IN SITU DEVELOPMENT OF Fe-Al INTERMETALLICS ON CARBON STEEL SURFACES THROUGH APPLICATION OF MIXED IRON AND ALUMINUM POWDERS BY THERMAL SPRAYING

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Abstract. *Fe-Al intermetallic compounds combine important features such as low density, good mechanical resistance and good resistance to corrosion. Processes currently known as capable of achieving Fe-Al intermetallic compounds are either not feasible for use in the field or are very costly - or both. For this reason, the oil industry which experiences considerable losses related to naphthenic acid corrosion, as well as many other segments of the productive sector, have shown interest in the development of new technologies for the in situ achievement of Fe-Al intermetallics. This study investigates the application of a mixture of iron and aluminum powders in the ratios of 10Al90Fe, 15Al85Fe and 20Al80Fe, onto carbon steel substrates through thermal spraying the oxyacetilenic flame and coatings qualified through bend test. These coatings were analyzed through the use of optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). In all the specimens, the formation of Fe-Al intermetallic compounds was verified during the process of coating deposition. Through SEM and EDS, test specimen - with a 20Al80Fe coating subjected to further heat treatment during one hour in furnaces at 700 ºC and at 900ºC - were also assessed. In this case, aside from lamellar formation, vertical columns of Fe-Al intermetallics were also verified. Thus, this study concludes that it is possible to form Fe-Al intermetallics through thermal spraying of mixtures of iron and aluminum powders onto carbon steel substrates without re-fusion or any further heat treatment as well as it is possible to achieve vertical columns of Fe-Al intermetallic by subjecting these coatings to further heat treatment. However, improvements to this process are still required for intermetallic compounds to develop in a homogeneously and steady fashion, to be effectively used in the oil industry and other industries in need of carbon steel corrosion control.*

Keywords: *Thermal Spray. Fe-Al Intermetallics. Corrosion Control.*

1. INTRODUCTION

Intermetallic compounds are materials consisting of an alloy of phases formed by two or more metallic elements, where atoms of one phase occupy specific points in the crystalline network of the other phase. Some compounds, especially those based on Aluminum and Silicon, present interesting combinations of characteristics such as low density, good mechanical resistance and good resistance to corrosion (Correa, 1990).

Many segments in the scientific environment and productive sector have expressed interest in the development of processes to achieve intermetallic compounds. For the oil industry, which experiences losses related to naphthenic corrosion in piping and oxidative corrosion in structures, it is very important to consider the coating of steel surfaces with Fe-Al intermetallic compounds that prove to reduce the corrosion rate of steel used in oil refining with high naphthenic acidity rate and which, therefore, increase the life cycle of facilities and decrease their final cost (Correa, 1990).

Besides application in the chemical industry, Fe-Al intermetallic compounds – since they show good resistance to oxidation – are also used in various other applications such as, for example, gas exhaustion systems in automotive engines, thermal turbines, heat exchangers and other industrial compounds.

Presently, various processes for the achievement of Fe-Al intermetallic compounds are known. Paredes (1998) demonstrated that it is possible to obtain diffusion of aluminum on steel during thermal spraying. Capra (2005) obtained in laboratory the formation of Fe-Al intermetallic compounds through thermal spraying of aluminum with thermal treatment and/or further refusion on the coated surface, in special furnaces, according to rigorously controlled parameters. However, the necessity of further treatments is a limiting factor to the use of this process in the field.

On the other hand, alonized steel, considered to be a point of reference in the comparison of results from other processes (Paredes et al., 2002), has a high cost and its manufacture in the field is unfeasible.

Silvério et al. (2003) obtained excellent results in the formation of Fe-Al intermetallics from the deposition of iron and aluminum powders through the Plasma Transferred Arc process (PTA).

According to Sampson (1997), in Thermal Spray processes (TS), deposition materials are melted or heated with a heat source generated in the nozzle of an appropriate pistol through gas combustion, electric arc or by plasma.

Immediately after fusion, the finely atomized material is accelerated by a transportation gas under pressure and launched against the surface to be coated, reaching it in a melted or semi-melted state.

Dorfman (2002) describes that, when striking the surface, particles get deformed, fragmented and adherent to the basis material and, subsequently, to the existing particles, thus giving origin to coating layers with typical structure, different from any other metallurgical format. These layers are composed of small deformed particles laid in parallel to the substrate, with typically lamellar structure containing oxides, porosities and empty spaces.

Flame Spray (FS) is the thermal spraying process that uses heat generated by combustion of a mixture of acetylene and oxygen (C_2H_2 + O_2) in the nozzle of the pistol. This heat is capable of melting the material to be coated; subsequently, a transportation gas jet atomizes the melted metal, launching it at high speed onto the substrate. The transportation gas is usually compressed air but an inert gas can also be used, with the advantage of reducing the presence of oxides. Compressed air is also used to cool down the pistol nozzle.

When the coating material used is in powder form, the powder is usually charged into the pistol through a gaseous media (nitrogen), where particles have their speed controlled by the carrier gas; at the moment of contact with the flame, they promptly melt and the transportation gas jet is projected onto the substrate (Lima e Trevisan, 1990).

After being deposited, coatings can be heated with the help of blowtorches or furnaces to melt or diffuse the deposited layer and reach the desired densification and adherence.

In this scenario it becomes evident that intermetallic Fe-Al coatings are a good protection for carbon steel but methods currently in use are expensive and/or unfeasible for field work.

Solving this problem implies coating carbon steel with intermetallic Fe-Al using more economic, feasible processes both in industries and in the field.

Therefore, this paper proposes:

- To develop, in situ, Fe-Al intermetallics using the process of powder thermal spraying with acetylenic flame and no further heat treatment, and different mixtures of iron and aluminum powder as coating material.
- To perform a preliminary observation of these coatings when they are subjected to further heat treatments. The proceedings of the COBEM 2011 will be published in the proceedings CD-ROM, in Adobe™ pdf format.

2. METHODOLOGY

During the preparation of coating materials, iron and aluminum powders, still kept separate, were previously dehydrated in a kiln at 110°C for a minimum period of 24 hours. Subsequently, they were sifted through #250 and #325 screen meshes of a vibrating screen at ¾ of total intensity, during approximately 12 minutes. Once sifted, only the powder retained in the #325 screen mesh was used, thus ensuring the desired granulometry with particles ranging between 44 μm and 63 μm.

Based on these preliminary tests, three different mixtures of iron and aluminum powders were prepared with the following ratios:

- 10% aluminum and 90% iron (10Al90Fe);
- 15% aluminum and 85% iron (15Al85Fe);
- 20% aluminum and 80% iron (20Al80Fe).

Each proportion of iron and aluminum powders was mixed in a metallic mixing recipient of the Y type, always clean and dry, rotated in a lathe at 50 rpm, for 2 hours.

The iron and aluminum powder mixtures were then kept in glass recipients and dehydrated in a kiln at 110°C for a minimum period of 24 hours. After this procedure, the recipients holding the mixtures were kept in the kiln at 50 ºC to remain dry until the moment of its use in the thermal spraying process.

Commercial iron and aluminum powders were used, with minimum purity levels of 98% and 99%, respectively.

Two test specimens were sprinkled for each powder mixture ratio onto substrates of an ABNT 1020 steel plate with size 90 mm x 50 mm x 3 mm, called as follows:

- Test specimens 1A and 1B for mixture 15Al85Fe;
- Test specimens 2A and 2B for mixture 20Al80Fe;
- Test specimens 3A and 3B for mixture 10Al90Fe.

Before the coating application, substrates underwent the recommended process of cleaning and surface roughness required for coating adherence. Therefore, abrasive sandblasting was performed with white aluminum oxide of granulometry 36 / Alundum 38 A, at a pressure of 100 psi and approximate distance of 100 mm. These procedures allowed all substrates to achieve a Sa3 cleaning degree, according to NACE RMN – 01/70 Standard. The equipment used in this operation was a sandblasting cabin of the CMV brand, model 65 9075.

Roughness measurement of the sandblasted surfaces to be sprinkled was performed by scanning in five different positions, through a Mitutoyo portable roughness tester with mechanical detector, model SJ-201.

Under the same conditions, nine ABNT 1020 steel plates sized 75 mm x 50 mm x 1.25 mm were also prepared as specimens for adherence tests through the bending test with the purpose of qualifying process parameters with regard to coating adherence to the substrate.

Once substrates and powder mixtures were prepared, the specimens were coated through a pistol (6P-II model) and a powder feeding unit (5MP model), both manufactured by Sulzer Metco.

After being sprinkled, the specimens were subjected to bending tests under the following conditions: knife diameter - 13 mm, support diameter - 32 mm, distance between supports - 22 mm and bending angle of 180º.

After results obtained with bending tests, the following parameters were defined for the process: oxygen flow - 40 m³/h, acetylene flow - 35 m³/h, nitrogen flow - 15 m³/h, nitrogen pressure – 40 psig, compressed air pressure – 60 psi, powder feed rate – 30 g/min, spray distance between pistol and substrate – 100 mm, speed of advance of approximately 10 mm/s, 4 passes, substrate pre-heating - 120°C. In order to verify the average thickness of the coatings, two measurements using a digital thickness caliper were made of each coated plate, with values ranging between 150 µm and 200 µm.

First, test specimens 1A and 1B were sprinkled with powder composed of 15% aluminum and 85% iron. Then, test specimens 2A and 2B were sprinkled with powder composed of 20% aluminum and 80% iron. Finally, test specimens 3A and 3B were sprinkled with powder composed of 10% aluminum and 90% iron.

For analysis of the results, test specimens were transversally cut in relation to the sprinkled surface, embedded in Bakelite and sanded with a polishing machine with 220, 320, 400, 600 and 1200 sandpaper grits, successively, then polished with alumina in wet felt.

The micro-structural characterization of the test specimens was obtained through optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The equipment used was an Olympus BX 51M microscope with a digital camera for image acquisition and a Philips XL Scanning Electronic Microscope.

In order to obtain images from the optical microscope, polished test specimens were attacked with 2% Nital reagent for 20 seconds.

In order to observe intermetallic Fe-Al coatings subjected to further heat treatment, other test specimens were prepared following the same previous procedures. However, the powder feed rate was reduced to 25 g/min and the number of passes was raised to five. Only the 20Al80Fe ratio was adopted during the observation. To avoid Bakelite contamination, these specimens did not undergo embedding. Therefore, it was not possible to view it with the SEM in addition to the image of the coating's transversal section, a top view of the coated surface.

3. RESULTS AND DISCUSSION

3.1 Micro-structural Analysis of 10Al90Fe Coatings

Observations were made through OM, SEM and EDS of specimens with coating material composed of a powder mixture with 10% aluminum and 90% iron in its weight.

Fig. 1 shows an image obtained through OM where, in the coating layer appearing between the Bakelite and substrate, the presence of 'pancakes' (typical thermal spray formation) can be observed, composed of aluminum, iron and intermetallic Fe-Al.

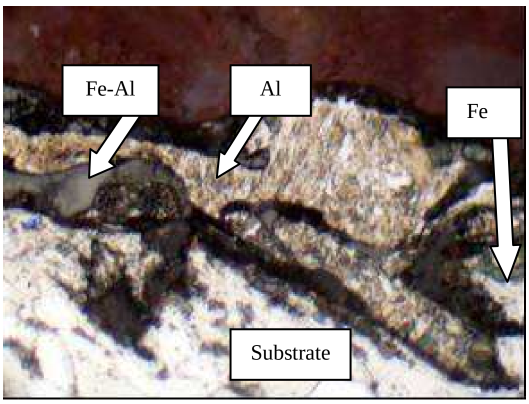


Figure 1 - 10Al90Fe coating and intermetallic Fe-Al formed – OM, 1000x amplification.

Fig. 2 presents an image obtained through SEM where the presence of iron and aluminum not diffused with formed intermetallic Fe-Al can be observed in the coating layer.

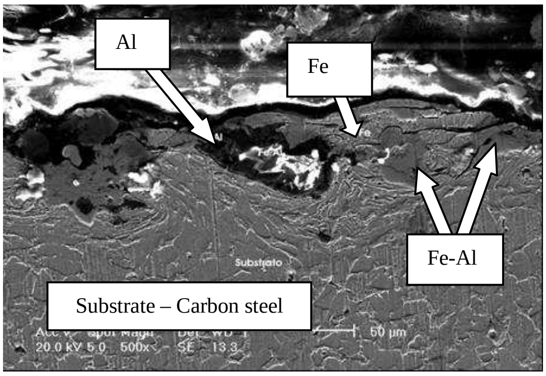


Figure 2 - 10Al90Fe coating and intermetallic Fe-Al formed – SEM, 500x amplification.

The EDS view relative to the point indicated in Fig. 2 by the presence of intermetallic Fe-Al is presented in Fig. 3.

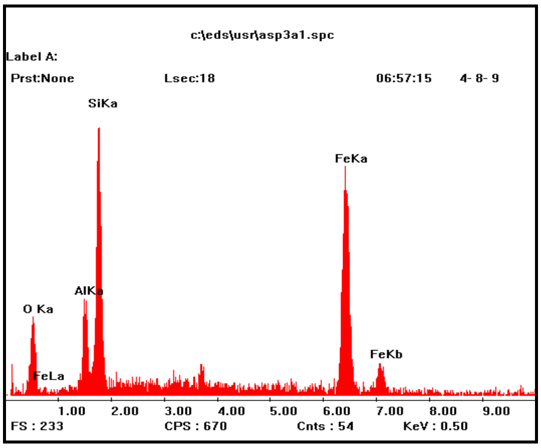


Figure 3 – EDS of coated specimen with 10Al90Fe.

At the focused point, atomic percentages of the elements found were: 37% Fe, 12% Al, 27% Si, 24% O. These results confirm the formation of intermetallic Fe-Al viewed through OM and SEM, as well as oxides and pores typically present in coatings applied by thermal spray. The presence of silicon was explained by the existence of sandpaper waste fouling, later found in this sample.

3.2 Micro-structural Analysis of 15Al85Fe Coatings

Views through OM, SEM and EDS of samples with coating material was a powder mixture composed of, by weight, of 15% aluminum and 85% iron.

In the coating presented in Fig. 4, the typical aspect of iron, aluminum and Fe-Al intermetallics can be observed. In this image, intermetallic Fe-Al can be observed in shades of grey evidenced by white arrows.

Fig. 5 presents an image obtained through SEM where the presence of iron and aluminum not diffused in conjunction with intermetallic Fe-Al formed can be observed in the coating layer.

The EDS viewing relative to the point indicated in Fig. 5 by the presence of intermetallic Fe-Al, is presented in Fig. 6.

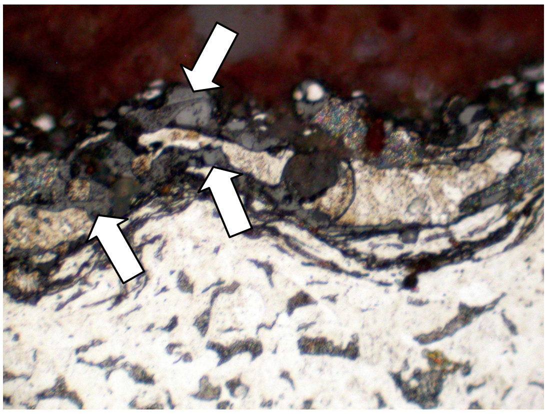


Figure 4: Intermetallic Fe-Al formed in 15Al85Fe coating – OM (500x amplification).

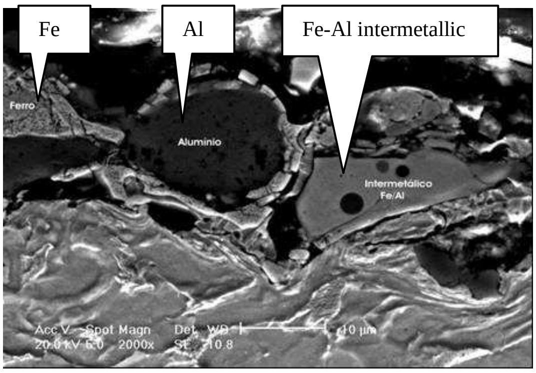


Figure 5: Demonstration through SEM (2000x), view of intermetallic Fe-Al formed in 15Al85Fe coating.

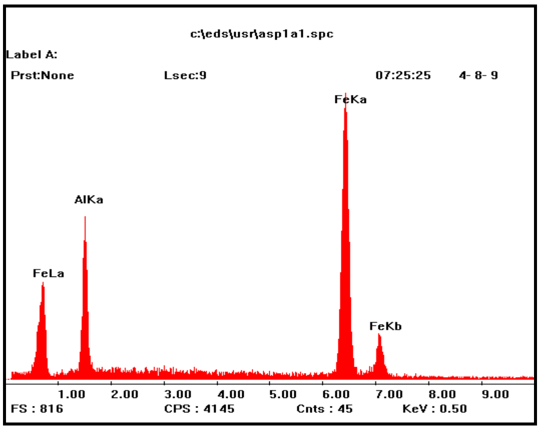


Figure 6 – EDS in sample coated with 15Al85Fe.

On the analyzed point, atomic percentages of elements found were: 68% Fe and 32% Al. These results confirmed the formation of intermetallic Fe-Al viewed through OM and SEM. Considering the percentage of aluminum, according to the literature, it is possibly the intermetallic FeAl.

3.3 Micro-structural Analysis of 20Al80Fe Coatings

Views through OM, SEM and EDS of samples with coating material made of powders composed by weight of 20% aluminum and 80% iron.

Fig. 7 shows an image obtained through OM where the presence of 'pancakes' formed of aluminum, iron and intermetallic Fe-Al can be observed in the coating layer.

Fig. 8 shows an image obtained through SEM where the presence of non-diffused iron and aluminum in conjunction with the intermetallic Fe-Al formed can be observed in the coating layer.

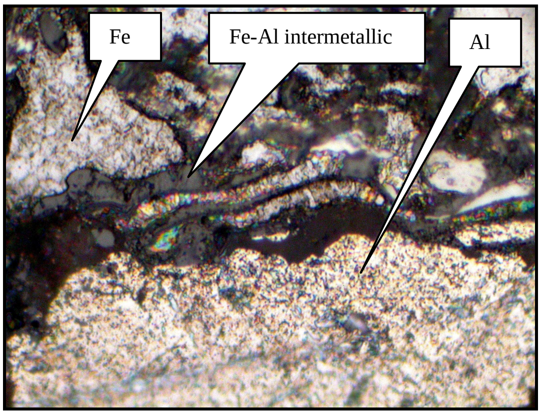


Figure 7 - 20Al80Fe coating and intermetallic Fe-Al formed – OM, 1000x amplification.

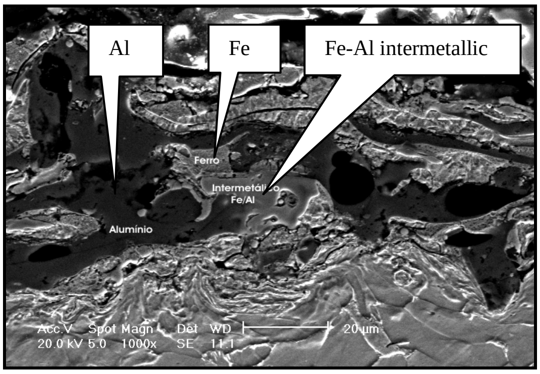


Figure 8: Demonstration in SEM (1000x) of intermetallic Fe-Al formed in 20Al80Fe coating.

The EDS view relative to the point indicated in Fig. 8 by the presence of intermetallic Fe-Al is presented in Fig. 9. In this point analyzed in sample 2A, atomic percentages of elements found were: 59% Al and 41% Fe. These results confirm the formation of intermetallic Fe-Al viewed in OM and SEM and, considering the percentage of aluminum, according to literature, it is possible the intermetallic FeAl3.

In all the samples analyzed through OM and SEM, different intermetallic Fe-Al formed in different quantities, sizes and distributions were viewed.

In samples coated with 20Al80Fe a higher quantity of intermetallic formed was verified, followed by samples coated with 15Al85Fe and, finally, samples coated with 10Al90Fe.

The semi-quantitative results of elements obtained through EDS of which values are presented in Table1 confirm the presence of intermetallic Fe-Al in all the samples. However, different atomic percentages of iron and aluminum found in the samples demonstrate that different intermetallic Fe-Al compounds were formed in the coating process by thermal spray with powder-flame.

By comparing the data presented in Table 1 to data obtained in corresponding literature (Massalski, 1990; Lison, 1998; Guimaraens et al., 2007), it is possible to deduce that the different intermetallic Fe-Al formed present compositions ranging from iron-rich such as, for example, Fe3Al to aluminum-rich such as, for example, Fe2Al7, with intermediary compositions such as FeAl, FeAl2, Fe2Al5 and FeAl3.

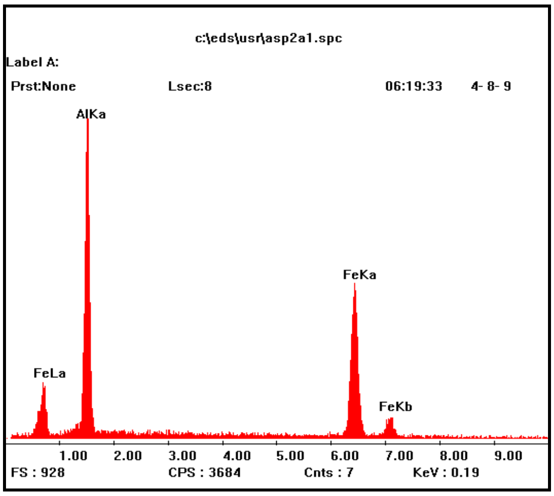


Figure 9 – EDS in sample coated with 20Al80Fe.

Table 1: Semi-quantitative Analysis of Elements.

Sample	Element	Ratio	Weight Percentage	Atomic Percentage
1A	Al	0.085	19	32
	Fe	0.915	81	68
1B Measurement 1	O	0.189	32	46
	Al	0.671	58	50
	Fe	0.141	10	4
1B Measurement 2	Al	0,288	46	66
	Fe	0.712	54	34
2A	Al	0,258	41	59
	Fe	0.742	59	41
2B	Al	0.410	54	71
	Fe	0.590	46	29
3A	O	0.053	11	24
	Si	0.154	22	27
	Al	0.053	9	12
	Fe	0.740	58	37
3B	No results were obtained.			

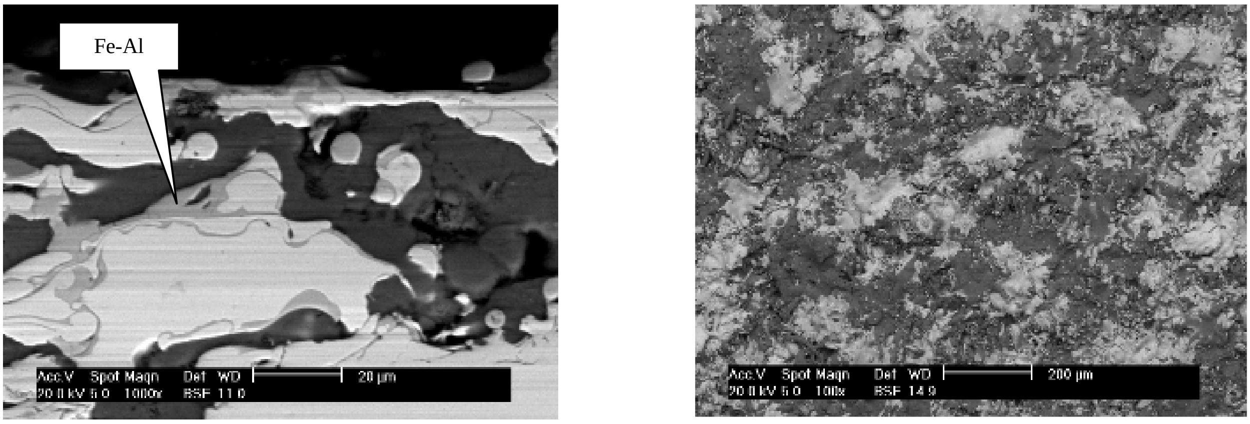
3.4 Micro-structural Analysis of 20Al80Fe Coating with further heat treatment.

Three situations were analyzed in non-embedded test specimens: a) without further heat treatment; b) with further heat treatment in a 900 °C furnace for one hour; c) with further heat treatment in a 900 °C furnace for three hours. SEM images of the transversal section and coating surface were obtained for each of these situations.

In Fig. 10a and 10b, presenting the transversal section and the surface of the 20Al80Fe coating without any further heat treatment, respectively, the existence of intermetallic Fe-Al formed can be observed.

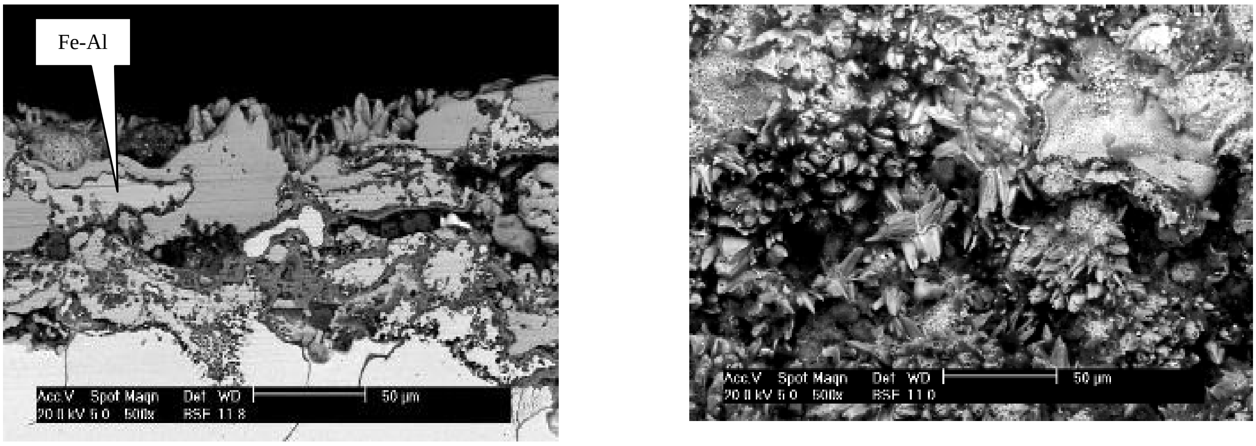
In Fig. 11a and 11b, presenting the transversal section and the surface of the 20Al80Fe coating with further heat treatment in a 900 °C furnace for one hour, the existence of different intermetallic Fe-Al formed can be observed.

In Fig. 12a and 12b, presenting the transversal section and the surface of the 20Al80Fe coating with further heat treatment in a 900 °C furnace for three hours, the existence of different intermetallic Fe-Al formed can be observed.



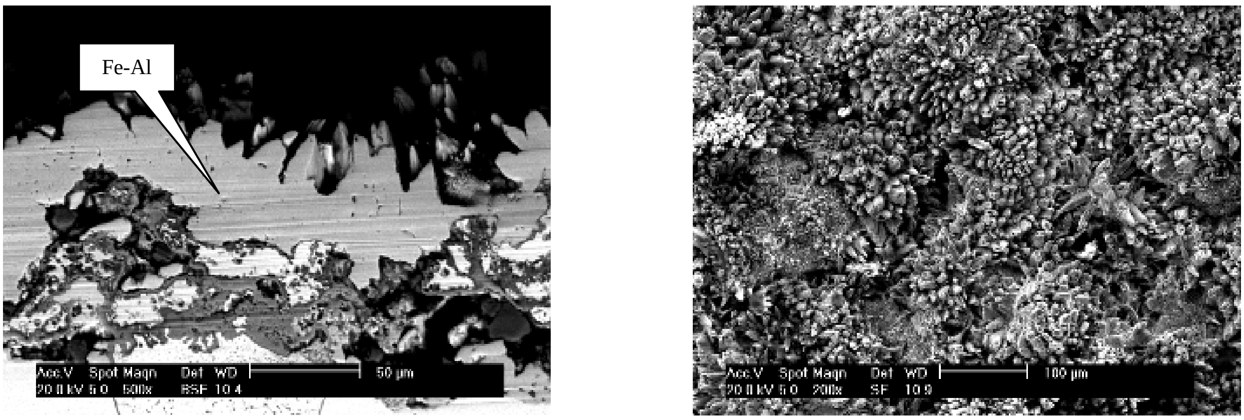
(a) (b)

Figure 10: SEM view of 20Al80Fe coating without any further heat treatment: a) transversal section; b)surface.



(a) (b)

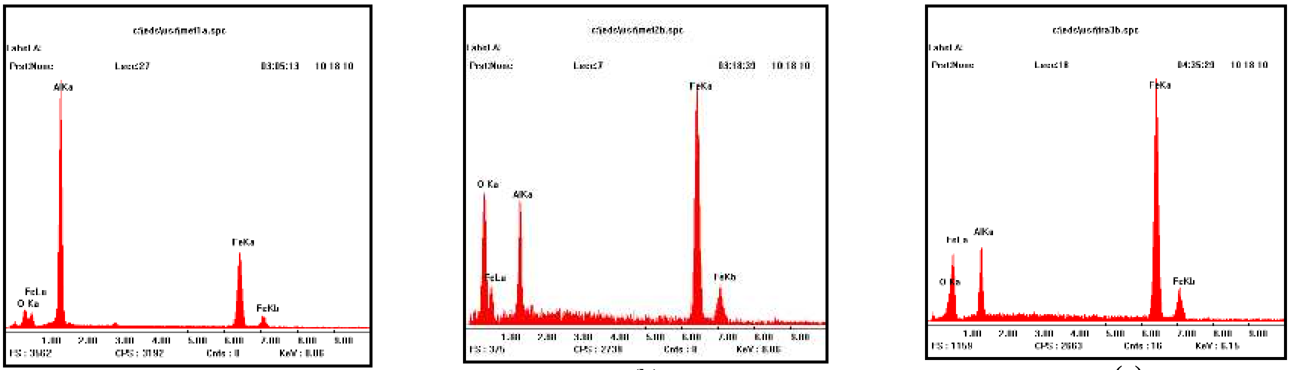
Figure 11: SEM view of 20Al80Fe coating with further heat treatment in a 900 °C furnace for one hour: a) transversal section; b) surface.



(a) (b)

Figure 12: SEM view of 20Al80Fe coating with further heat treatment in a 900 °C furnace for 3 hours: a) transversal section; b) surface.

SEM views obtained in the points indicated in Figs. 10a, 11a and 12a are presented, respectively, in Figs. 13a, 13b and 13c proving the formation of different types of intermetallic Fe-Al and iron and aluminum oxides.



(a) (b) (c)

Figure 13: SEM view of 20Al80Fe coating: a) no heat treatment; b) further heat treatment in a 900 °C furnace for 1 hour; c) further heat treatment in a 900 °C furnace for 3 hours.

4. CONCLUSIONS

Based on micro-structural analyses of the coatings obtained through OM, SEM and EDS, it was concluded that it is possible to obtain in situ, through Thermal Spray with Oxyacetilenic Flame without further re-fusion, the formation of Fe-Al intermetallic compounds onto a carbon steel substrate, if the material deposited is a metallic powder composed of iron and aluminum. Among the different mixture ratios tested, the formation of intermetallic Fe-Al was the most intense when the 20Al80Fe coating was used. Second, in terms of intensity of intermetallic Fe-Al formation we have the 15Al85Fe mixture and, third, the 10Al90Fe mixture.

In the sprinkled layers, in conjunction with intermetallic Fe-Al formed in a discontinuous and non-homogeneous fashion, non-diffused iron and aluminum are present, as well as some oxides and pores.

Further heat treatment intensifies the formation of intermetallic Fe-Al and leads to a change in the coating's surface texture, generating sharp elevations.

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6. REFERENCES

Capra, A. R., 2005, "Desenvolvimento de Intermetálicos Fe-Al através de Aspersão Térmica e Tratamento Posterior". Dissertation, 137 p., Curitiba, Brasil.

Correa, L. A., 1990, "Resistência da liga Ferro-Alumínio à corrosão pelo ácido naftênico". Boletim Técnico Petrobrás, Jan/Mar Rio de Janeiro, Brasil, Vol. 33, pp.73-79.

Dorfman, M. R., 2002, "Thermal Spray". Advanced Materials & Processes, Vol. 160, n. 10, pp. 66-68.

Guimaraens, E.; Laukant, H.; Glatzel, U., 2007, " Metallurgical characterization of aluminum steel joints joined by laser weld-brazing process using different filler materials and welding parameters". University of Bayreuth, Germany.

Lima, C. C.; Trevisan, R., 2001, "Aspersão Térmica – Fundamentos e Aplicações". Artliber Editora, São Paulo, 1 ed, 148 p.

Lison R., 1998, "Wege zum Stoffschluss über Schweiss und Lötprozesse" – DVS-Verlag GmbH.

Massalski, T. B., 1990, "Binary Alloy Phase Diagrams". Second Edition, v. 1, p. 147.

Paredes, R. S. C., 1998, "Estudo de Revestimentos de Alumínio Depositados por Três Processos de Aspersão Térmica para a Proteção do Aço Contra Corrosão Marinha". These, UFSC.

Paredes R. C.; Rodrigues, R. M. P. H.; Bond, D.; Silva, P. S. C. P.; Lima, D. F. B., 2002, "Comparação da obtenção de Intermetálicos Fe/Al através de Aspersão Térmica com alumínio e Alonização". Anais do 2º Congresso Brasileiro de P&D em Petróleo e Gás. Rio de Janeiro, RJ.

Sampson, E. R., 1997, "Thermal Spray Coatings for Corrosion Protection: Na Overview", Coatings & Linings, Vol. 36, n. 12, pp. 27-29.

Silvério, R. B.; Paredes, R. C.; Oliveira A. S. C. M., 2003, "Iron Aluminide Alloy Development Using Plasma Transferred Arc Coating Process". Proceedings of the 17th Brazilian Congress of Mechanical Engineering, v. CD-ROM, São Paulo, Brasil.

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