EVALUATION OF NiAl ALLOYS USED AS RESISTANT COATING DEPOSITED BY POWDER FLAME SPRAYING

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Abstract. Thermal spray is used to produce coating, when there is a need to elevate the life of parts and systems, and in some cases, may also recover them. To resist in certain conditions such as high temperature, corrosive ambient and mechanical stress is necessary to develop specific alloys to withstand the various service conditions. This article aims to produce and study alloys in situ, during the deposition process, for the development of high temperature resistant coatings, as well as procedures for their application. Different mixtures of NiAl were deposited using Powder Flame Spraying process, on substrates of AISI 304 austenitic steel. It was evaluated the influence of pre and post heating. The sample were submitted to tensile test to measure the adherence. Preliminary results of the analysis obtained by optical microscopy, X-ray diffraction and microhardness of coatings showed high adhesion, low porosity and oxide inclusions.

Keywords*: Flame Spraying, NiAl coatings, Intermetallics.*

1. INTRODUCTION

The NiAl intermetallics are of great interest because of their properties of strength, oxidation and corrosion resistance at high temperatures (Carvalho, 2007). The nickel-aluminum phase diagram shows two stable intermetallic compounds, Ni3Al and NiAl, formed on the nickel-rich end (Tamarin, 2002).These aluminides favor the formation of the α-Al_2O_3, which is a stable oxide and the primary responsible for the protection against oxidation in these alloys (Peng e Wang,2011). One way to increase the materials superficial strength is to change the surface, applying a coating consisting of a nobler material, in order to increase his durability and resistance to an aggressive ambient.(Santos, 2008). These characteristics can be achieved by applying NiAl coatings through the Thermal Spray, n which it is expected that during the deposition process, NiAl intermetallics can be produced (Birks et al., 2006). In this work it was studied the deposition of NiAl coatings by Flame Spray Process, with different procedures, although these are normally applied in the industry by HVOF and Plasma Spray processes, which, in accordance with the literature, resulting in lower porosity and inclusion of oxides, although they are much more expensive, thus achieving good results with the FS process, aided by heat treatment of the substrates, the costs can be reduced (Paredes, d'Amico and Oliveira, 2006). After the substrates were subjected to tensile tests to measure adherence, preliminary results show coatings with high adherence, low porosity and oxide inclusions, furthermore, in the alloys deposited from commercial powder it was found the presence of Ni_3Al and NiAl intermetallics, which have attractive properties at high temperatures.

2. METHODOLOGY

The methodology consisted in the evaluation of the deposition of layers of the commercial alloy Diamalloy 4008 NS (95%Ni5%Al) (Sulzer,2010), and of the prepared mixtures with 73%Ni27%Al and 83%Ni17%Al,both with grain size 45µm deposited through Flame Spray process in substrates of AISI 304L with 1.3 mm thick. The deposition parameters are found in Table I.

Table I – Temperature and Identification of the Substrates AISI 304L for Coatings Deposited by Flame Spray Process

Conditions / Alloys	Substrate in Room Temperature	Substrate with Pre-Heating (200°C) for 2 min	Substrate with Pre and Post-Heating (200°C) for 2 min
Diamalloy4008NS – 95%Ni5%Al	A1	A2	A3
73%Ni 27%Al	B1	B2	B3
83%Ni 17%Al	C1	C2	C3

2.1 Experimental

For the activities realization were used the following materials and equipment:

- Preparation of Nickel/Aluminum alloys in powder for the metallization: Dryer, Automatic Sieving VIBROTECH CT-025, automatic Y-mixer;

- Grit Blasting: shot-blasting machine of 100 psi; alumina in powder grain size 36/ Alundum 38A;

- Thermal Spray: Cabin of metallization with exhaustion system and removal of dust via the wall with water blade; Thermal Spray machine fabricated by Sulzer Metco, Model 5MPE with 6P-II Thermospray gun and RP5 feeder, and funnel through which passes the powder with constant feeding. The gases used were oxygen, acetylene, nitrogen;

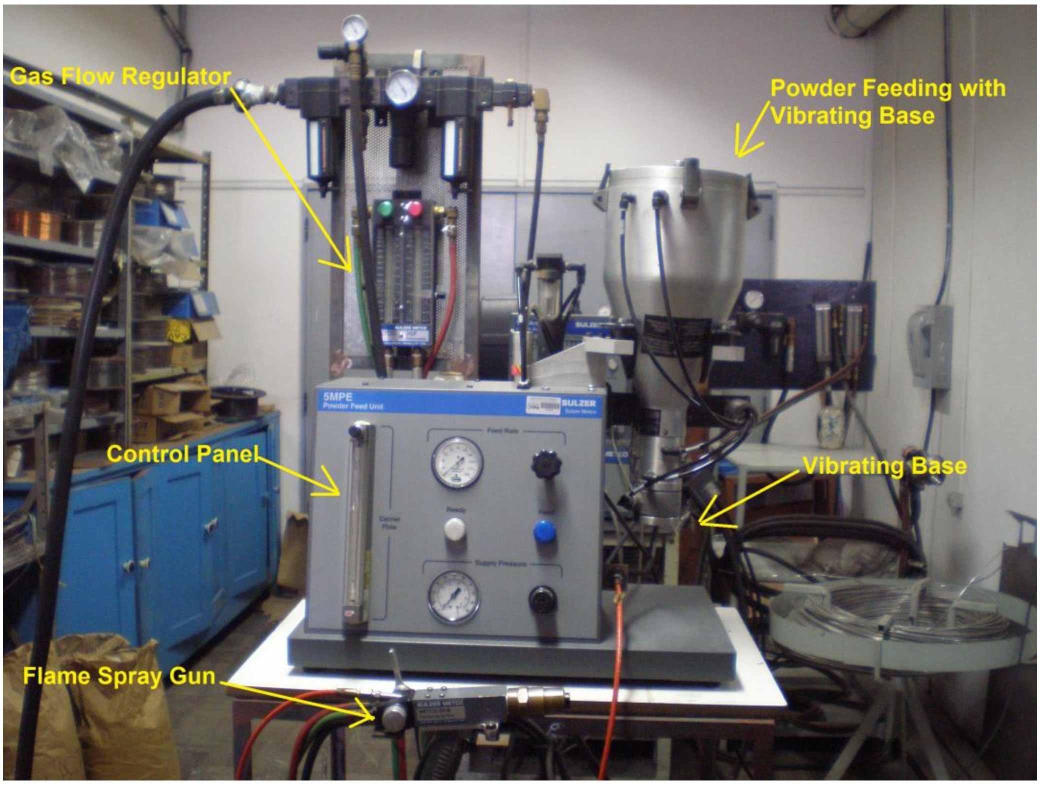

Figure 1 – Thermal Spray equipment - Flame Spray Process - UFPR- LAMATS

- Heating of the Substrates: The substrates were pre and post-heated by the Flame of the Gun without the powder feeding, using a pyrometer to measure the temperature of the substrate;

- Materials for the metallography of the substrates: cutting discs smooth, granulated bakelite for the embedding of the substrates, sandpapers with different grain sizes, polishing cloth for use with diamond paste, diamond paste with grain size 2-4 mm;

- Equipment used for the metallography of the substrates: metallographic cutter, polishing machine, automatic mounting press, metallographic optical microscope Olympus BX51M and digital camera;

- X-ray Difratometry: Shimadzu D7000;

- Hardness Test: Micro Hardness Tester.

- Tensile Test: Instron, model 1467

2.2.1 Experimental Methodology and Thermal Spray Parameters

They were used 18 substrates cylindrical of 1020 carbon steel for the tensile test (Ø25mmx25mm) and another 18 substrates of AISI 304L stainless steel in the form of plates (85x39x1,3mm) to metallographic analysis.

All 36 substrates, initially, suffer grit blasting with Sa3 cleaning. After that, they were metalized with the following parameters, showed in Table II:

Table II – Thermal Spray Parameters

Substrate-Gun distance	200mm
Number of Layers	10
Nitrogen Flow	15 scfh
Oxygen Flow	80 scfh
Acetylene Flow	35 scfh
Nitrogen Pressure	55 psi
Oxygen Pressure	60 psi
Acetylene Pressure	17 psi
Approximate thickness obtained in the coated layer	± 100 µm (plates) ± 300 µm (cylindricals)

The substrates A1, B1 and C1after the grit blasting were metalized. The substrates A2, B2 e C2 were pre heated at 200°C for 2 minutes. The substrates A3, B3 e C3 were pre and post heated at 200°C for 2 minutes. After the deposition, all substrates were protected of environment, placed in an hothouse (at 50 º C), where they remained for at least 24 hours prior to testing and metallography.

2.3 Tests

2.3.1 Tensile Test:

The tensile test was realized in a equipment Instron Model 4467. To unite the specimens it was used an epoxy adhesive Araldite Professional, with a drying time of 12 hours. The specimens metalized were glued in the grit blasted substrate, of equal dimensions, with white aluminum oxide, according to ASTM C-633 and Petrobrás N-2568 (Lima and Guilemany, 2007). It was used an elongation velocity between 0,013mm/s and 0,021mm/s until the rupture moment, and the data of load and rupture tensile were collected.

2.3.2 X-Ray Difratometry (XRD):

After the deposition, the substrates were cut in the dimensions of 1mm wide and 1mm long and analyzed by XRD in a Difatrometry Shimadzu D7000.

2.3.3 Micro Hardness Vickers Tester:

The specimens were embed in a Arotec Pre-30, with dark Bakelite, and then sanded and polished. They were made 5 indentations in each substrate, with no pre-defined spacing, but taking care to make the indentations at different phases, verified by the difference in coloration, as shown in Figure 2. The load applied it was 300g with a dwell time of l5 seconds, the equipment used was the HMV Shimadzu.

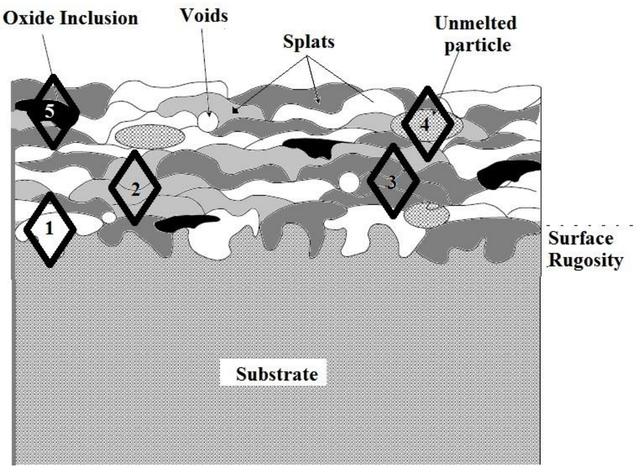

Figure 2 – Schematic drawing of indentations. Adapted from Marques, 2003

3. RESULTS AND DISCUSSION

3.1 Adherence between Substrate and Coating

Table III show the values of the stress rupture and the respective load for each specimen tested. In A1, A2 and A3 the rupture occurred between the lamellae and the stress rupture were lower than B and C alloys.

The coatings pre and post heating show higher values for the stress rupture, this indicates that both the pre and post-heating provide an increasing to the adhesion and adherence to the substrate. In these 3 cases the pre-heating caused an increase in tensile strength of the coatings, however, the post-heating was effective only in the alloy B while in the other alloys, the tensile strength was compromised, probably due to the higher presence of oxides. It is important note that these values are equivalent to coatings deposited by HVOF, which are normally much higher than the values obtained by FS (Pawlowski, 2008). The Figures 3, 4 and 5, present the coating surfaces of the specimen after tensile test.

Table III – Values of Tensile Test

Specimens	Load [kN]	Stress Rupture [MPa]	Rupture	Figures
A1	6,93	13,68	between lamellae	3
A2	8,62	17	between lamellae	
A3	6,73	12,27	between lamellae and interface	
B1	7,97	15,72	between lamellae	4
B2	11,70	23,09	between lamellae	
B3	14,53	28,68	between lamellae and interface	
C1	10,2	20,13	between lamellae and interface	5
C2	14,61	28,84	between lamellae and interface	
C3	11,59	22,88	between lamellae and interface	

A1 A2 A3

Figure 3 – Specimens surface after Tensile Test - A1, A2 and A3 alloys.

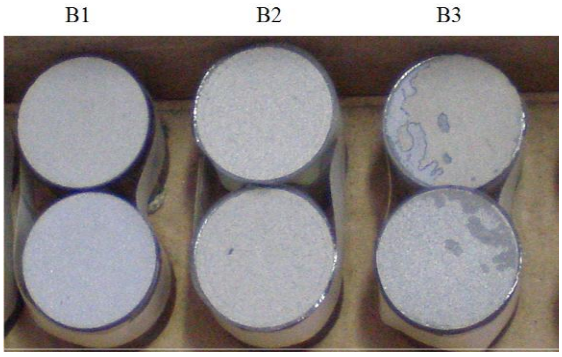

Figure 4 – Specimens surface after Tensile Test - B1, B2 and B3 alloys.

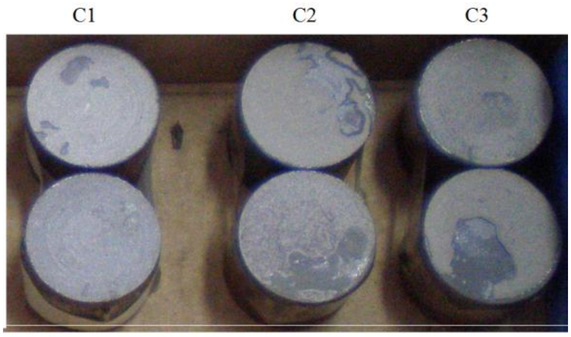

Figure 5 – Specimens surface after Tensile Test - C1, C2 and C3 alloys.

It can be observed yet in samples A3, B3, C1, C2 and C3, that part of the rupture occurred in the interface and part occurred between the lamellae. It denotes the good adherence of the coating; furthermore, maybe the interlamellar rupture occurred due to the inclusions of NiO between the splats.

3.2 Phases Obtained During Flame Spray Process

The Figure 6 presents a comparison of the XRD patterns for the Diamalloy (95%Ni5%Al) deposited in the conditions A1, A2 e A3. According to showed in the difratograma, were found peaks of NiAl and Ni_3Al that confirm the formation of intermetallics. Peaks of NiO were also found

These Nickel aluminides, as previously described, are stable intermetallics and show excellent oxidation resistance at high temperature, inducing to the transformation/formation of a protective oxide layer α-Al_2O_3 when used at temperatures above 800°C(Dong. et al.,2010).

It is noteworthy that the 95%Ni5%Al alloy has suffered a transformation in the deposition process (flame, transport and substrate) for NiAl, Ni_3Al and NiO.

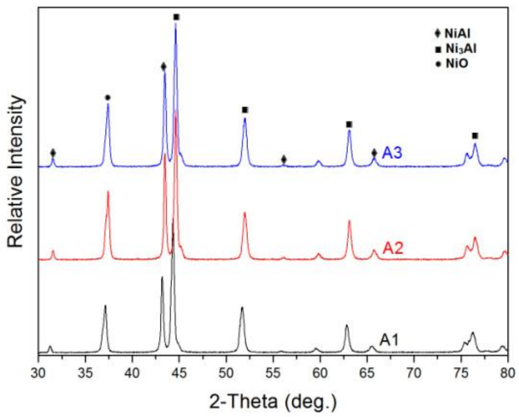

Figure 6. Present phases in specimens A1, A2 and A3.

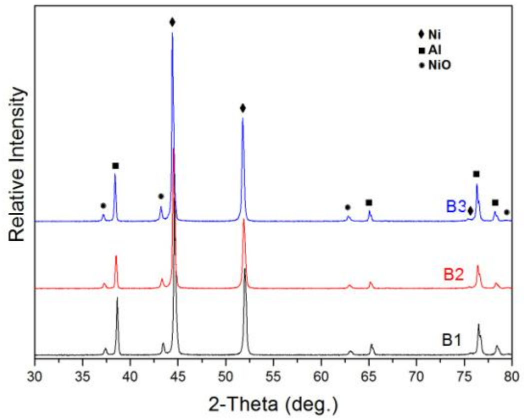

Figure 7. Present phases in specimens B1, B2 and B3.

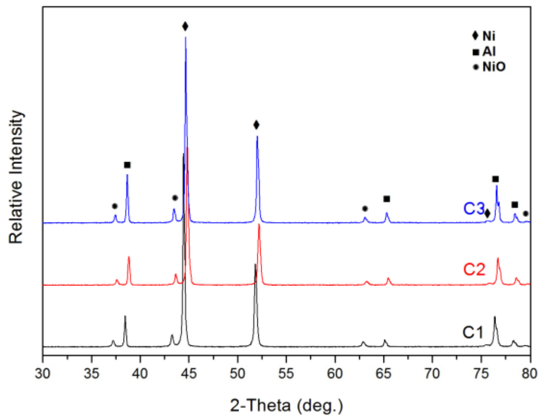

Figure 8. Present phases in specimens C1, C2 and C3.

The Figures 7 and 8 show XRD patterns for the mixtures containing 73%Ni27%Al and 83%Ni17%Al. Both present similar patterns, containing Ni, Al and little peaks of NiO. There wasn't the formation of NiAl intermetallics. It is believed that the formation of NiO, in all cases, occurred during the deposition. It can be perceived that the treatment of pre and post heating didn't interfere in formation of any different phase. The exposure time of the powder in the flame temperature was not sufficient for the occurrence of NiAl and Ni_3Al intermetallic, which as described before, in oxidizing environments form a protective oxide layer of Al_2O_3. The properties of these intermetallics at high temperatures (oxidation resistance, mechanical strength, etc..) are higher than the properties of the pure Ni and Al.

3.3 Micro Hardness of the Coating

Table IV present the average values for the result of micro hardness Vickers in each specimen. The average values are plotted in a graph, in which is also the Standard Deviation.

Table IV – Average Values of Indentations

Specimens	Indentations [$HV^{0,3}$]
A1	174,2
A2	267
A3	192,4
B1	129,18
B2	129
B3	178,2
C1	155,4
C2	132,2
C3	106,34

In the coatings A2, A3 and A1 were found the higher hardness values, according to showed in Figure 9, being $424HV^{0.3}$, $279HV^{0.3}$ e $250HV^{0.3}$, respectively. The XRD analysis revealed that in these specimens there was the formation of NiAl and Ni_3Al, which lead to the conclusion that the indentations that obtained the higher values, they probably were made above these intermetallics. The coatings B1, B2, B3 and C1, C2, C3 have the lower values to the micro hardness, but with a lower standard deviation. The XRD analysis shows that in these substrates were found, Ni and Al, and a small amount of NiO. The peaks of higher hardness in the graph for these coatings probably are attributed to NiO.

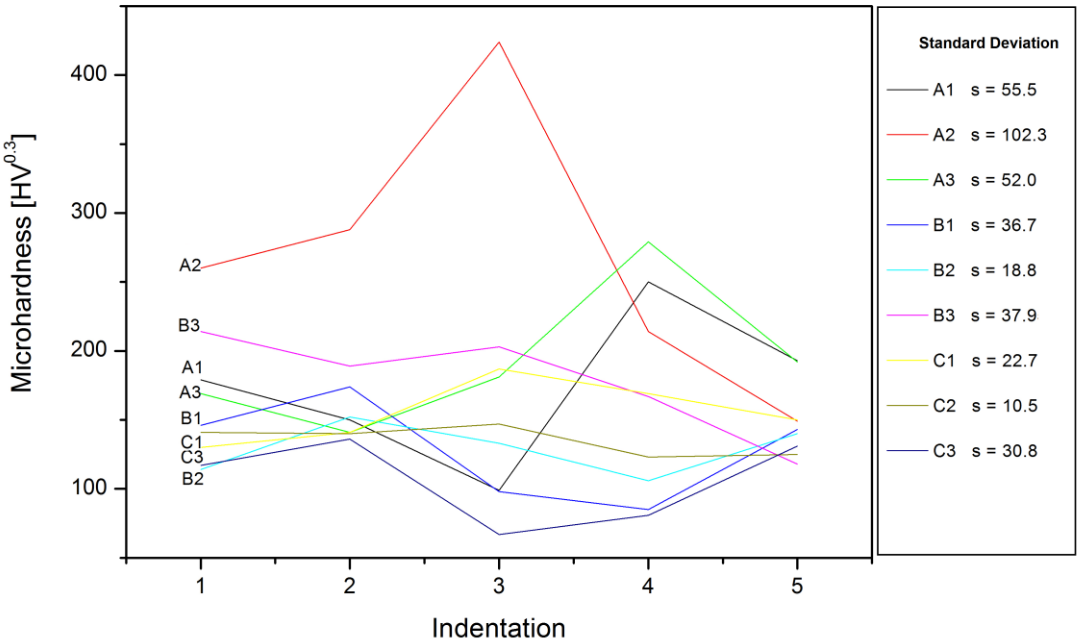

Figure 9 – Graph of Average Values of Micro Hardness

3.4 Microstructure of the Coatings

The Figures 10, 11 and 12 present the optical microscopy of the substrates(cross section in the coated specimen). By comparing the photographs of the samples without heat treatment, those who suffered pre and post-heating, it can be seen that the splats are thinner and more homogeneous in samples A2, A3, B2, B3, C2 and C3, due to the powder feed that is constant and the better wetting on the heated splat/substrate, this is in agreement with literature. (Paredes et al., 2006). It can be noted that there was a coarsening of some grains in the substrates pre and post-heated, forming thicker lamellae. The amount of oxides also increases as seen in Figure 9, but beyond the oxide between the lamella, it is possible to observe a continuous oxide layer that surrounds all the splats. These oxides according to XRD are NiO. The specimens A3 and B2 showed a higher amount of oxides between the layers and this may have influenced in their mode of fracture in adherence test, which occurred between the lamellae, primarily the specimen A3.

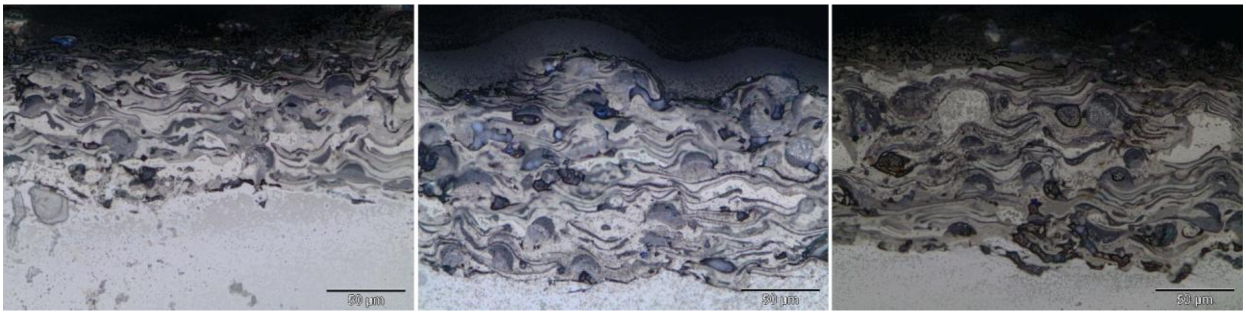

Figure 10 – Optical Microscopy of specimens A1, A2 e A3, Diamalloy 4008NS

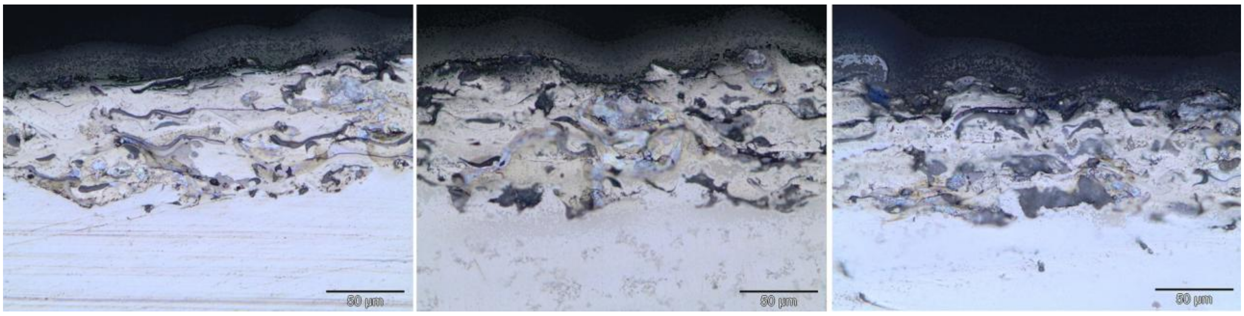

Figure 11 - Optical Microscopy of specimens B1, B2 e B3, 73%Ni27%Al

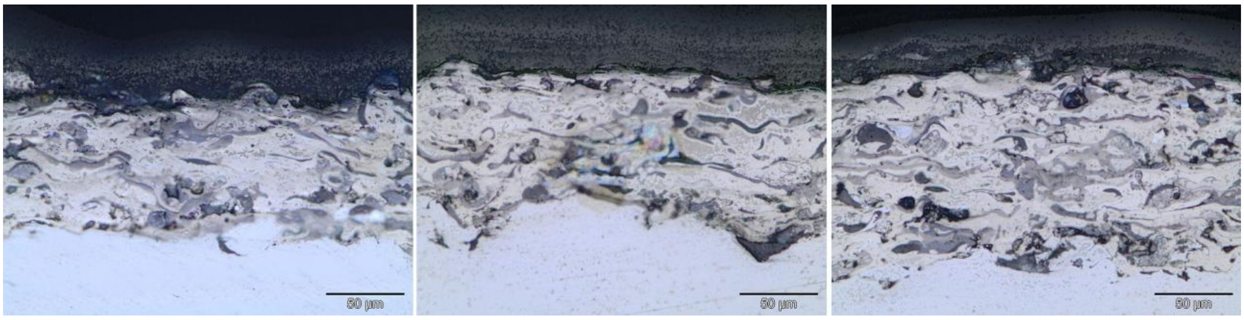

Figure 12 - Optical Microscopy of specimens C1, C2 e C3, 83%Ni17%Al

In the Figures presented above, it is possible to see that the amount of pores is very small, being comparable to a coating deposited by HVOF process (as seen in Cheng and Wang, 2004), showing that these coatings deposited are dense and have low porosity. The literature predicts porosity between 10 and 20% for coatings deposited by FS (Pawlowski, 2008). Observing Figure 10 (commercial alloy Diamalloy), it can be noted that when deposited at room temperature there are few pores, but after the pre and post heating there is an increasing in the amount of oxides. This isn't seen in the Figure 11 (liga 73%Ni27%Al) after pre and post heating, the coating is totally homogeneous with few oxides and without visible porosity. In the case of Figure 12 (83% Ni17% Al), there is a layer very homogeneous and without visible pores, only after the post heating is appearing a few points of oxides.

For calculating the percentage of pores, it was used the software AnalySIS. This software converts the image to a 8 bits gray-scale image, analyzing the desired phases, in this case the pores, by differences in the shades of gray. In each image it was taken the measures of porosity in ten different points, and the medium valor was calculated, according Table V.

Table V – Porosity percentual.

Specimen	Porosity (%)
A1	2.6
A2	3.7
A3	2.7
B1	6.2
B2	4.1
B3	2.7
C1	4.8
C2	2.8
C3	9.1

4. CONCLUSION

With observed data it can be concluded that:

- The analysis of present phases observed in XRD of the samples A1, A2 and A3 show the formation of Ni_3Al intermetallic, NiAl and NiO, due to transformation of 95%Ni5%Al during the deposition process (flame, transport and substrate).
- The time of exposure at the high temperature of the flame, during the deposition, was not sufficient for the formation of α-Al_2O_3, but small peaks of NiO were found.
- In the samples B and C were found Al, Ni and NiO, and there was no formation of any intermetallic. This probably occurs because the temperature of 200°C for the pre and post heating and the time of exposure of the powder to the flame during the deposition process was not sufficient to the formation of intermetallics.
- The highest hardness values were found for the coatings A1, A2 and A3, in which there was formation of NiAl intermetallic.
- The optical microscopy showed that the coatings heat-treated, showed a lamellar structure finer and more homogeneous.
- The commercial alloy Diamalloy had a higher oxidation after suffering heat treatment. The alloy with 73%Ni27%Al showed that even after the pre and post heating there was no appearance of visible pores or oxides. In the alloy with 83% Ni17% Al was observed after the post heating, some points of oxides, but no visible pore.
- Although the results of the tensile test have obtained lower values for the stress rupture than that coating deposited by Plasma Spray, these results are equivalents to HVOF and really high to a coating deposited by FS process.
- The coatings obtained high adherence, low porosity and few oxide inclusions in the mixtures B and C, which makes the FS process viable and economical to the deposition of NiAl coatings, which are normally deposited by another processes.

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