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Characterization of FeCr and FeCoCr alloy coatings of carbon steels for marine environment applications

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Abstract

This paper presents the adhesive strength results of FeCr and FeCoCr deposits produced by electric arc thermal spray process on carbon steel plates. Five chemical compositions were tested to give a large panel of possibility. Coatings were characterized by several methods to result in a performance screening. The main assessment of microstructural morphology was made by scanning electron microscopy (SEM). The mechanical strength of coatings was evaluated by standard pull-off test. The corrosion resistance was analyzed in salt-spray test. The morphology of coatings exhibits characteristics of lamellar microstructures with incompletely melted particles together with a distribution of similarly oriented oxides. The adhesive strength of FeCoCr alloy coatings was higher amongst all studied conditions. All sealed conditions presented low corrosion in salt-spray exposure. Additionally, a new FeCoCr alloy was studied to reduce pores and microcracks that are frequently found in traditional FeCr and FeCrNi alloys. Based on the performed characterizations, the findings suggested that the FeCoCr deposition, with an epoxy sealing, is suitable to be used as an efficient coating of carbon steel in aggressive marine environments.

Keywords: Carbon steel; Thermal spray; Salt-spray test; Adhesion test; FeCoCr coating

Background

Thermal spraying (TS) is a deposition technique where a spray of molten particles is directed to the substrate to form the coating. It is used for protection of parts against wear, corrosion and high temperatures. Thus TS improves the properties of engineered surfaces. Thermal spraying processes are also applied for repairing damaged and worn parts [1–4].

According to Fukanuma et al. [4], the thermal spray consolidation of particulate materials is essentially a thermomechanical forming process, involving a combination of solid (unmelted or partially resolidified) and liquid phases. Some material can also be vaporized, but this is generally less than 0.1% wt. The thermal energy of the process heats the injected particles at temperature close to their melting points as well as the coating/substrate surface, during the deposition.

Adhesion of thermal sprayed layer to a substrate has been a primary concern to engineers as it is for any coating process. It is generally accepted that the adhesive strength of thermal spray coatings is controlled by three main forces caused by mechanical, physical and metallic interactions [4,5].

Mechanical forces originate from coating wedging or keying to substrates and they interact with surface asperities; metallic forces originate from chemical reactions between the coating and the substrate; and physical forces are related to van der Waals interactions [5].

The bonding between particles and substrate is critical to ensure the quality of coating. Cracking and debonding of coating from the substrate are two main types of failures. Consequently, the structural integrity evaluation of coatings is important to ensure the safety and the reliability of coated parts [4].

The protection of carbon steel against corrosion in marine environment by metallic coatings obtained from thermal spray process has been used in the last years [6–9]. Besides, the increasing aggressiveness of new oil and gas environment, mainly in the Brazilian pre-salt region of ultra-deep exploitation, represents a challenging application to traditional materials such as ordinary steels. Therefore, offshore industry has increased the use of thermal spray as a method to protect the mechanical parts of equipments against corrosion and wear. For this purpose, wire arc spraying is used because of its simplicity, low operation cost and high efficiency [10].

Coatings are suitable for use when good cohesion of deposit and high adherence of coating on substrate are required [11]. Conversely, if the adhesion is insufficient, a common choice is the use the others alloy coatings. On the other hand, the adhesion of the coating to the substrate is assumed to be created by a mechanical interlock between the substrate surface and the first coating layer. Then, a certain degree of surface roughness – usually created by grit blasting – is generally necessary to achieve good results [11].

Residual stresses appear through the deposit thickness when a sprayed coating has several millimeters. Moreover, this stress affects the coating adhesion. The adhesion strength depends on the coating-substrate bonding as well as the coating microstructure. Finally, the residual stress distribution influenced strongly the bonding and the microstructure [2].

In the present investigation, the adhesive strength is evaluated for five electric arc sprayed coatings based on FeCr, FeCoCr, FeCoCrNi and FeCrNi alloys. These metallic systems are interesting because the deposits are expected to simultaneously resist to the typical wear of bearing applications as well as to the corrosive environments such as the pre-salt oilfields. In this application, the evaluation of new chemical compositions of coatings besides the fine adjusts of operational parameters of spray deposition has technological interest. Thus, in this paper, the characterization of coated carbon steel from microstructural, adhesion and corrosion aspects are presented.

Methods

Steel plates were cut to form 150 mm × 100 mm × 4.5 mm specimens. The specimen surfaces were previously grit-blasted with Al_2O_3 particles. The coatings were prepared by electric arc thermal spray process on carbon steel plates. Initially, an intermediate bond was applied to increase the adhesion of coating. Pure argon gas was used as powder carrying agent and shielding atmosphere. All the process parameters, including the spray distance, were kept constant throughout the coating process. The main parameters were the electric voltage and the distance of pistol (*circa* 100 mm). Carbon steel samples were grit blasted before electric arc spraying. Epoxy resin was applied to a group of samples as a bond coat after the final TS coating. A control group was tested without epoxy application. Four wires were used; their chemical compositions are depicted in Table 1. Each wire was labeled as A, B, C, and D for convenience. Wire C is a cobalt alloy and the others are ferrous base alloys. From all possible combinations of wires and intermediate bonds, five combinations were chosen, as shown in Table 2. Although the high price of cobalt alloy, in specific industrial applications where aggressive environment is present, it can be a suitable choice. Two intermediate bonds were chosen: the ordinary 95Ni5Al which produces a known good adherence also but presents some defects; and 78.3Ni20Cr1.4Si0.3Fe as an alternative alloy. Each combination of wire-intermediate bond was identified, as depicted in Table 2. The condition 1 will be hereafter labeled as FeCr; conditions 2 and 3 as FeCoCr; condition 4 as FeCoCrNi and condition 5 as FeCrNi, considering the main alloy elements present in the deposits.

During the thermal sprayed deposition process the following average parameter values were used: voltage 40 V, current intensity 100 A and deposition rate of 2.34 kg hr^{-1}. The equipment used for deposition has two entrances for 2.6 mm diameter wire reels. After deposition, some samples were additionally sealed with epoxy resin. This sealant blocks the porosity that could connect to the carbon steel substrate.

The microstructures of coatings were examined by scanning electron microscopy (SEM). The surface chemistry was studied by X-ray energy dispersive spectroscopy (EDS) microanalysis with point-wise and spectral mapping of elements. The samples for microscopic examination were prepared by standard metallographic techniques.

Adhesion test was performed according to ASTM D4541 standard [12]. A pull-off test was done by applying a tensile stress perpendicular to the surface. These tests were performed in duplicate. The studs, with diameter of 10 mm, were fixed with epoxy resin. The drying-time was 10 minutes and cure-time was 24 hours at room temperature. The testing apparatus was attached to the loading fixture and then aligned before the application of normal stress. The force increases gradually and it was monitored up to the instant that a portion of coating detached, or a previously specified stress was reached.

Samples of coated carbon steel were tested in salt-spray camera at 35°C for 36 hours. The aqueous solution was 5.0% NaCl. The evaluation of corroded area was done by optical microscopy (OM) and SEM.

Results and discussions

SEM micrographs of coating are shown in Figures 1, 2, 3 4. The morphology of coatings exhibit characteristics of lamellar microstructures with the long axis of impacted splats oriented along the substrate surface (see Figure 1c). Lamellar structure is layered, a sandwich-like structure. This kind of structure occurs owing to the successive layers

Table 1 Chemical composition of wires (% wt)

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				
D	68.5		19.6	9.1		1.5		0.5	0.02	0.3	0.4	0.03	0.07	0.01

Table 2 Experimental combination of wires and intermediate bond

Condition (Principal elements)	Combination of wires	Intermediate bond
1 (FeCr)	A + B	95Ni5Al
2 (FeCoCr)	A + C	95Ni5Al
3 (FeCoCr)	B + C	95Ni5Al
4 (FeCoCrNi)	C + D	78.3Ni20Cr1.4Si0.3Fe
5 (FeCrNi)	D + B	78.3Ni20Cr1.4Si0.3Fe

of deposition. Lamellar structure is not isotropic, therefore different properties can be found in parallel or transversal directions in respect the coating thickness [1,2]. Incompletely melted particles together with a distribution of similarly oriented oxides are observed for the five coating types. Oxides are hard particles and increase coating hardness. Conversely, abundant and continuous oxide networks can lead to cohesive failure, Figure 4, of coating and contribute to excessive wear damage of bearings. Consequently, it is important to assure that oxide content of coatings be limited.

EDS measurement results of SEM facilities show agreement between phase compositions of substrate (see Figures 1, 2, 3) for all conditions. Line analysis shows the distributions of elements between the substrate and coating. The observed variation in the alloying content can be ascribed to the non-uniform cooling conditions of individual

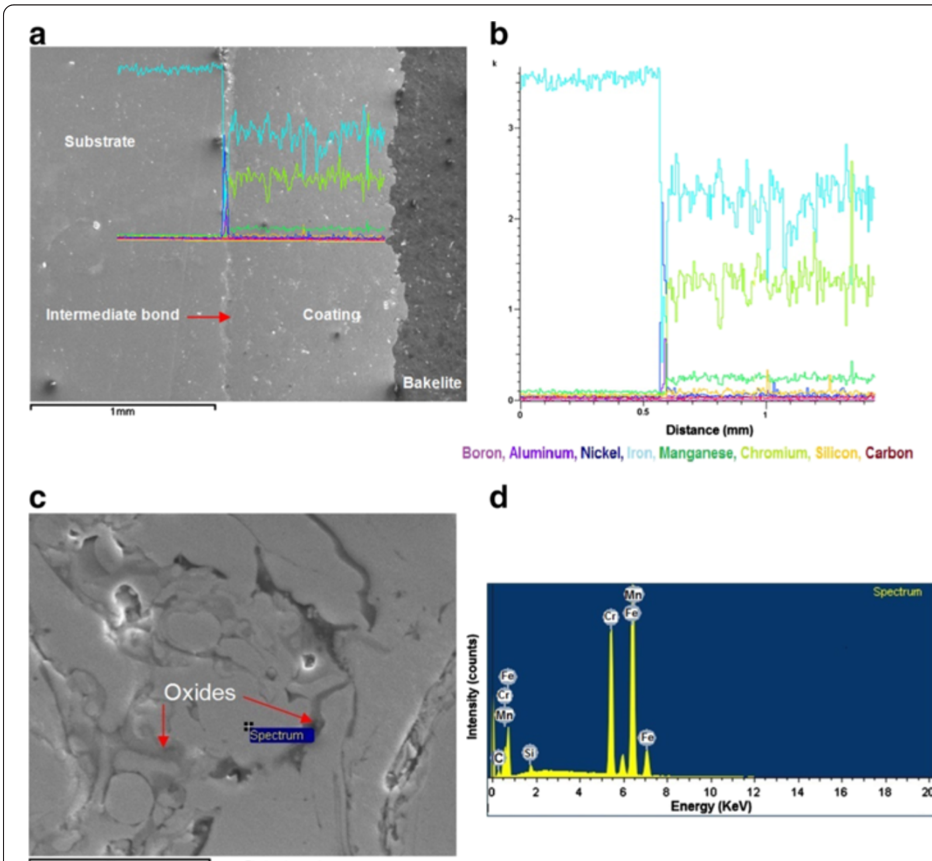

Figure 1 Presence of microcracks, porosity, and oxides (c) imaged by SEM. (a) cross-section of coating layer. Line **(b)** and point **(d)** analysis by EDS spectra reveal the element presence. Condition 1.

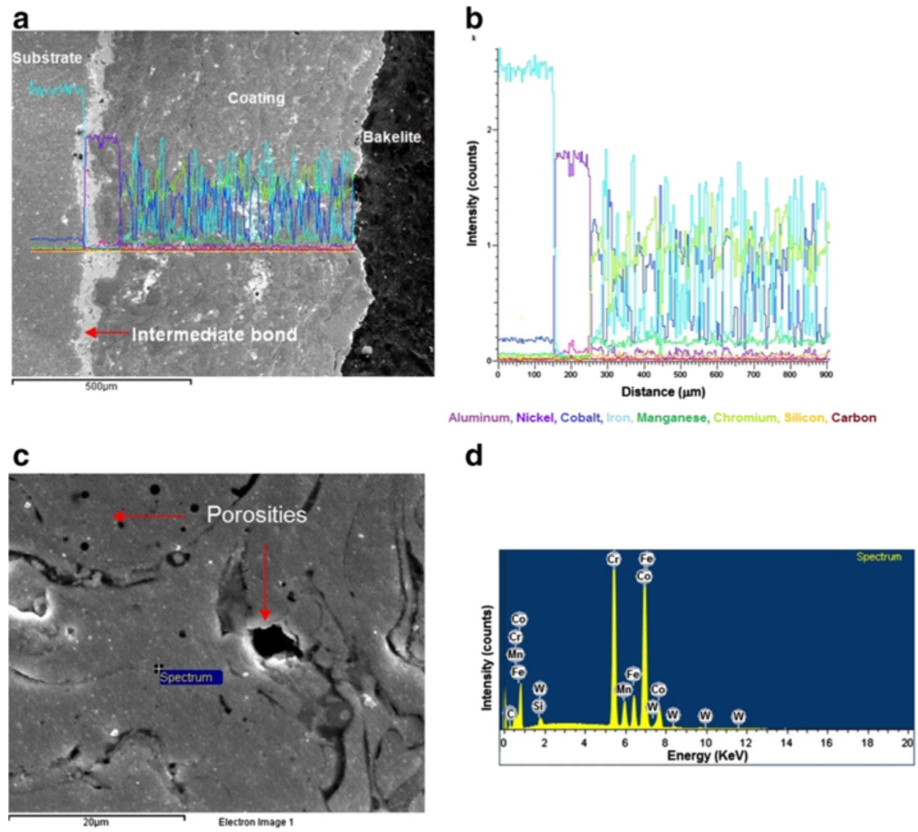

Figure 2 SEM micrographs: presence of microcracks, porosity (c), and oxide. (a) cross-section of coating layer. EDS spectra: line **(b)** and point **(d)** analysis. Condition 2.

particles on impact. The short cooling times, as well as the differences of temperature, size, shape and velocity of particles do not ensure the same deposition conditions for all particles. Less amount of porosity was obtained by electric arc of thermal spray process for all conditions, Figure 2c. This result is in agreement with some other authors [13,14] who found as low as 0.2% of porosity in electric process. Generally, the porosity of thermal spray coatings is typically inferior than 5% of total volume, however, this flaw affects the heat transfer of certain mechanical component [15] being, in this application, very important. The retention of some unmelted and/or resolidified particles can produce deposits with low cohesive strength, especially in the case of "as-sprayed" materials without post-deposition heat treatment or fusion. Besides, high oxide content can be observed in Figure 4a (condition 1). Figure 4b depicts the microcracks at coating of condition 1. These microcracks are flaws of coatings and can generate additional problems such as low adhesion and even low resistance to corrosion [11].

Figures 5, 6, 7 shows the results of adhesion tests of alloy coatings studied. Figure 6 depicts the surface after the adhesion test. The adhesive strength on coatings appears slightly dependent on chemical composition. It is also shown that the adhesive strength on the FeCoCr and FeCoCrNi alloys are a slightly higher than that of other conditions. The aspect of alloy coatings surfaces after adhesion test is shown in Figure 7, summarizing the experimental results.

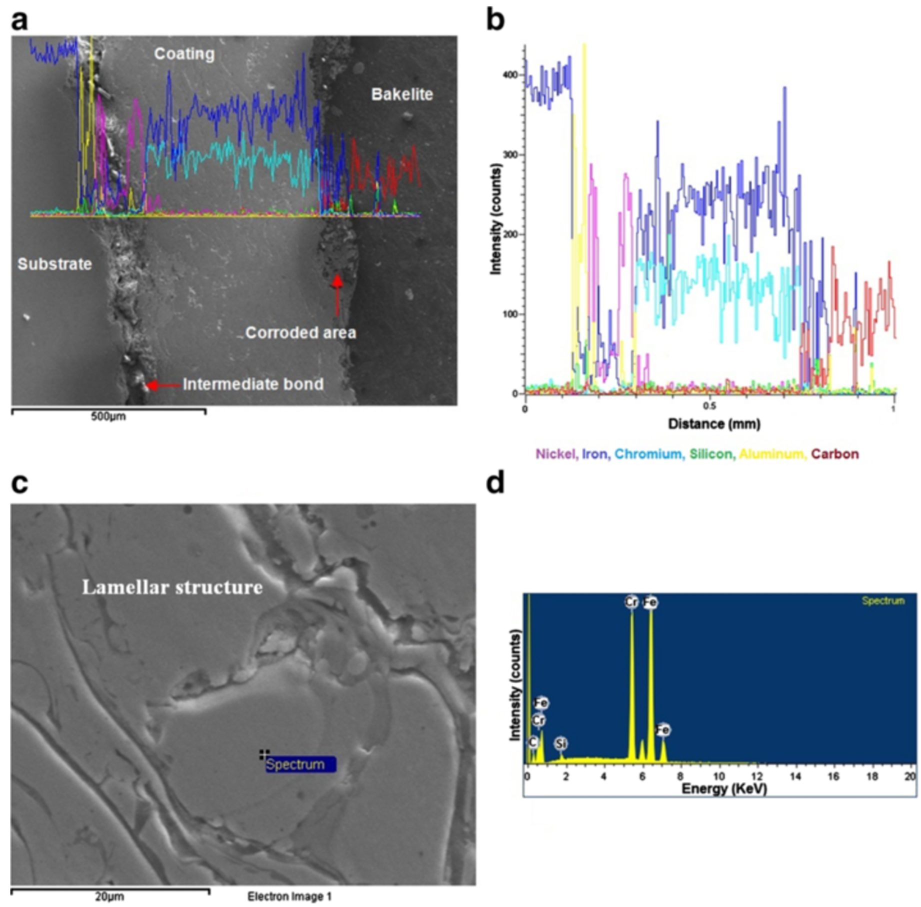

Figure 3 SEM micrographs after salt-spray: a) cross-section of coating layer with intermediate bond and corrosion areas, b) elemental profile, c) lamellar structure, d) local spectrum. Condition 1.

Low porosity produces compact coatings and good substrate-coating bonds. Indeed, close examination of coating–substrate interface of these layers shows neither gaps nor cracks. The absence of flaws is a characteristic of good adhesion of coating-substrate. Moreover, the results of adhesion test, presented in Figure 7, confirmed these characteristics of deposits. The metallic coating presents good adherence of both interfaces (intermediate bond-deposit and intermediate bond-substrate). The observed limits of bond strength ranged from

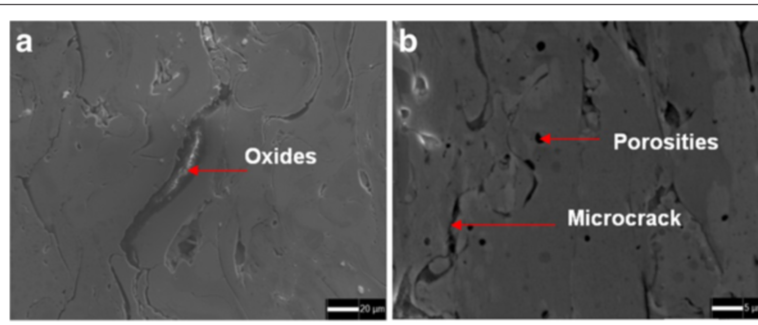

Figure 4 SEM micrographs after salt-spray. Presence of oxides **(a)**; and microcrack and porosity **(b)**. Condition 1.

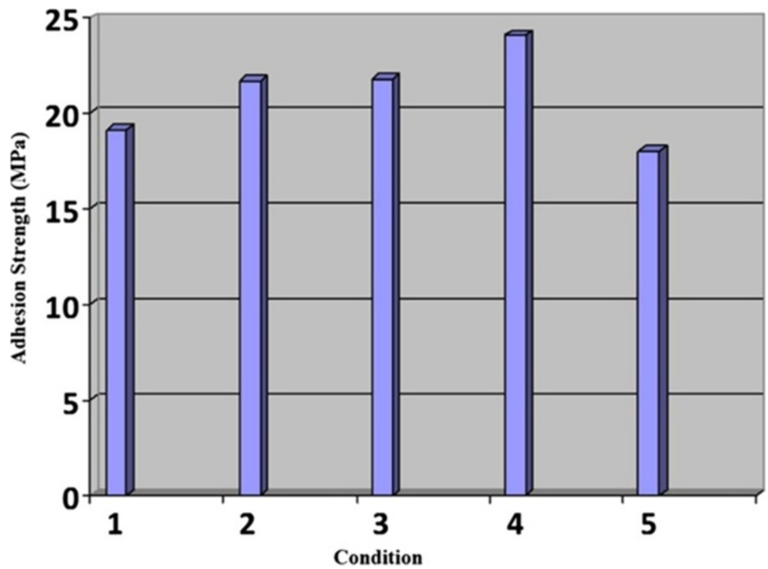

Figure 5 Adhesion strength of studied alloy coatings. Average of two results.

14.0 MPa to 25.3 MPa for the five conditions, with a global average adhesion tensile strength of 19.6 MPa. This strength is considerably higher than the typical mean values obtained with other process by Young et al. [16]. The prevalent mode of fracture of samples is adhesion failure, which is the fracture between the adhesive and the coating. Other modes of fracture more critical (conditions 1 and 4) exist, such as coating-substrate interface, that expose approximately half of the substrate, as shown in Figure 7d (condition 4). However, even this kind of fracture produced high strength, as depicted in Figure 5. Indirect evidence indicated that adhesion is limited both by insufficient particle velocities and thermal energies for coarse particles. The limitation for fine particles is likely caused by the high oxide content.

Sobolev et al. [17] conducted an analysis of several effects that affect the coating adhesion. The oxide content and magnitude of the residual stresses were shown to be

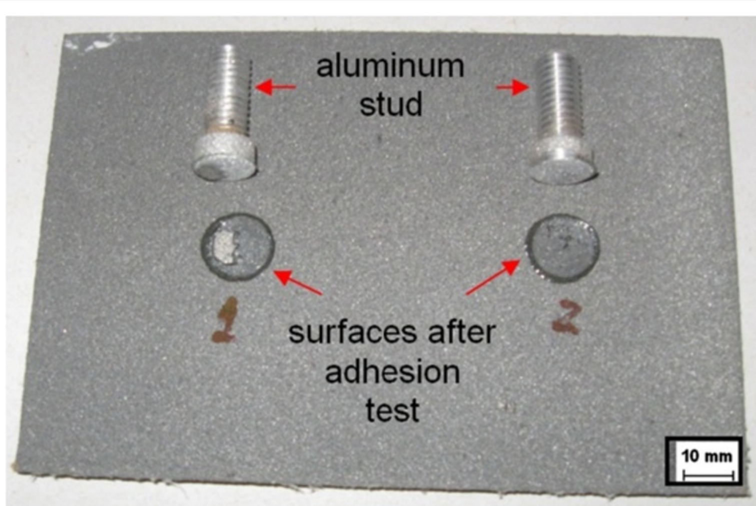

Figure 6 Aspect of samples after adhesion test. Condition 1. Duplicate measurement.

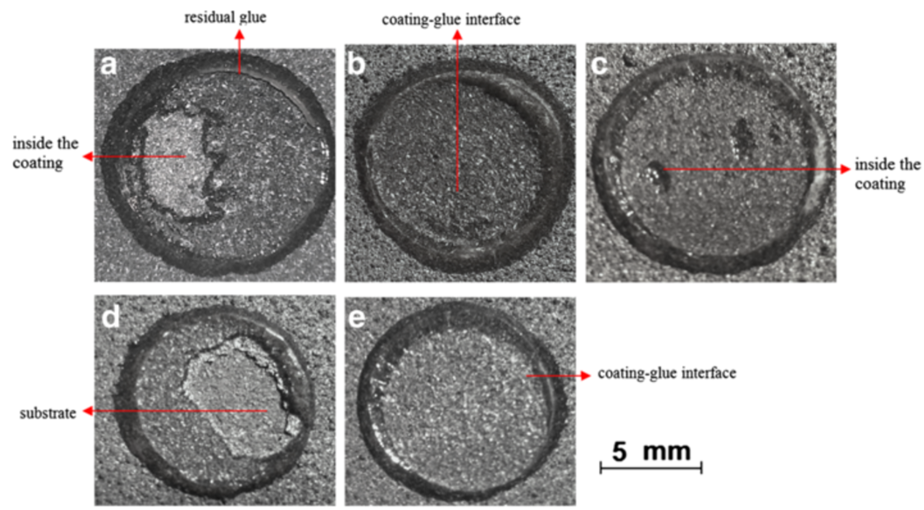

Figure 7 Surfaces after adhesion test. Conditions: a) 1, b) 2, c) 3, d) 4 and e) 5. OM micrographs.

detrimental for adhesion. Furthermore, it was pointed out that the adhesion increases with higher particle velocity and with increasing thermal energy of droplets. Besides, the poor inter-splat interactions found in coarse coatings are related to low velocity of particles. Then, low coating adhesion occurs when this condition is present in thermal spray process.

According to Berndt et al. [18], adhesion can be expressed in various ways. For example,' basic adhesion' represents the interfacial bond and it is the sum of all intermolecular or interatomic interactions. The actual adhesion test, as performed in this paper, is normally called 'practical adhesion'. In this case, it reflects the basic adhesion and the factors that resist to the work required to detach a film or a coating off the substrate.

Coated samples were additionally tested in salt-spray camera for 36 hours at 35°C to obtain their resistance to corrosion in chloride environment. After this exposure, all samples were gently cleaned and observed in optical microscopy to evaluate the fraction of surface that was attacked. The presence of black/brown rusty region was considered as corrosion. Figure 8 shows the aspect of surface for coatings with and without sealant after salt-spray test. In addition, electrochemical corrosion results of these conditions also reveals the positive effects of sealants [9]. The samples with epoxy sealant were attacked at negligible intensity. Therefore, the lack of corrosion of epoxy-coated samples indicates that its presence is important to ensure a high resistance against corrosion, even for noble deposits on carbon steel. Even considering the negligible corrosion intensity, and below the quantification limit of the used method, the microscopy evaluation reveals that condition 2 exhibited the lowest corroded area. The exposure of samples in aggressive condition of salt-spray is an important screening test for brine environment corrosion performance and the salt-spray exposure was useful to discriminate the corrosion intensity of unsealed samples.

Figure 3(a) shows the cross-section of coating imaged by SEM after salt-spray test. Although the microstructures reveal pores, they are not critical for corrosion resistance because they are small and shallow and do not penetrate deep enough to reach the interface substrate-coating.

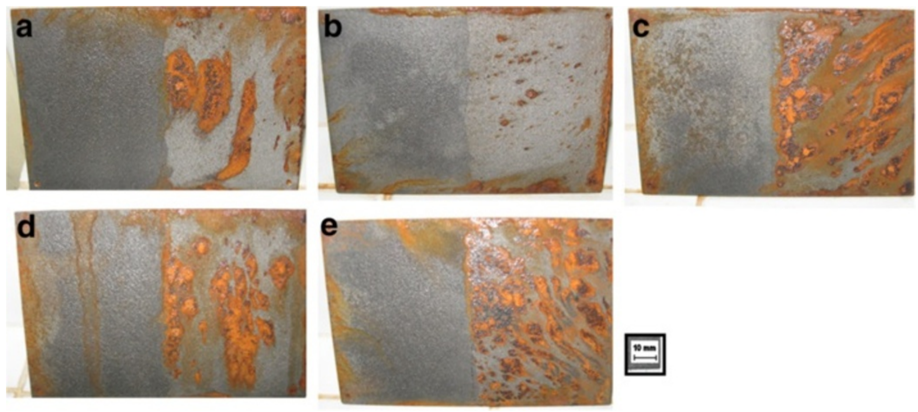

Figure 8 Surfaces of coatings with and without sealant after salt-spray test. Conditions: **a)** 1, **b)** 2, **c)** 3, **d)** 4 and **e)** 5. The left half area of each sample has sealed with epoxy.

Taking into account the global aspects of microstructure, corrosion resistance after salt-spray exposure and adhesion results of thermal spray coatings, the condition 2 presented the best average performance. This coating was deposited with (66.1Fe27.0Cr3.5B1.8Mn + 58.4Co28.8Cr4.9 W3.6Fe1.9Ni) alloy plus (95Ni5Al) intermediate bond on carbon steel substrate.

Salt-spray exposure has long been used as a method to determine the corrosion resistance of materials and its correlation to actual service performance has been extensively discussed [19]. The test is easily performed, being acceptable method for comparing with the behavior of materials and coatings. The observable characteristics of salt-spray tested surface are used to evaluate the uniformity of thickness and degree of porosity of coatings [19,20]. However, no straightforward correlation exist between the corrosion intensity for a given test duration such as the salt-spray camera and the expected life of the coating, since corrosion is a complex process that can be influenced by many external factors.

Conclusions

The adhesive strength of alloy coatings using thermal spray process has been studied and related to chemical composition. Five combinations of wires and intermediate bonds were used. The coatings were characterized by morphological aspects, corrosion and adhesion tests, and the most relevant conclusions are summarized as following:

- The results indicate good uniformity of deposited layer and the presence of small oxides. The observed porosity was very low for the conditions without epoxy sealant.
- The global measured bond strength varied from 14.0 MPa to 25.3 MPa for the five studied conditions, with an average adhesion tensile strength of 19.6 MPa. The prevalent mode of fracture of samples was adhesive failure, which is the fracture between the adhesive and the coating.
- The best adhesive strength was found for FeCoCr alloy coatings. Specifically, the thermal spray coating with (66.1Fe27.0Cr3.5B1.8Mn + 58.4Co28.8Cr4.9 W3.6Fe1.9Ni) deposited alloy plus (95Ni5Al) intermediate bond presented the best average performance. This evaluation takes into account the microstructure, corrosion resistance after salt-spray exposure and adhesion aspects.

- The samples sealed with epoxy presented a high resistance against corrosion.
- The metallic coatings deposited on carbon steels produced a mechanically strong layer with anti-corrosion properties in aggressive marine environments.

Competing interests
The authors declare that they have no competing interests.

Authors' contributions
FJ carried out the coatings applications studies, participated in the assessment of microstructural morphology and analysis and interpretation of data. VR carried out of samples and salt-spray test preparation and have made substantial contributions to conception and design. IN participated in the design of the study and have been involved in drafting the manuscript or revising it critically for important intellectual content. HR conceived of the study, and participated in its design and coordination and helped to draft the manuscript and have given final approval of the version to be published. All authors read and approved the final manuscript.

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