18th IFHTSE CONGRESS
International Federation for Heat Treatment and Surface Engineering
IFHTSE

ANAIS
PROCEEDINGS
ISSN 1516-392X

INFLUENCE OF DILUTION LEVEL ON OXIDATION RESISTANCE OF PLASMA TRANSFERRED ARC NiCrAlC COATINGS[1]

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Abstract

NICRALC coatings processed by Plasma Transferred Arc (PTA) are a new proposal to protect the components exposed to high-temperature oxidation environments. This study evaluated the relationship between the compositional changes in the coatings due to the different levels of dilution, and the morphology and phase constitution of the developing protective oxide scale. Elementary powders were mixed and deposited by PTA welding onto AISI 316L stainless steel, varying current intensity (100 and 130 A). The microstructure of specimens was characterized by means of scanning electron microscopy with local chemical analysis and by X-Ray diffraction. The coatings were subjected to thermo-gravimetric balance (TGA), using temperatures range of 700-1,000 °C during 5 hours. Results revealed the alumina formation, independent on the compositional variation. For low dilution level transient q-alumina was observed, while for high dilution level resulted in a stable a-alumina. This difference was attributed to the complexity of aluminum diffusion in intermetallic structures. The accumulated mass were smaller than other materials employed to high-temperature, such as as-cast NiCrAlC, indicating better oxidation resistance of the tested coatings.

Keywords: Intermetallics; NiCrAlC; Oxidation resistance; PTA.

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[1] *Technical contribution to the 18th IFHTSE Congress - International Federation for Heat Treatment and Surface Engineering, 2010 July 26-30th, Rio de Janeiro, RJ, Brazil.*

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INTRODUCTION

Some specific characteristics are necessary to consider an oxide as protective: (i) be stable; (ii) has a low growth rate, and; (iii) be adherent to substrate.[1]

Components exposed to high-temperature oxidation environments contain alloying elements in order to form Cr_2O_3, Al_2O_3 or SiO_2 oxides.[2-3] At temperatures higher than 900 ºC,[4] the Cr_2O_3 reacts with O_2 forming CrO_3, a volatile oxide. Therefore, at temperatures above 1100°C the films based on Al_2O_3 and SiO_2 may present a superior performance.

Intermetallic systems such as Ni–Al, Co–Al, Nb–Al, Ru–Al and Fe–Cr–Al are useful for operations within 1000–1900°C. During high-temperature oxidation, these materials form protective films based on Al_2O_3. Nickel aluminides have properties similar to cobalt aluminides, but are significantly less expensive.[5]

In 1996 a new class of Intermetallic Coumpoud (IC) named NiCrAlC was proposed by Yoshimura and Goldenstein.[6] The motivation for this development was the similarity between Ni-Cr-C and Fe-Cr-C phase diagrams considering the *liquidus* projections. The alloy design aims to obtain good oxidation and abrasion resistances at high temperatures, constituted in Ni_3Al intermetallic matrix with a dispersion of hard chromium carbides.

These alloys can substitute the Co-based alloys, as well many refractory steels and Ni-based alloys in applications where high-strength at high temperatures must be coupled with good oxidation properties. A previous study[7] showed that the as-cast NiCrAlC presented a good oxidation performance when comparing with Stellite 6 and a ferrous alloy. Unfortunately, NiCrAlC presented problems with casting. An alternative process for this material is the powder metallurgy. Benegra et al.[8] deposited atomized NiCrAlC powder by HVOF. These coatings showed higher corrosion resistance than the AISI 316L substrate in an HCl 5% aqueous solution for 40ºC. Additionally, its abrasion wear rate was much smaller than that described in the literature for as-cast materials with similar composition, and only one order of magnitude higher than as-cast and heat treated (aged) NiCrAlC alloy.

The aim of this study is to evaluate the relationship between the compositional changes in the coatings due to the different levels of dilution, and the morphology and phase constitution of the developing protective oxide scale.

EXPERIMENTAL

Elementary powder mixtures of nickel, aluminum, chromium carbide and iron boride were used to obtain NiCrAlC coatings onto 316 L stainless steel substrate (100 mm X 80 mm X 7 mm). As-received chemical compositions of the substrate and powder materials are presented in Tables 1 and 2, respectively. The nominal composition of mixture coating is presented in Table 3.

Table 1. Chemical composition of the 316L stainless steel (% mass)

C	Mn	P	S	Si	Ni	Cr	Mo	Cu	Al	Co	N
0.017	1.43	0.039	0.028	0.40	10.12	16.62	2.05	0.36	<0.005	0.11	0.06

Table 2. Chemical composition of the as-received elementary powder

Powder	Composition (% mass)	Grain size distribution
Ni	99.8 min	75-250 *μm*
Cr	99.5 min	75-250 *μm*
Al	98 min	75 – 250 *μm*
Iron boride	Fe + 14% B	< 250 *μm*
Chromium carbide	Cr: 87 min, C: 10-13, Si: 0.5 max., Al: 1.0 max., Fe: 0.7 max.	60 – 300 *μm*

Table 3. Nominal composition of the elementary powder mixture (% mass)

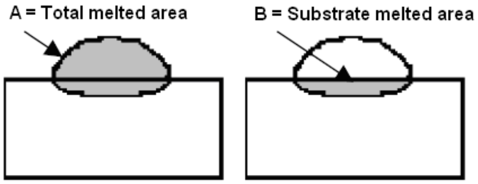
Cr	Al	chromium carbide	iron boride	Ni
10	15	8	0.1	Bal

The plasma transferred arc (PTA) process was conducted varying only the current intensities. Processing parameters for PTA are presented in Table 4.

Table 4. Process parameters for PTA deposition of NICRALC alloys

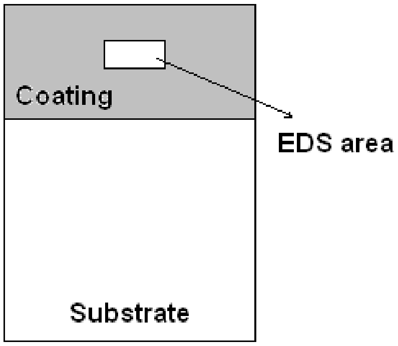
Current Intensities	100 or 130 A
Powder feeding rate	500 g/min
Welding speed	100 mm/min
Distance torch - specimen	10 mm
Plasma gas flux	2 l/min
Protective gas flux	15 l/min
Feeding gas flux	2 l/min

The quality of surfaces was visually evaluated, with respect to the presence of porosities and cracks. Dilution levels (d) were determined at the cross-sections of the coatings by means of: (i) quantitative metallography, which was used to determine the area ratio, as shown in Fig. 1, and (ii) iron content methodology, using semi-quantitative Energy Dispersion Spectroscopy (EDS) analysis of the iron profile (Fig. 2).



$$d_{area} = \frac{\text{Substrate melted area}}{\text{Total melted area}} * 100 = \frac{B}{A+B}$$

Figure 1. Dilution levels determined by the quantitative metallography.



$$d_{\%Fe} = \frac{\%Fe_{Final} - \%Fe_{Inicial}}{\%Fe_{Substrate}}$$

Figure 2. Dilution levels determined by the iron content [citar yaedu].

The microstructures were revealed using scanning electron microscopy (SEM).

Oxidation tests were conducted in a Shimadzu 50 thermo-gravimetric balance (TGA), using temperatures range of 700-1,000 °C. The oxidation test parameters were: heating rates of 20°C.min^{-1}, 20 mL.min^{-1} flow of synthetic air, and all steady-state temperatures were kept constant by 5 hours. The specimens were cut into about 2x2 mm coupons, as shown in Fig. 3. The specimens were polished, washed and ultrasonically degreased in acetone. After this preparation, the specimens' dimensions were measured. The oxides morphology and their growth were investigated by means of SEM and EDS. In addition, as-deposited coatings were submitted to X-ray diffraction (XRD) analysis, using Shimadzu equipment.

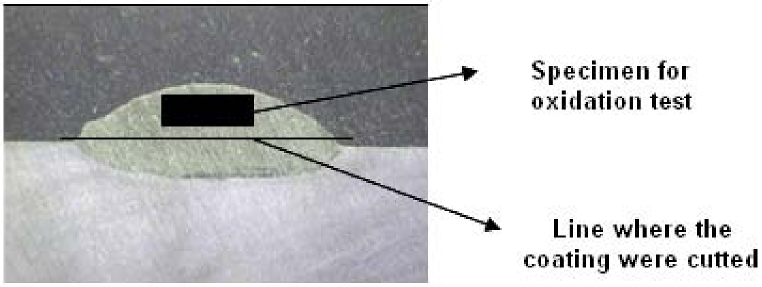


Figure 3. Illustration of region where specimens were extracted for oxidation test.

The specimens were also submitted to a heat treatment in a furnace for 72 hours, without synthetic air. This test intends to reveal the oxidation of a transversal section and to measure the oxide thick.

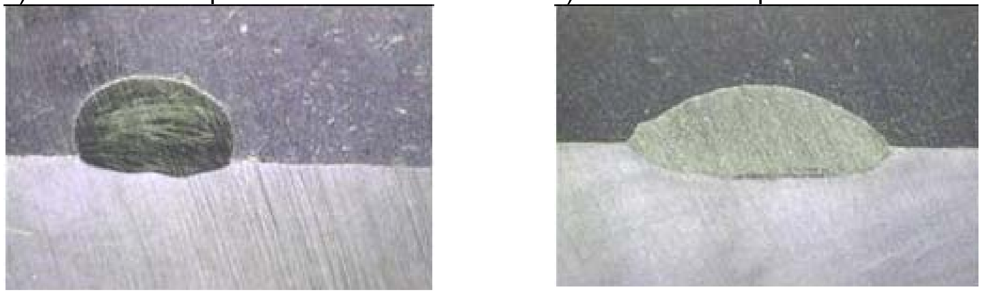
RESULTS AND DISCUSSION

As-deposited Coating Characterization

The quality of coated surfaces deposited using 130 A was satisfactory. In these coatings, pores, cracks or other imperfections were not observed. Higher dilutions levels can be attributed to the higher current intensity (130 A), as show in Fig. 4 Thus, more energy was inputed in the process; consequently a high volume of substrate was melted, incorporating iron to the coat. This increase in iron content can result in an increase in the toughness.

On other hand, the coating deposited with low current intensity (100 A) presented cracks. A possible reason can be its low toughness, since less dilution was observed, and consequently less iron was incorporated to the coating.

The transversal section of the coats shows the current intensity effect in the geometrical characteristic and, consequently, in the dilution levels.


a) NiCrAlC as deposited with 100 A

b) NiCrAlC as deposited with 130 A

Figure 4. Transversal section of the coats showing the geometrical characteristics.

Fig. 5 shows that the dilution level is mainly determined by the intensity current, following the previous works. This behavior is attributed to higher heat input, which allows melting a higher substrate volume.

The elementary powder mixtures have insignificant amount of iron (Table 2). For this reason, the iron diffusion from the substrate to the coating is a good indicative of the dilution level. Fig. 5 shows the dilution levels obtained using both methods.

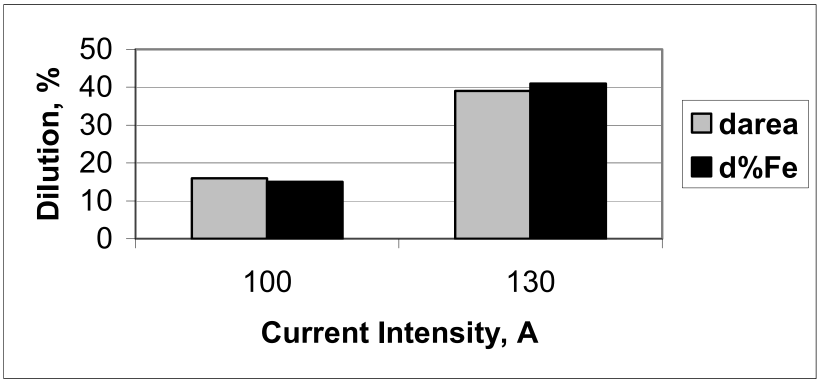


Figure 5. Dilution level determined by means of two methodologies for different current intensities employed in PTA.

The dilution values are similar for the same intensity current for both compositions. The small difference is attributed to the fact that the iron content method does not consider the geometrical characteristic of the coating. According to Fig. 4, the heat input is responsible to higher dilutions levels.

Chemical analyses, considering a large area, are presented in Table 5. The variation in the current intensity from 100 to 130 A caused an increase of 63% in the iron content, and a reduction of aluminum in 18 %. On the other hand, the chromium content did not vary with current intensity.

Table 5. Chemical analyses by EDS.

Current intensity, A	Al	Si	Mo	Cr	Mn	Fe	Ni
100	12.14	0.42	0.46	13.63	0.57	10.29	62.49
130	9.94	0.62	0.9	13.43	0.99	27.73	46.39

The oxidation is very dependent on the chemical composition. As the aluminum and iron contents varied with the current intensity (Table 5), this study intends to describe how this variation could change the oxidation kinetics and the oxide morphology.

Fig. 6 presents the composition profiles for Fe, Ni, Cr and Al, determined by EDS from the surface to the substrate. One can observe that did not have compositional variation in the coating. Iron contents change along the coatings profile, increasing from the external surface to the fusion line. This is a characteristic of processes such as PTA, where a metallurgical bond between the substrate and coating is observed. However, the TGA tests will be performed only in the coating, removing the substrate melted area.

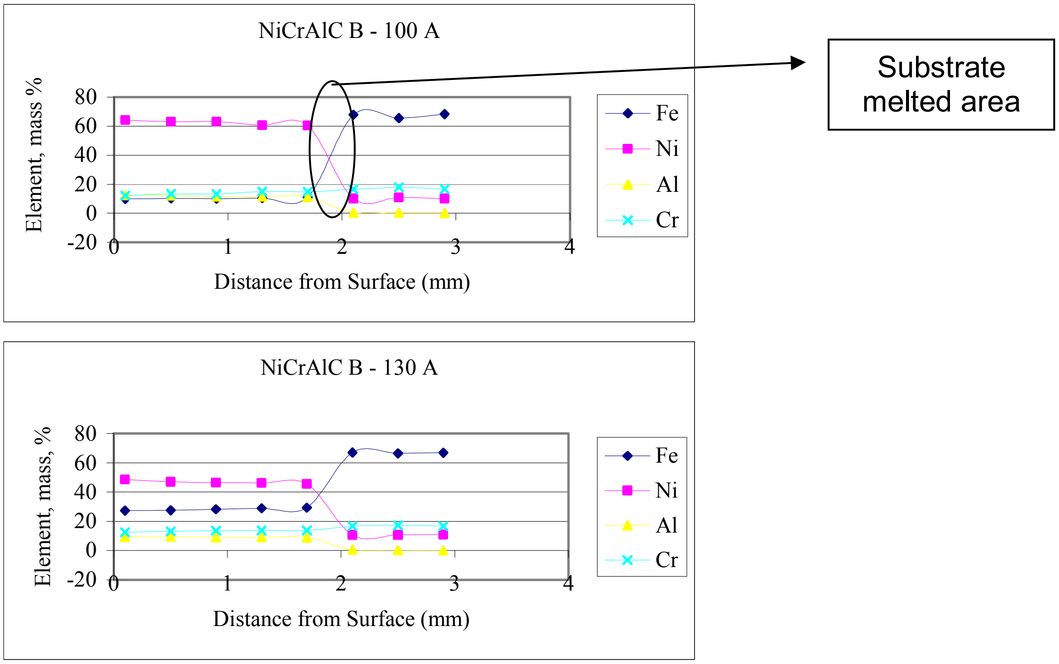
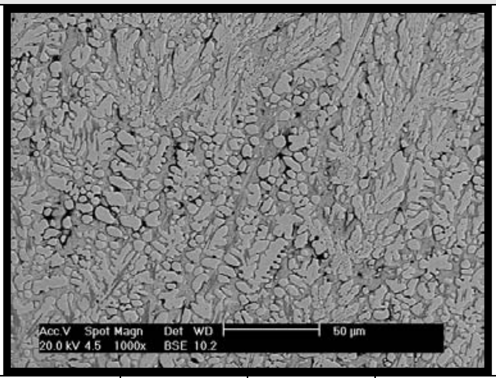


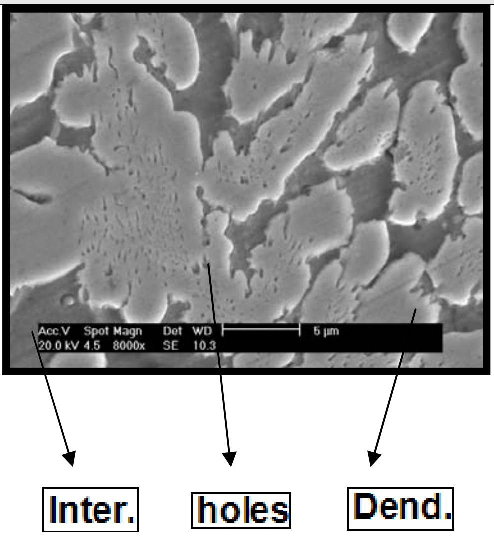
Figure 6. Chemical composition profiles of Fe, Ni, Al, and Cr, determined by EDS.

Fig. 7 presents the microstructure of as-deposited coatings. For these cases, the local chemical compositions are also presented. The cooling rates of PTA process promoted a dendritic solidification.

The microstructures presented in Fig. 7 allow concluding that the alloys are constituted by two phases. A dentritic region is rich in aluminum, indicating the NiAl formation, further confirmed by XRD analysis. An interdentritic region has a lower amount of aluminum and it is rich in chromium, which can constitute a solid solution or the Ni_3Al intermetallic phase formation.

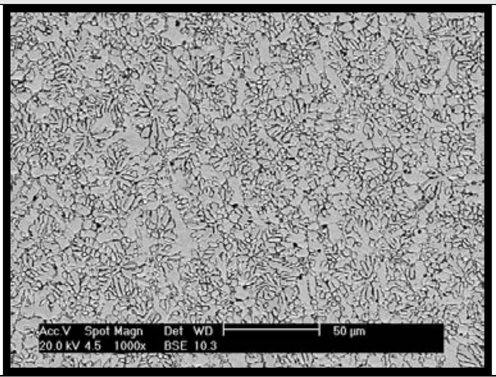
NiCrAlC as deposited with 100 A

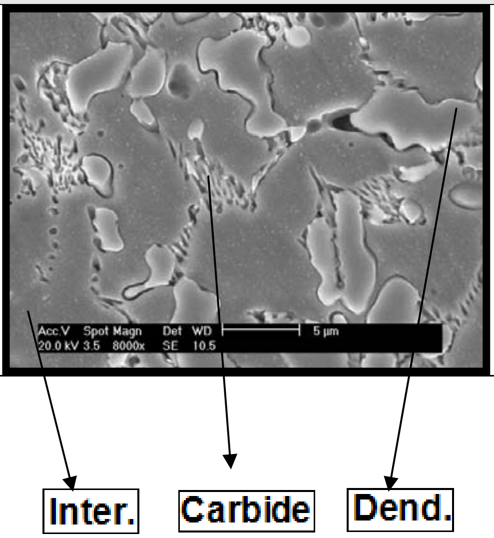




% W	Dend.	Inter.	holes
Al	15.48	6.76	15.43
Si	0.37	0.27	0.30
Mo	0.26	0.51	0.37
Cr	7.62	16.46	14.08
Mn	0.55	0.51	0.38
Fe	8.17	12.90	7.68
Ni	67.55	62.63	61.77

NiCrAlC as deposited with 130 A

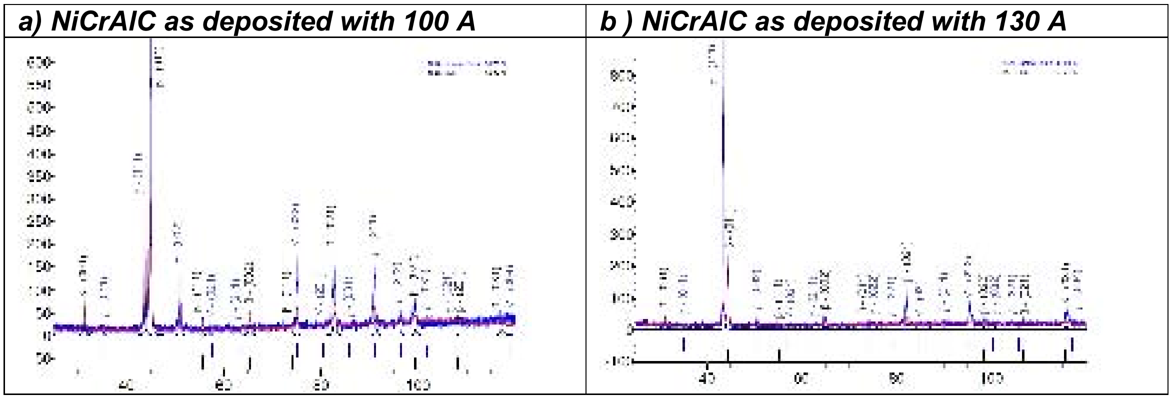




% W	Dend.	Inter.	Carbide
Al	13.48	6.31	5.83
Si	0.42	0.42	0.50
Mo	0.42	0.48	1.09
Cr	8.18	15.84	17.34
Mn	1.08	0.79	0.93
Fe	21.04	33.14	32.57
Ni	55.38	43.02	41.74

Figure 7. Microstructures and chemical analysis of NICRALC coatings.

The XRD patterns are presented in Fig. 8a and 8b for coatings deposited with 100 A and 130 A, respectively.



a) NiCrAlC as deposited with 100 A

b) NiCrAlC as deposited with 130 A

Figure 8. XRD patterns of NICRALC coatings.

The β phase corresponds to NiAl intermetallic phase with structure *Pm*3*m* (221), γ' phase corresponds to Ni3Al intermetallic phase with structure *Pm*3*m* (221), γ phase corresponds to Ni solid solution with structure *Fm*3*m* (225) and Cr_7C_3 carbide has structure *Pmcn* (62). During the Rietveld refinement it was verified a strong texture (preferred orientation) for (111) plane of γ' for NICRALC 130A and (110) plane for NICRALC 100A. In order to verify it, March's model[12] was applied with α parameter of 0.15 for 100A and 0.36 for 130A.

Due to the use of texture correction algorithm, it was not possible to quantify the volume fraction of phases. However, it can be qualitatively observed that γ' phase and β phase have significantly different fraction in the two samples. The major phase identified in NICRALC 100A was β, while in NICRALC 130A was γ'. This difference can be attributed to the different dilutions resulting from the processing parameters used in each sample. Disordered γ phase was identified only in NICRALC 100A sample. The presence of Cr_7C_3 carbide was verified in both samples.

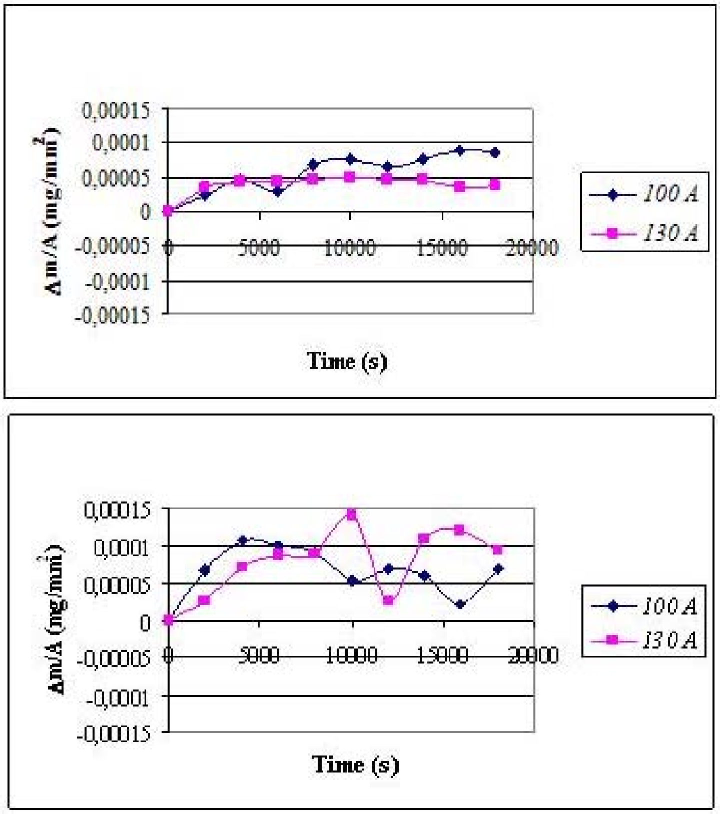
Oxidation Behavior

Fig. 9 presents the accumulated mass for 900 and 1,000 °C as a function of test time.

One can be noted that at 900 ° C the oxidation behavior is more stable, there is a mass gain with time, and . the spalling phenomen did not take place.

For 1,000 C the mass increased sometimes and in others it diminished also. These observations could relate to the spalling phenomena, due to the thickness increase with the higher temperature. As the coating presents sufficient Aluminium content for the alumina formation, the cycle is repeated.

It is possible to conclude that the tested alloys were very resistant to the oxidation in synthetic atmosphere, and a clearly evidence for this is the fact that only from 1,000 °C the oxide morphologies could be noted in SEM. For temperatures below 1,000 °C, the surfaces seemed very unaffected by the oxidation, and their aspect was very similar with the original surfaces before the tests. The morphologies of oxidized surfaces for 1,000 °C are shown in Fig. 10.



a) accumulated mass (900 °C)

b) accumulated mass (1,000 °C)

Figure 9. TGA results for NICRALC coatings for isothermal temperatures, showing accumulated mass as a function of test time.

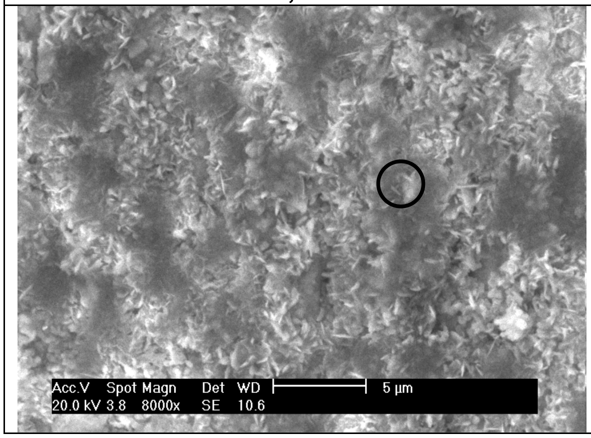
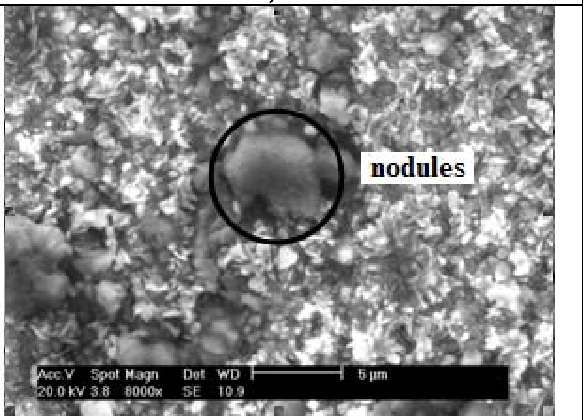
NiCrAlC* – *100 A*, tested for *1000ºC	***NiCrAlC* – *130 A*, tested for *1000ºC***
	

Figure 10. Surface aspects revealed by SEM after TGA tests.

For coatings deposited with less intensity current, one can observe features as acicular. Lee et al.[1] describe the acicular morphology as the initial monoclinic metastable θ-Al_2O_3 phase. This transient phase corresponds to the early stage of oxidation, when the oxides nucleate and grew to form an acicular shape. In the further oxidation, the θ-Al_2O_3 would transform into the equilibrium α-Al_2O_3 phase. This result is in accord to the oxidation behavior of NiAl.

At higher current intensity the oxide is composed of grains where nodules are present. According to Houngniou et al.[10] this oxide morphology is composed mainly of α-Al_2O_3 phase.

The observed difference in those morphologies can be attributed to the diffusion rate of aluminum at the surface during TGA tests. For specimens processed with lower current intensity, probably a large amount of intermetallic phase was formed, and in this structure the atoms are in more stable positions. Consequently, more energy is required to active the aluminum movement, retarding the oxidizing process.

Fig. 10 also shows a continuous layer and the microcracks, voids or spalling is not visible. This consideration suggest that the formed layer is adherent to the substrate, according to the very low rate of oxidation. Reinforcing these observations, a transversal section of the coating submitted to 1,000 °C for 72 hours can be seen in Fig. 11.

NiCrAlC – 100 A, tested for _1000ºC during 72 h_

% W	Oxide
O	30.9
Al	58.4
Si	1.12
Mo	0.37
Cr	3.07
Mn	1.21
Fe	1.69
Ni	3.31

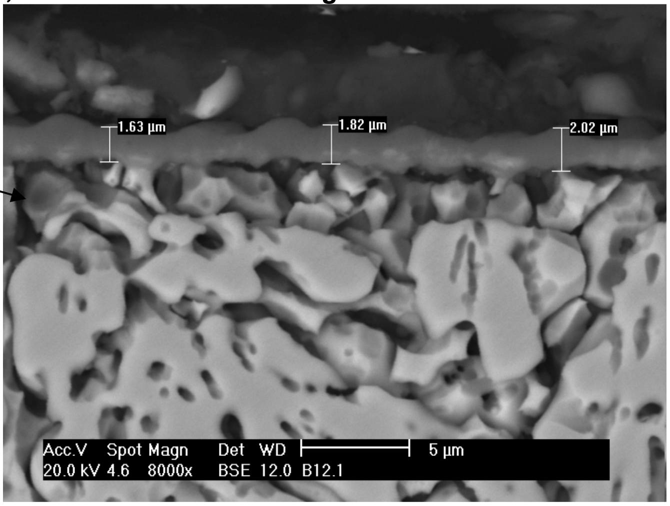


Figure 11. Transversal section of NiCrAlC deposited with 100 A submitted for 1,000 ºC during 72 hours. The oxide scale and their respectively thickness are present.

Compositional analyses of the surfaces submitted to five different temperatures shows that aluminum grown substantially to the oxide surface (Fig. 12). On the other hand, the contents of other elements decreased as temperature testing. The temperature increase helped the aluminum diffusion and its preferential affinity with oxygen gave rise to the alumina formation.

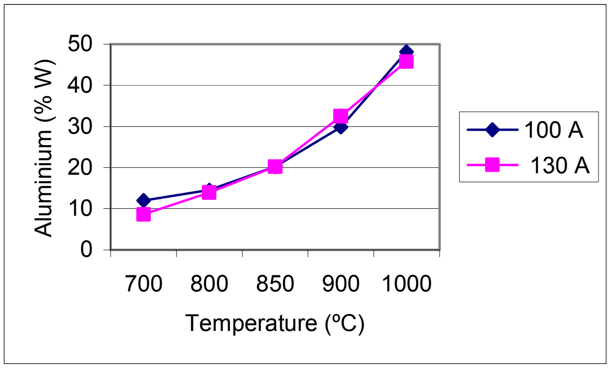


Figure 12. Aluminum content as a function of the testing temperature (TGA experiments).

Finally, an important comparison can be made with results obtained by Kunioshi et al.[7] These researches verified the oxidation behavior of as-cast NiCrAlC, and competitive materials as the Stellite 6 and a commercially petrochemical ferrous alloy using the same test methodology employed in this study. Their results showed that the oxidations rates were two orders of magnitude higher than those observed for NICRALC processed by PTA. Moreover, the performance of Stellite 6 and a ferrous alloy tested by ref.[7] was worst than that observed for NICRALC processed by PTA. The Stellite 6 presented less adherent oxide, with the apparent spalling phenomena, and the ferrous alloy presented lower oxidation resistance up to 900 °C. As-cast NiCrAlC shows the presence of CrO3 oxide, which is volatile in temperatures about 950 °C.

CONCLUSIONS

This study presented a Ni-based alloy processed by PTA, with variation of current intensity, which results in two dilution levels. The oxidation behavior of these coatings was studied, leading the following conclusions:

- The compositional differences attributed to intensity current did not affect the mass variation and the alumina formation.
- The oxide formation was only observed for tests conducted for 1,000°C.
- For high dilution level a stable a-alumina was observed, while for low dilution level a transient q-alumina was detected.
- NiCrAlC alloy deposited by PTA presented two orders of magnitude lower than the competitive materials tested by Kunioshi at al. (Stellite 6, a ferrous alloy and NiCrAlC as cast).
- NiCrAlC alloy deposited by PTA did not presents spalling phenomena and were not observe the volatile oxides as the NiCrAlC as cast.
- NiCrAlC alloy deposited by PTA presents better oxidation behavior than as-cast NICRALC, and of other alloys employed for high-temperature oxidation environments (Stellite 6 and a ferrous alloy).

Further developments are necessary in order to verify the effect of longer testing time in diffusion of aluminum.

Acknowledgements

Authors would like to thank Laboratório de Corrosão do CCTM-IPEN, Universidade Tecnológica Federal do Paraná (UTFPR), CAPES for its financial support to the present work.

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