# MICROSTRUCTURAL EVOLUTION OF COATINGS IN CARBON STEEL BY THERMAL SPRAYING

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*The protection against the steel substrate corrosion in marine environment, obtained by metallic coatings thermally sprayed, has been studied and largely used throughout the last years. The corrosive process occurs easily if the materials are not resistant to the corrosion or if they do not possess an adequate system of protection. We can find coatings produced by thermal sprayed in bridges, tanks and petrochemical structures, antennas, steel towers, electrification poles, ships components, offshore structures, etc. Amongst the diverse areas that use these protective systems, the offshore industry, that in the past used painting projects as the main form of protection against corrosion of structures exposed to severe marine environments, is significantly increasing the use of the thermal sprayed in their steel structures. The main objective of this work is the evaluation of properties of materials formed by the deposition of coatings via the process of thermal sprayed in carbon steel substrate SAE 1020 previously prepared with abrasive blasting, and was applied sealant in some samples. In this study had been evaluated 3 coatings based in Cr, Fe, Ni, Co, sprayed through the Electric Arc process and then studied the behavior of microstructure, hardness, porosity, morphology and especially the resistance to corrosion. Microstructural evolution has been correlated with the progress of salt spray tests as well as scanning analysis electron microscopy (SEM) and optical microscopy (OM). The results presented in this work consider both, the evaluation of oxide layer behavior and its participation as protective element of the steel substratum and the register, through metallographic examination, of how the layer is affected by the test saline environment. It can be concluded that in the salt spray corrosion test, the superficial corrosion products can be adherent and act as additional protection barrier. Moreover, its propagation for the interior of the covering depends on the adherence and cohesion of the deposited layer. The coatings with percentage of Co had better corrosion resistance.*

***Keywords**: Thermal Spraying, coatings, salt spray*

## 1. INTRODUCTION

The offshore industry comes significantly increasing the use of the thermal spray. Among the techniques used to improve materials performance the deposition on the surface of components is a proper way of recovering worn elements. Thermal spraying processes were developed on the last years and they are a very suitable method to obtain layers with high hardness for protecting or repairing the base component. Employing these processes it is possible to overlay metallic substrates with polymers, metals and ceramics, e.g.: HVOF, Arc-Spray and Flame-Spray. All these techniques permit the deposition of coating materials, generally ductile, with self-lubricating properties and improved corrosion and wear resistance. The impact against the substrate surface flats the particles and produces adhesion to the substrate in a direction parallel to it by the interlocking of the molten or semi-molten, according to Braday et al. (2008) and Sampson (1997).

Dorfman (2002) reported that thermal spray is a deposition technique that involves the melting of powder particles or wires and their rapid solidification upon impacting a substrate. The coating process develops by the successive impingement and interbonding among the splats (solidified individual particle). The multitude of interdependent process parameters results in a range of thermal histories for the molten particles, producing a wide distribution of particle velocities and temperatures within the stream.

This work has as main objective the evaluation of properties of three coatings formed by the sprayed of alloys on carbon steel substratum. Metallic coatings sprayed by electric arc process were made. Afterward, an assessment of the microstructural morphology measured by means of the optical microscope (OM) and scanning electron microscope (SEM) were made. The resistance to corrosion was tested in salt spray during 40 hours.

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## 2. METHODOLOGY

In the present investigation, three coatings had been evaluated, on the basis of Fe-Cr-Ni-B-Co sprayed by the electric arc process. Initially, the coatings were characterized according to their porosity and morphology. Tables 1 and 2 show the chemical composition of the four wires, used to form the coating, and the combination of three conditions of coating, respectively. The selected substrate material was carbon steel SAE 1020. The steel samples were cut to form specimens of approximately 100 mm x 150 mm x 4,5 mm. .

The process of thermal spray was done with the following parameters: voltage about 40 V, current about 100 A and deposition rate of 2,34 kg/h. The equipment has two entrances for the reels with wire of 1.6 mm in diameter to be deposited.

An assessment of the microstructural morphology by optical microscope (OM) and scanning electron microscope (SEM) coupled with an X-ray energy dispersive spectroscopy (EDS) was made and compared with microhardness Vickers (HV 500) test and porosity quantification. The samples for microscopic examination were prepared by standard metallographic techniques. The resistance to corrosion was analyzed in salt spray during 40 hours, Fig. 1, according to ASTM B 117.

Microhardness testing was performed using a Vickers microhardness tester (Wilson Instruments, model 422MVD) with a load of 500 g. Microhardeness analysis were made from the surface of the coating to the substrate, passing through the intermediate bond of adherence in order to evaluate an average value and a standard deviation of this parameter.

The coating porosity was determined by quantitative image analysis on the basis of optical micrographs taken from cross sections at magnifications of 100X or 500X.

The porosity quantification was made in accordance to the methodology proposed by Vreijling (1998), who classified seven types of porosity in the coatings produced by thermal spraying. Afterward, was estimated the percentage of area in the porous coating.

**Table 1**. Chemical composition of four wires used in process electric arc.

| wire | %Fe | %Co | %Cr | %Ni | %B | %Mn | %W | %Mo | %C | %Si | %Cu | %P | %N | %Nb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (a) | 66,1 | | 27,0 | | 3,5 | 1,8 | | | | 1,6 | | | | |
| (b) | 65,7 | | 25,7 | 2,9 | | 1,9 | | 0,8 | 1,6 | 1,4 | | | | |
| (c) | 3,6 | 58,4 | 28,8 | 1,9 | | 0,9 | 4,9 | 0,02 | 1,1 | 0,3 | | | | |

**Table 2**. Details of three conditions studied with combination and intermediate bond.

| **Condition** | **Combination of wires** | **Intermediate bond** |
|---|---|---|
| 1 | a + b | 95Ni; 5Al |
| 2 | a + c | 95Ni; 5Al |
| 3 | b + c | 95Ni; 5Al |

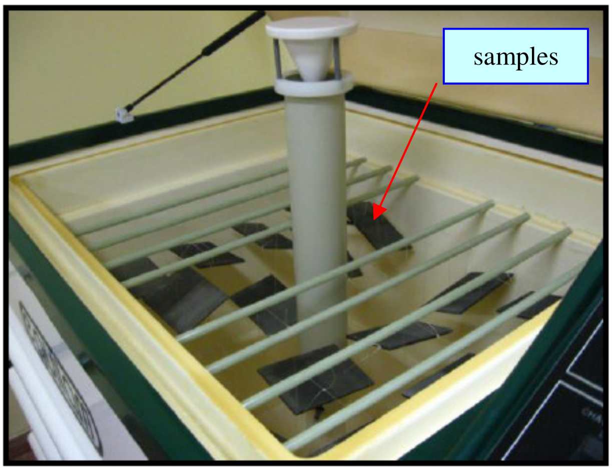



Figure 1. Disposition of samples used in salt spray test.

## 3. RESULTS AND DISCUSSIONS

The results obtained by MO and SEM indicate that the three conditions had shown uniformity in the deposited layer with lamellar structure and oxides and little oxide, microcracks and porosity, according Fig. 2. The results show that the morphology of the coatings exhibit characteristic lamellar microstructures with the long axis of impacted splats oriented parallel to the substrate surface, and incompletely melted particles together with a distribution of similarly oriented oxides for three coatings studied.

Oxides may increase coating hardness and may also provide lubricity. Conversely, excessive and continuous oxide networks can lead to cohesive failure of a coating and contribute to excessive wear debris. Based on that, when selecting materials, coating processes, and processing parameters, it is important that oxide content and structure be controlled to acceptable levels.

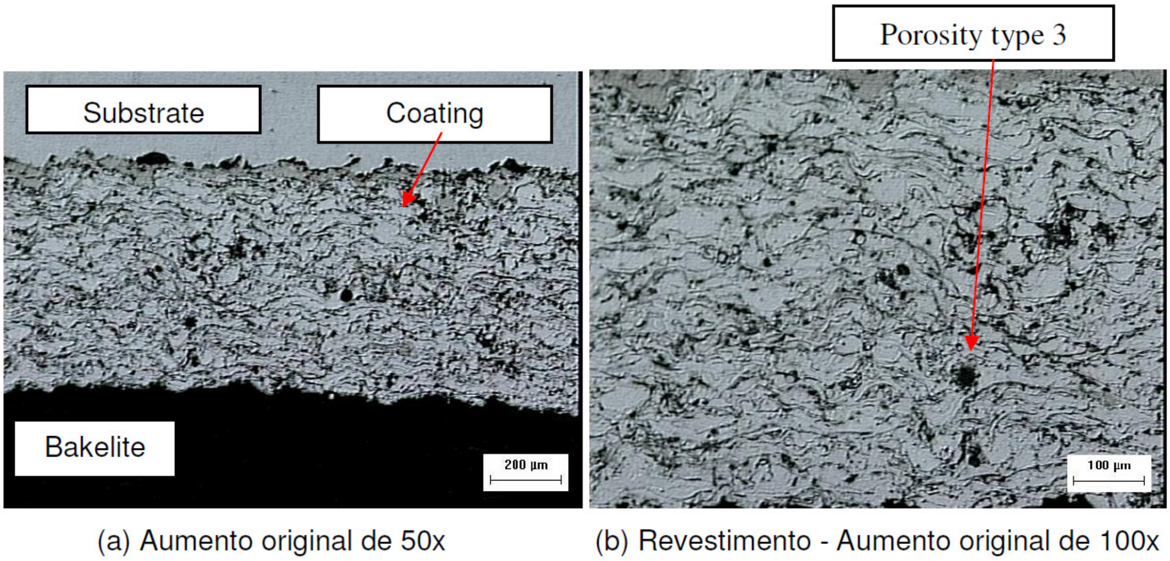



Figure 2. OM micrographs a) aspect of condition 2 (Fe-Cr-Co) show substrate, coating and bakelite. (50X), b) details lamellar structure and oxides of coating (100X).

The occurrence of porosity was very low for all conditions studied, reaching a maximum of 3.9% in condition 1 (Fe-Cr) and a minimum of 1.6% in condition 3 (Fe-Cr-Co ).

According to the methodology proposed by Vreijling (1998), it is possible to observe pores in all samples, but it is in the condition 3 that was found the greatest amount of porosity in the form of lamellae and microcracks. The conditions 1 and 2 had a higher amount of porosity in the form of bubbles, probably formed after cooling of the metal.

Basically, two main parameters influenced the porosity (Sampson, 1997): particle velocity and temperature. Increasing the flow rate leads to an increase in the particle velocity and a decrease, simultaneously, in the diameter of the particle. Consequently, smaller and faster spray particles are produced forming a denser structure. At the same time, higher oxide content can be observed.

**Table 3.** Percentage of porosity obtained.

| **Coatings** | **Porosity (%)** |
|---|---|
| Condition 1 | 3,9 |
| Condition 2 | 2,8 |
| Condition 3 | 1,6 |

These results show the importance of the process of electric arc in terms of porosity amount. Paredes et al. (Paredes et al.-2003) found less porosity in the samples produced by arc (3.9%) compared with the percentage of porosities found in samples produced by means of conventional flame (5.5%).

The porosity of thermal spray coatings is typically lower than 5% in volume. The retention of some unmelted and/or resolidified particles can lead to lower deposit cohesive strength, especially in the case of "as-sprayed" materials with no post-deposition heat treatment or fusion.

The three coatings, with a low porosity, are dense and well bonded to the substrate. The examination of the coating–substrate interface on an overall length shows no gaps or cracks, which are characteristic features of good adhesion between the coating and the substrate.

Considering the resolution limits, porosity within a microstructure can be easily detected by image analysis due to the high degree of contrast between the dark pores (voids) and the more highly reflective coating material. Work by Cortés (1998) has shown that image analysis can reproducibly detect and measure microstructural features (pores, cracks, etc.) within thermal spray coatings. The reliability of these methods for specific experiments and metallographic conditions was statistically tested to give a 95% confidence level, (Cortés, 1998).

Figures 3 and 4 show the cross-sectional SEM micrographs of the analyzed coating. Although the microstructure has revealed pores, they are not critical for corrosion resistance because of their small sizes and because they don't penetrate the coating layer and intermediate league. The results of phase identification by the EDS analysis in SEM show the same phase composition as the feedstock material (spectrum figure 2) for all conditions studied.

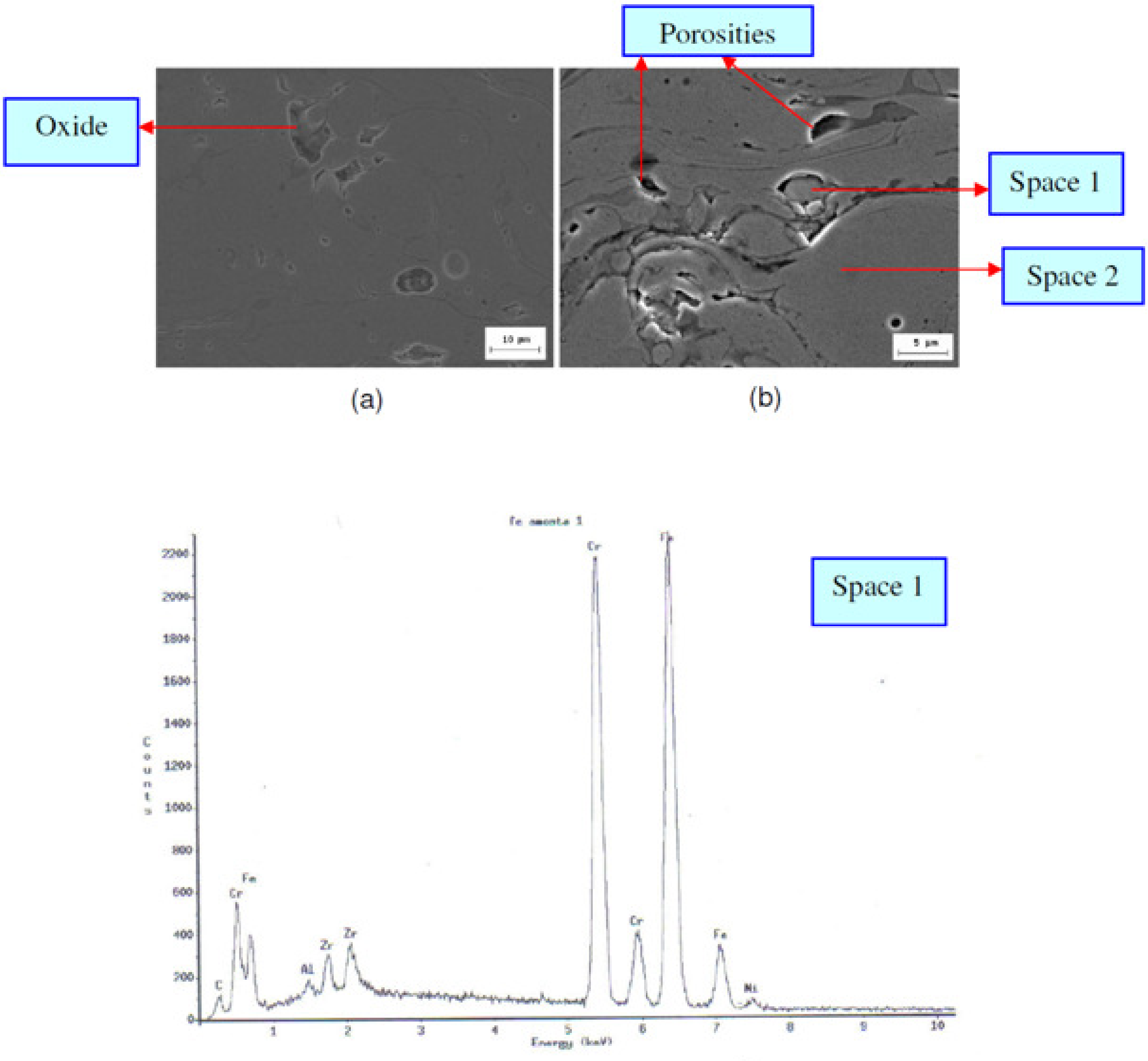



Figure 3. SEM micrographs of condition show the presence of microcraks, porosity and oxide. The spectrum of condition 1, space 1. (a) Magnitude 1500X, (b) Magnitude 2000X

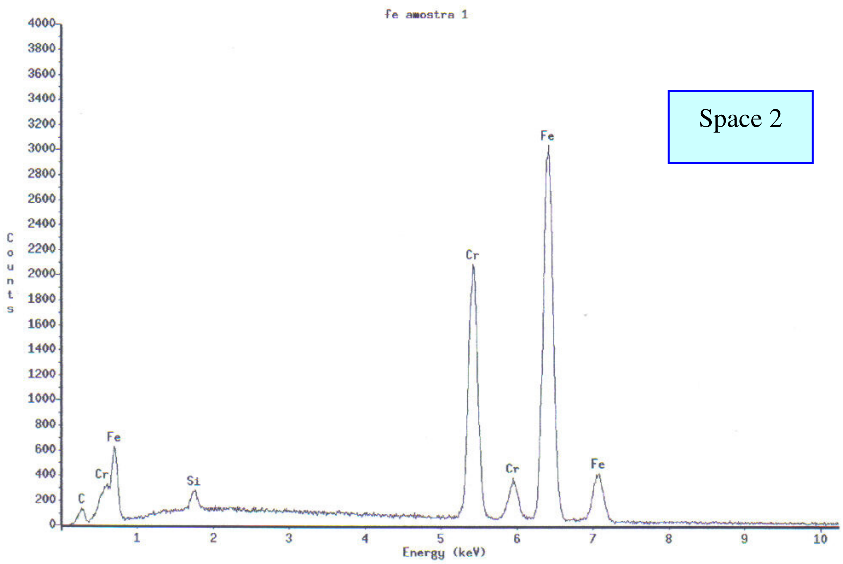



Figure 4. The spectrum of condition 1, space 2.

A thick oxide scale is revealed which seems to have grown up in the form of laminar layers. There is presence of cracks, which are some of them parallel to the surface of the base steel, while some others are perpendicular to the surface of the steel.

The microhardness along the coating layer showed similar results of microhardness between conditions 1, and 2, Figs. 5 and 6, which presented more Cr and Ni elements.

The higher hardness of these three mentioned coatings can be attributed to the fine microstructure of individual lamellae and the inclusions of iron oxide. Thus, the coatings exhibited the higher hardness, which would contribute to increase in wear resistance. The advantage is that coatings with high hardness would contribute to wear and corrosion resistance.

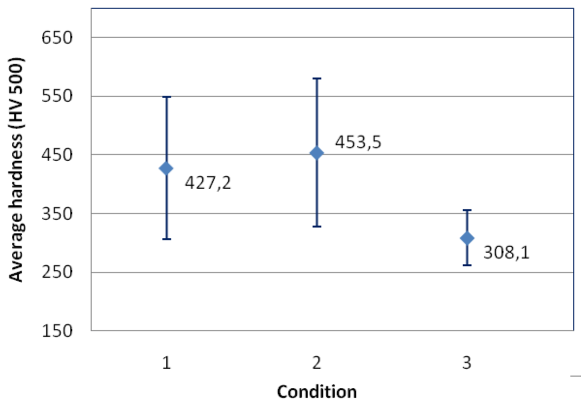



Figure 5. Average standard deviation of the values of hardness (HV 500) along the layer for each coating condition.

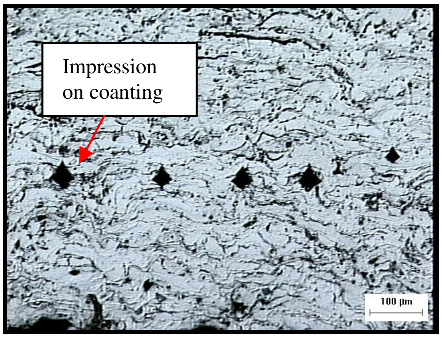


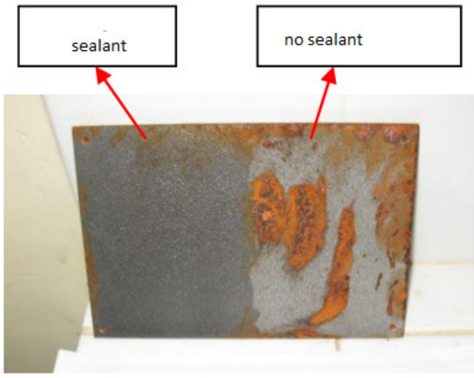

**Figura 6.** Example of microhardness impressions on coating.

The presence of chromium (between 19% and 29%) in the coatings due to the fact that the alloying element oxide forms relatively ease, (Terres, 2006), increases the hardness of the coating, and increases the corrosion resistance (Capra, 2005). Moreover, chromium is also used as a grain refiner to decrease the incidence of cracks resulting from stress.

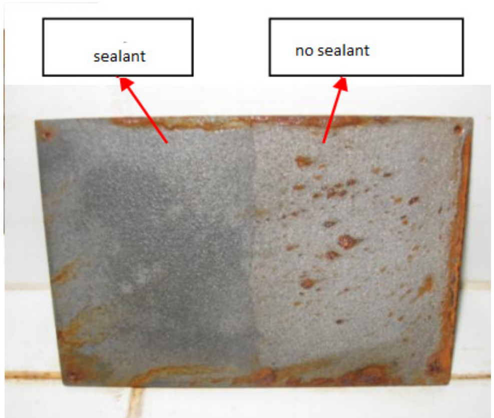
In another study, which also evaluates the effect of chemical composition of coatings obtained by thermal spraying, Schiefler (2004) indicates that hard phases (usually borides) are formed during the solidification of the material, increasing its hardness and improving wear resistance of deposited coatings. This behavior indicates that the highest average hardness of conditions 1 and 2 were found due to the probable formation of borides.

It was possible to identify a major difference between the average hardness of the substrate (132.8 HV) and the average hardness of the coatings. This difference shows the efficiency of thermally sprayed metallic coatings on carbon steel substrates, for applications in environments that require high mechanical hardness.

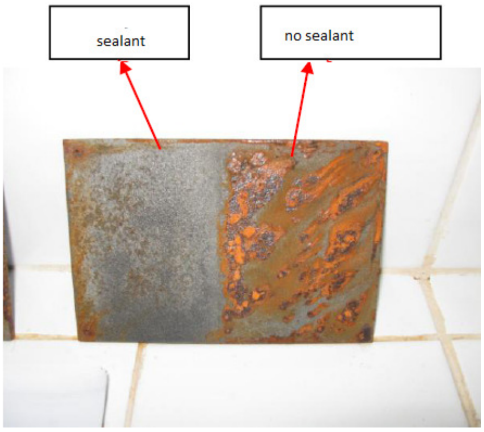
The results show, according Fig. 7, that on the corrosion process for the salt spray technique, the superficial products of corrosion (sealant) can be very adherent and it also can promote an additional barrier of protection. When was analyzed the side of the sample without sealant the best result was condition 2, Fig. 7, that contain a significant percentage of Co.




Condition 1




Condition 2




Condition 3

Figure 7. Aspects of samples of salt spray for 3 conditions.

## 4. CONCLUSIONS

This work has as main objective the evaluation of properties of three coatings formed by the sprayed of alloys on carbon steel substratum. The results obtained by MO and SEM indicate that the three conditions had shown uniformity in the deposited layer with lamellar structure and oxides and little oxide, microcracks and porosity presence. The conditions that contain a significant percentage of Co had better corrosion resistance and higher hardness than the other condition studied. It was possible to identify a major difference between the average hardness of the substrate and the average hardness of the coatings. This difference shows the efficiency of thermally sprayed metallic coatings on carbon steel substrates, for applications in environments that require high mechanical hardness.

**5. ACKNOWLEDGEMENTS**

The authors would like to acknowledge the support of the Brazilian Research Agencies CNPq, CAPES, Laboratory of Microscopy of UFRJ and VGK Company.

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