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Corrosion Resistance of Coatings Produced by Spraying Powders Under a Laser Beam in a Saline Environment NaCl 3% by the Electrochemical Method

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Abstract: The manuscript focuses on the study of corrosion resistance in NaCl medium of a 304L type stainless steel after application of protective nickel-based and cobalt-based coatings produced by powder spraying under a continuous CO_2 laser (10.6 µm wavelength) beam. Using polarization and electrochemical impedance spectroscopy methods, the results found confirm that metallic coatings produced under high energy beams offer excellent protection up to an efficiency of E = 98.12% in aggressive environments with salinity to 3%.

Keywords: Corrosion; stainless steel, salinity, electrochemical methods, laser cladding, efficiency.

1. Introduction

The flexibility and efficiency of high-energy beams such as CO_2 lasers have allowed the versatility of their application in several industrial domains [1], [3]. One of the major problems encountered in industry is the degradation of certain machine parts under the effect of corrosion, which requires their protection in order to extend their life and reduce economic costs [4], [5].

In order to ensure protection against corrosion and abrasion, nickel and cobalt alloys are widely used in industry for the coating of machine parts working at very high temperatures [6], [7]. Surface treatments carried out under high energy beams by powder injection offers the possibility to apply a broad variety of metallurgical coatings on the surface of materials, and they can be effective and economical solutions [4].

Indeed, the importance of this type of treatment is asserting itself more and more, because it is one of the rare means easy to implement and to reduce the cost of production. With this new technology, the coatings produced can give new properties to the base materials [8].

Studies have shown the effect of the treatment on the geometric quality of the laser sheath obtained by powder injection [9], [10]. However, the effectiveness of protecting coatings against corrosion remains to be examined. Due to the interaction of stainless steel with aqueous solutions, especially during desalination (water treatment) and petrochemicals process in which the alloy is in contact with highly concentrated saline and acidic environments, corrosion problems arise [11], [12]. Research in the field of stainless steels corrosion used in chlorinated media is of great practical value. The initiation of pitting by chlorides causing rupture of the passive film occurs at a so-called pitting potential. To explore pitting of steel many investigations have been made, the theories estimate that Cl^- penetrates and migrates through passive films. Between pitting potential and Cl^- concentration a linear relationship has been reported elsewhere. Some researchers have attributed the influence of the interaction of chlorides with nitrogen and sulfur included during the bites. Others have studied the effect of pH on the corrosion of stainless steels [13].

The present paper is a study of corrosion resistance generated by deposits of nickel base and cobalt base alloys produced by powder projection under CO_2 laser beam in a NaCl medium. Coaxial injection of powder is used to localize the powder flow for production of deposits on a 304L stainless steel. Polarization and electrochemical impedance spectroscopy methods were used as an experimental tool for this research [14], [16].

2. Experimental procedure

2.1 Materials

Samples of an austenitic stainless steel as substrates are chosen. Indeed, this type of steel exhibits virtually no allotropic transformation on heating and cooling [17]. Prior to coating, the cubic shaped (1 x 1 cm^2) X3CrNi18-10 (304L) (0.03% C, 0.75% Si, 18% Cr, 68.7% Fe, 10% Ni, 1.5% Mn, 0.02% P) were cleaned with acetone and rinsed with alcohol. Before any deposition, the powders of Cenium 36 (Ce36) (36% Ni, 30% Cr, W, 1% C) and METCO 18C (M18C) (40% Co, 18% Cr, 26.8% Ni, 20.5% Fe, 0.2% C, W, 3.5% Si, Mn, 3% B, 6% Mo) undergo a drying treatment for approximately 30 minutes at 200° C. The two working electrodes are prepared from a 304L stainless steel one coated with nickel and the other with cobalt. The models are presented by the figures below.

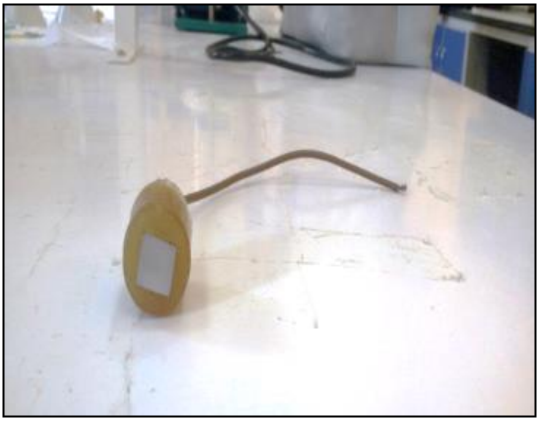

Figure 1: Working electrode 304L

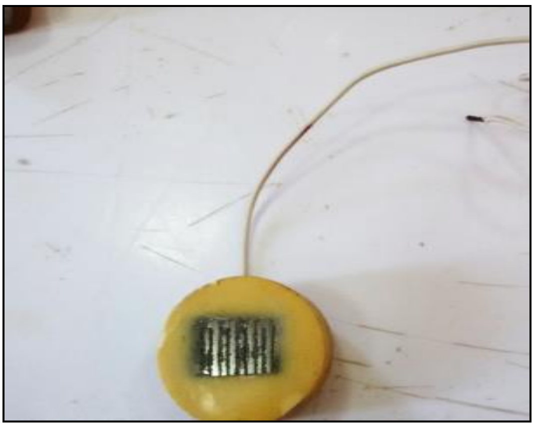

Figure 2: Working electrodes 304L nickel coating

With 1200 grade emery paper the exposed area was mechanically abraded because the good quality of the surface state of the deposits made does not require the use of repeated polishing. It is then washed with distilled water, degreased with acetone and finally dried before each experiment. The corrosive medium is a 3% NaCl solution prepared by dissolving 30 g of powdered NaCl crystallized in a liter of distilled water, then stirred to obtain a homogeneous solution. Before their microstructural characterization, samples were polished and cleaned using the following reagent: 150 cm^3 HCl, 25 g $K_2Cr_3O_7$, 50 cm^3 H_2O Keller's reagent**.**

2.2 Laser claddings

The heat source used is a continuous CO_2 laser (CILAS CI 4000) whose output power from the cavity varies between 200 and 3600 W. To focus the beam on the surface of the sample, a focal lens of 191 mm is used. The manufacturing process involves injecting powder into a bath of molten metal on the surface of the workpiece under the laser beam. This moves with a constant speed with respect to the beam. The powder dispenser used is of type 4MP (METCO). A system of nozzles, arranged around the lens and the focused beam, directs the powder and the protective argon jet towards the part, in the same axis as the laser beam *(Fig. 3).* The processing parameters have been previously optimized: energy density (95.103 W / cm^2); travel speed (5 mm / s); powder flow rate (20g / min); workpiece nozzle distance (20 mm); powder / beam tilt (15 degrees), *Fig. 3.*

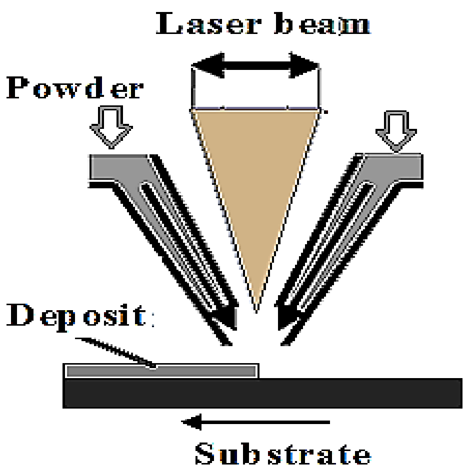

Figure 3: Powder spray coating process

2.3 Electrochemical measurement setup

The experimental setup is an electrochemical cell composed of conventional three electrodes which are: the working electrode made up of the steel to be tested with an (1 x 1 cm^2) exposed area to the corrosive solution. The reference electrode (calomel) and the auxiliary electrode consisting of a platinum plate (1 x 1 cm^2). A Volta lab PGZ 301 potentiostate controlled by Tacussel model corrosion analysis software (Voltamaster 4 and EC-lab demo) was used for electrochemical measurements. In Nyquist representation the EIS data were given.

3. Results and discussion

3.1 Laser claddings microstructure

The microstructure of the deposit M18 cobalt-based powder / 304L obtained by SEM is presented in *Fig. 4*. The structure is mixed type, the balance is cellular or dendritic, oriented randomly. The existence of various growth regimes therefore leads to very distinct structures with different properties, which is confirmed by other studies [18]. The 1.2 mm thick sheathed layer obtained has a good morphological appearance with a low dilution rate.

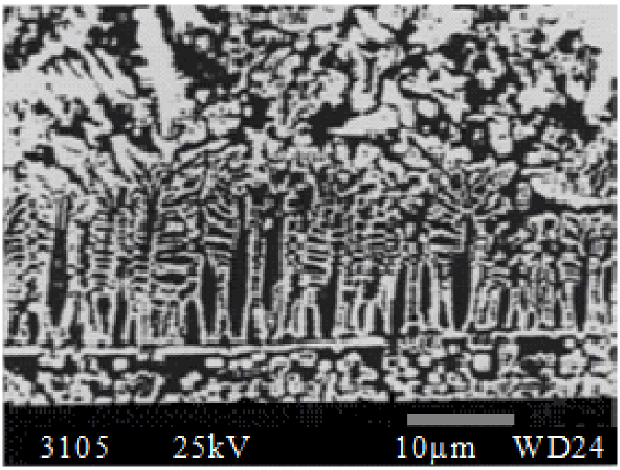

Figure 4: Microstructure at the coating-substrate (Metco18) / 304L

Several areas can be distinguished. A slightly marked transition zone with the substrate is associated with an interface probably characterized by solidification with a flat front. It is a monocrystalline and homogeneous growth layer. An area adjacent to the interface in which an austenitic primary phase develops.

3.2 Microhardness profile

A Vickers's microhardness tester was used. The microhardness measurements under a load of 200 g (*Fig. 5*) were taken along a cross section of the deposit. The fluctuations recorded at the level of hardness correspond to the various zones described by the morphologies presented in *Fig. 4*. The hardness filiation carried out highlights the existence of different mechanical properties between the various parts of the deposit and the support. Indeed, from the point of view of hardness, an appreciable gain was recorded due to the change brought about by this surface treatment.

The results of the literature confirmed that during processing, precipitates of complex borides and carbides of the M7C3 type form, which strengthen the matrix and therefore give it new properties such as good resistance to friction [19-21].

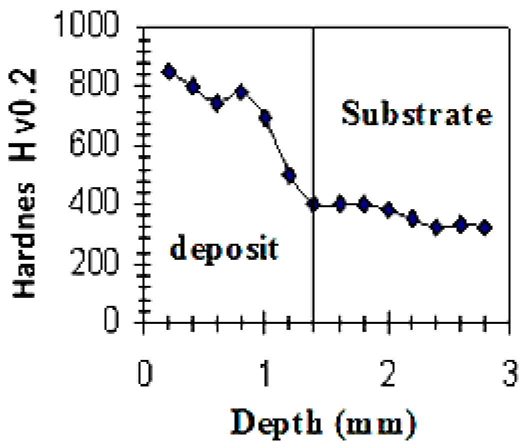

Figure 5: Microhardness profile along the deposit

3.3 Polarization curves

The potentiodynamic polarization curves for stainless steel in the 3% NaCl medium in the absence and presence of nickel-based and cobalt based coating are shown in *Fig 6, Fig 7*. It can be seen that anodic and cathodic reactions of stainless steel with the saline environment are inhibited in the presence of protective deposits which reduces the dissolution of stainless steel by delaying the degradation reaction. In presence of this coating the corrosion potential is moved to the more noble value (positive) playing the role of anodic corrosion inhibitor. Obtained by extrapolation of the Tafel lines, the electrochemical corrosion parameters as a corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel slopes (β_c, β_b) are grouped in *Table 1*. The efficiency of inhibition (E%) is determined from the following relation:

$$E\% = \frac{1 - i_{corr}}{i^0_{corr}} \cdot 100 \,. \tag{1}$$

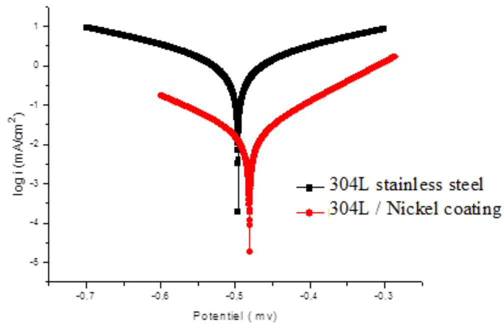

Figure 6: Polarization curves of 304L steel in 3% NaCl in absence and presence of nickel coating

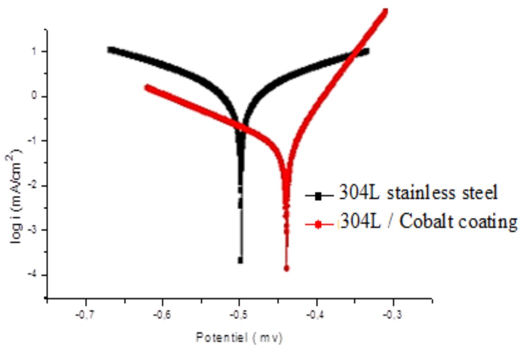

Figure 7: Polarization curves of 304L steel in 3% NaCl in absence and presence of cobalt coating

In the presence of coatings, the corrosion density (i_{corr}) expressed in mA·cm^2, directly proportional to the corrosion rate, decreases, which probably inhibits corrosion and remarkably for nickel compared to results *Table 2* [22] from the literature, which prove the effectiveness of the laser process used. The current density and corrosion polarization resistance of 304L steel in 3% NaCl are 0.2993 (mA / cm^2) and 57.69 (Ω·cm^2), respectively. These values change by the application of the nickel and cobalt based metallic coating ((304L / Ni coating.) (304L / Co coating), therefore leading to a decrease in i_{corr} and an increase in R_p, which confirms the high value of efficiency presented in *Table 1*, the effective protective barrier role of the applied coating.

Table 1: Potentiodynamic polarization parameters for stainless steel in 3% NaCl in absence and presence of Ni and Co coating at 298 K

	E (*i*=0) (mV)	R_p (Ω·cm²)	i_{corr} (mA/cm²)	β_a (mV)	β_c (mV)	*Coeff.*	*E* (%)	Corrosion rate Cr (μm/year)
304L	-488.8	57.69	0.364	78.8	-125.3	1	-	3.96
304L/ Ni coating	-486.3	647.10	0.026	72.5	-89.7	0.9993	98.12	0.25
304L/ Co coating	-481.1	149.28	0.084	52.2	-64.8	0.9953	83.22	0.96

Table 2: Corrosion rate of 304L stainless steel specimens, coated in a chlorinated nickel bath [22]

Concentration Al_2O_2 (g/l)	Corrosion rate (μm/year)	Current density (μA/cm²)	E_{Corr}/E_{CS} (mV)
Uncoated	4.635	0.3963	-354.7
0	3.006	0.3743	-363.3
5	1.284	0.1098	-356.5
10	1.656	0.1415	-361.5
15	2.651	0.2267	-336.3
20	1.961	0.1638	-364.7

3.4 Electrochemical impedance spectroscopy measurements

Schematized by *Fig.8* and *Fig.9*, the diagrams of impedance in Nyquist representation traces in the absence and presence of metallic coatings reduce to unreformed capacitive semicircles indicating that corrosion process has been controlled by a single phenomenon which is the transfer of charge.

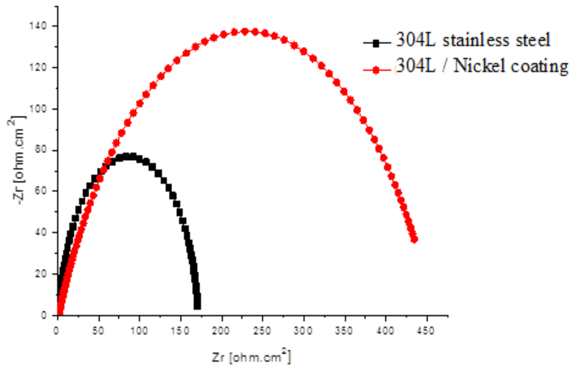

Figure 8: Nyquist diagrams of 304L stainless steel in 3% NaCl medium in the absence and presence of the nickel-based coating

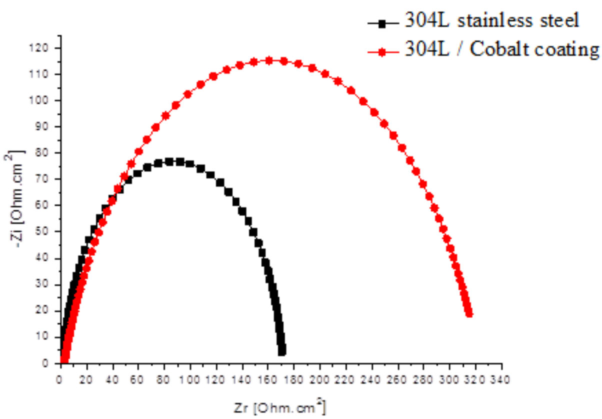

Figure 9: Nyquist diagrams of 304L stainless steel in 3% NaCl medium in the absence and presence of the cobalt-based coating

The simulated curves essentially follow the experimental data. *Table 3* presents the values of solution resistance (R_s), load transfer resistance (R_{tc}), total capacitance (C_{dl}), which were calculated by simulating the experimental data with the EC-Lab software.

It is noted that the diameter of the semicircles is proportional to the transfer resistance which is higher in the presence of deposits and remarkably for nickel. The undeformed regular shape indicates a homogeneous and complete distribution of the protective film on the substrate surface which is confirmed by the results obtained and carried on the *Table 2*, showing that there is an increase in the transfer resistance R_{tc} load with coating application as capacitance values decrease.

Table 3: Values associated with the impedance parameters stainless steel in 3% NaCl in absence and presence of Ni and Co coating at 298 K

	R_S ($\Omega \cdot cm^2$)	R_{tc} ($\Omega \cdot cm^2$)	C_{dl} ($\mu F/cm^2$)	E (%)
304L	16.20	150.2	$0.4827\ 10^{-3}$	-
304L/ Ni coating	8.82	2008.0	$0.4002\ 10^{-3}$	91.82
304L/ Co coating	9.24	1840	$0.4055\ 10^{-3}$	83.22

4. Conclusion

From the electrochemical study for the characterization of the corrosion behavior in saline environment of coatings made under laser beam we conclude that:

With an efficiency of E = 98.12 % and a distribution homogeneity according to the results obtained from the study using the methods of polarization and electrochemical impedance spectroscopy the coatings carried out under high beam can constitute a solution for the fight against corrosion in the case of parts working in saline environments and can act effectively as a corrosion inhibitor for steels.

The difference between the efficiency values obtained for the two cases of coating nickel base, cobalt base respectively (E (%) 98.12; 83.22) brings us back to reflect on the influence of the quality of the powders used as filler material.

The very low corrosion rate obtained in the case of laser coatings shows that this method offers better protection against corrosion.

The laser process according to the impedance curves ensures continuity and uniformity of the protective layers deposited.

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