and 0.054 m s^{-1} on powder coating thicknesses of 250, 500 and 1 000 μm . As an example, **Fig. 1b)** shows both single as well as five overlapping tracks for a 500 μm initial coating thickness sample laser treated at the three scanning rates.

Figures 2, 3 and 4 show the cross section views of a whole track including the overlapping zone between two tracks for samples of 1 000, 500 and 250 μm initial coating thicknesses laser treated at scanning rates of 0.017, 0.036 and 0.054 m s^{-1} , respectively. The sections shown are

Fig. 2. Cross section of multiple overlapping tracks of Ni-Cr-W-Mo-Cu-C-B 1000 μm initial coating thickness laser treated at different scanning rates (with 3% nital etching).

Fig. 3. Cross section of multiple overlapping tracks of Ni-Cr-W-Mo-Cu-C-B 500 μm initial coating thickness laser treated at different scanning rates (with 3% nital etching).

representative of the remainder of the treated samples. The examination of these samples revealed the existence of three different areas, from the core to the surface of

Fig. 4. Cross section of multiple overlapping tracks of Ni-Cr-W-Mo-Cu-C-B 250 μm initial coating thickness laser treated at different scanning rates (with 3% nital etching).

the sample: the unaffected substrate, a heat affected zone (HAZ), and finally, the melted coating.

In all conditions studied, a transformation to martensite in the heat affected zone (HAZ) of the base steel occurs, as can be seen in Figs. 2, 3 and 4. The depth of the HAZ increased as the scanning rate decreased. Also, all the samples presented a good adherence and the melted layer-base material interface and heat affected zone (HAZ) were crack-free.

Figure 5 shows the profile of melted layer thickness at different scanning rates for all the samples studied, including both central track as well as overlapping areas. The sample of 1000 μm initial thickness and laser treated at the lowest scanning rate, 0.017 m s^{-1} , presented a very homogeneous coating thickness in the treated surface (Figs. 2 and 5). As the laser scanning rate increased, the thickness and uniformity of the treated surface decreased. For 500 and 250 μm initial coatings the thickness of the melted layer was halved when the scanning rate increased from 0.017 to 0.036 m s^{-1} . Furthermore, for these samples there were a substantial difference in melted layer thickness between the centre and the overlapping tracks. For 250 μm initial coating, the irregularities were high and the surface alloy even disappeared in some overlapping areas, as we could see in Fig. 4.

The optical microscopic observations of the etched samples revealed that the substrate/melted coating interface was characterized by a strip without a defined structure, which corresponds to a plane front growth (**Fig. 6**). The chemical composition obtained by EDAX at this zone revealed the existence of nickel, chromium, tungsten and molybdenum and a high iron content.

Fig. 5. Melted layer thickness variation of multiple overlapping tracks of Ni-Cr-W-Mo-Cu-C-B coatings for 1000, 500 and 250 initial thicknesses according to operating conditions of 4.7 kW and 0.017, 0.036 and 0.054 m/s^{-1} . (OL - overlapping between two tracks, T - number of track).

With respect to the melted coating, the samples presented a dendritic microstructure with eutectic carbides in interdendritic areas, as can be seen in the micrographs of Fig. 7. EDAX spectra taken on the dendrite stem and interdendritic zones are shown in Fig. 8. The size of the dendritic microstructure decreased as the scanning rate increases (Fig. 7).

3.2. Corrosion Behaviour

In order to find possible differences in the corrosion behaviour between samples of single and multiple tracks, both types of samples have been studied. As an example, Fig. 9 shows the evolution of the corrosion potential,

Fig. 6. Plane front growth and dendritic microstructure of a 1000 μm initial coating thickness sample laser treated at scanning rate of 0.017 m/s^{-1} .

Fig. 7. Variation of morphology and size of dendritic microstructure as a function of the laser scanning rate for 1000 μm initial coating thickness samples.

Fig. 8. EDAX analysed composition of dendritic and interdendritic areas of 1000 μm initial coating thickness sample laser treated at a scanning rate of 0.036 m s^{-1} .

E_{corr} , and the corrosion current density, i_{corr} , for samples with single and multiple overlapping tracks on 1000 μm initial thickness and with a laser scanning rate of 0.017. This good corrosion behaviour observed in samples with overlapping zones is difficult to achieve. In other studies,⁸⁾ carried out with Ni-P coatings, a high concentration of defects at the overlap zones were observed. Also in the surface laser treatment of steel, the most problematic area was the interface between treated and untreated zones, and the overlapping zones. In these zones aligned pitting occurred both at the interface and at the overlap zones.³⁾

The results obtained from metallographic characterization of the powder coatings after laser treatment revealed that the samples with 250 and 500 μm initial coating thicknesses presented numerous defects and a high degree of dilution with base material as will be seen later. For this reason the corrosion results about these samples are omitted.

Figure 10 shows the corrosion current density, i_{corr} , values for 1000 μm initial coating thickness samples laser treated at different scanning rates. These corrosion

Fig. 9. Evolution of i_{corr} and E_{corr} values for samples with single and overlapping tracks of 1000 μm initial thickness laser treated at a scanning rate of 0.017 m s^{-1} .

Fig. 10. Evolution of i_{corr} values for samples of 1000 μm initial thickness laser treated at different scanning rates.

current density values, i_{corr} , present appreciably different corrosion behaviour for the different scanning rates. Between the samples treated at minimum and maximum scanning rates a difference in corrosion current density values at least of one order of magnitude is observed. The lowest corrosion current density was obtained at the highest scanning rate, 0.054 m s^{-1} .

In order to complete the electrochemical characterization of these samples, electrochemical impedance

Fig. 11. Nyquist and Bode diagrams for samples of 1000 μm initial coating thickness laser treated at different scanning rates.

measurements were carried out. **Figure 11** exhibits the Nyquist and Bode diagrams for 1000 μm initial coating thickness samples laser treated at the different scanning rates. The most widely opened semicircle corresponds to laser treated samples at the maximum scanning rate. The extrapolation of these semicircles with the real impedance axis gives transference resistance, R_T , of about $10^5 \Omega \text{cm}^2$ for 1000 μm initial coating thickness laser treated at 0.054 m s^{-1} . This value is of the same order of magnitude as the value obtained by the polarization resistance method. The Bode diagrams (Fig. 11) show the impedance modulus and the phase angle *versus* frequency, which decreases as the scanning rate decreases.

After the impedance experiments, anodic polarization curves were performed. **Figure 12** shows anodic polarization curves for 1000 μm initial coating thickness samples laser treated at 0.054 and 0.017 m s^{-1} . In this figure for the sample treated at the highest scanning rate, a passivity range with a passivation current density of $10^{-6} \text{ A cm}^{-2}$ can be seen. This passivation is broken after applying a polarization of 347 mV over corrosion potential value. For a scanning rate of 0.017 m s^{-1} an active state was observed, as can be inferred from the anodic polarization curve in Fig. 12.

4. Discussion

After series of treatments necessary to optimise the laser processing conditions samples with three coating thickness were treated at the best conditions. With laser-surface-alloying is pretended to obtain a wide surface with high corrosion resistance.

As a consequence of the laser treatment the melted

Fig. 12. Anodic polarization curves for 1000 μm initial coating thickness samples laser treated at scanning rates of 0.054 and 0.017 m s^{-1} , respectively.

coating presents dendritic solidification. The dendritic and interdendritic areas are formed by a solid solution rich in Ni and Cr and eutectic chromium and refractories elements carbides, respectively (Fig. 8). Nickel and chromium in the surface alloy are quite homogeneously distributed. However, the estimated iron amount varies from the interface to the surface (**Fig. 13**).

A good chemical homogeneity is found in overlapping tracks samples. This homogeneity explains the excellent corrosion behaviour obtained in overlapping samples

Fig. 13. EDAX spectra for dendritic structure at the surface and near the melted layer-base material interface for 1000 μm initial coating thickness samples laser treated at 0.054 ms^{-1} .

that is not found in another laser treatments and coatings.^{3,8)}

The size of the dendritic microstructure depends on the scanning rate in the laser processing. The high scanning rates involve a low interaction time thus a faster solidification rate takes place. This effect produces a refinement of the dendritic microstructure (Fig. 7).

The interaction of the laser with the material is so high that besides melting of Ni-Cr-W-Mo-Cu-C-B coating a dilution effect with the substrate takes place. Due to this dilution there exists a good adherence between coating and base material. In addition, both melted layer-base material interface and heat affected zone (HAZ) are free of cracks (Figs. 2, 3 and 4).

The degree of dilution has been measured by the penetration of the surface alloys into the base steel, as can be seen in Fig. 14. The lower dilution degrees are attained at the highest scanning rates. At this velocity, the 250 μm initial coating presents irregularities and thickness variations so drastic that the technological applications are discarded. The 1000 μm initial coating at these high scanning rates shows the lowest penetration. The presence of high nickel and chromium elements at

Fig. 14. Average penetration of Ni-Cr-W-Mo-Cu-C-B initial coatings into the base material for the different coating thicknesses and laser scanning rates.

Fig. 15. EDAX spectra for dendritic structure at the surface for 1000 μm initial coating thickness samples laser treated at scanning rates of 0.017 and 0.054 ms^{-1} .

the surface promotes the formation of a passive layer with a good corrosion resistance (Fig. 10). In addition, the attack pitting susceptibility is low due to the high

Fig. 16. Metallographic observation of a cross section view of 500 μm initial coating thickness samples laser treated at a scanning rate of 0.017 m s^{-1} after corrosion test.

breakdown potential value, E_b , in Na_2SO_4 solution (Fig. 12). When the samples have been processed at the lowest scanning rate—1 000 μm and 0.017 m s^{-1} —the degree of dilution was so high that a considerable iron content at the surface is obtained. (Fig. 15). The presence of this iron diminishes the corrosion resistance two order of magnitude, as could be seen in Fig. 10. For these samples, the pitting corrosion susceptibility studied by means of the anodic polarization curve showed an active state (Fig. 12) due to the formation of a less protective layer.

The higher degree of dilution in samples with 250 and 500 μm initial thicknesses was achieved, leading to a great iron enrichment in the melted coating. Consequently, a martensitic transformation and cracks in the melted layer were produced. In these cases a drastic decrease in the corrosion resistance was obtained, as can be seen in Fig. 16, where the corrosion attack progresses through the cracks until reaching the base material and also in the martensitic structure of the melted coating.

5. Conclusions

(1) After laser treatment a dendritic microstructure for all coating thickness and laser scanning rates was observed. The size of the dendrites depends on the conditions of the laser processing.

(2) The lowest degree of dilution of base material into the laser surface alloy was obtained with a 1 000 μm

initial coating thickness and the maximum laser scanning rate, 0.054 m s^{-1} . The high content of chromium and nickel on the surface promotes the formation of a passive layer with a good corrosion resistance.

(3) Samples with 250 and 500 μm initial coatings have a higher penetration of base material into surface alloy and martensitic transformations even took place in the melted layer.

(4) Given the good corrosion behaviour of the 1 000 μm coatings treated at 0.054 m s^{-1} in wide testing areas where there are overlapping zones it is possible to consider their use in diverse technological applications in the future.

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