MODIFICATION OF NiAl INTERMETALLIC COATINGS PROCESSED BY PTA WITH CHROMIUM CARBIDES[1]

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Abstract

Equipments that operate under high-temperatures can be protected with NiAl intermetallic coatings mainly because of their metallurgical stability. This study as it evaluates the effect of chromium carbide added to Ni-Al intermetallic coatings processed by PTA. Three Ni-Al-$Cr_{23}C_6$ powder mixtures with different carbide fractions (15, 30 and 45 wt%) and another without carbides were deposited by PTA on an AISI 304 stainless steel plate, using two different current intensities (100 and 150A). Coatings were evaluated regarding the presence of welding defects, and resultant microstructures were characterized by X-ray diffraction and scanning electron microscopy. Vickers microhardness and EDS chemical composition were also determined. NiAl and Cr_7C_3 development was confirmed by X-ray diffraction analysis. A combination of NiAl/Cr-Fe-Ni phases was identified. The hardness was strongly related to the formed phases and their amounts. Besides presenting advances toward the development of coatings which can withstand severe operation conditions, the present study shows that PTA hardfacing is able to produce reinforced intermetallic coatings for high-temperature applications.

Key-words: NiAl coating; Chromium carbide; Plasma transferred arc.

MODIFICAÇÃO DE REVESTIMENTOS INTERMETÁLICOS NiAl PROCESSADOS POR PTA COM CARBETO DE CROMO

Resumo

Equipamentos que operam sob altas temperaturas podem ser protegidos por revestimentos intermetálicos de NiAl, principalmente por sua estabilidade metalúrgica. Este estudo avalia o efeito de carbeto de cromo adicionado em revestimentos intermetálicos NiAl processados por PTA. Três misturas de pó de Ni-Al-$Cr_{23}C_6$ com diferentes frações de carbeto (15, 30 e 45%) e outra sem carbetos foram depositadas por PTA em uma placa de aço inoxidável AISI 304, utilizando-se duas intensidades de corrente (100 e 150A). Revestimentos foram avaliados em relação a presença de defeitos de soldagem e as microestruturas resultantes foram caracterizadas por difração de raios-X e microscopia eletrônica de varredura. Perfis de microdureza Vickers e composição química (EDS) também foram determinados. O desenvolvimento de NiAl e Cr_7C_3 foi confirmado pela difração de raios-X. Um comportamento binário NiAl/Cr-Fe-Ni foi identificado e a dureza foi fortemente dependente da quantidade das fases formadas. Além de apresentar avanços para o desenvolvimento de revestimentos que podem suportar condições severas de operação, o presente estudo mostrou que a aplicação de revestimentos por PTA é capaz de produzir revestimentos intermetálicos reforçados para aplicações em altas temperaturas.

Palavras-chave: Revestimentos NiAl; Carbeto de cromo; Plasma arco transferido.

1 INTRODUCTION

Equipments that operate under severe conditions can be protected with coatings of resistant materials. Intermetallic materials are a good alternative for high-temperature, corrosion[1] and wear-resistance applications.[2]

The NiAl intermetallic s considered a high-temperature structural material[3] due to its high melting temperature, low density, high thermal conductivity and good oxidation resistance, and efforts have been devoted to apply this aluminide on gas turbines applications.[4] However, its application has been very restricted due to the low ductility and toughness at room-temperature.[5] Although the addition of ternary elements has been extensively studied in order to solve this problem, an alloy with both room-temperature ductility and high-temperature strength has not been developed yet.[3]

Different processing techniques have been used to obtain nickel aluminides, such as casting, extrusion[6] and powder metallurgy routes with hot isostatic pressing (HIP)[7] and hot pressing consolidations.[8] PVD technique with different substrates,[9] high velocity oxyfuel (HVOF) with additions of CeO_2 or Cr[10] and self-propagating high temperature synthesis (SHS) with different characteristics[11-13] are presented as surfacing processes used to produce NiAl. However, few studies reported the use of PTA to produce these alloys.

PTA hardfacing process can be used to deposit high-quality welded coatings at lower production costs when compared with other welding processes, like oxyfuel gas welding (OGW) and gas tungsten arc process (GTA).[14] In comparison with thermal spray processes, such as air plasma spray and high velocity oxyfuel (HVOF), the major advantage of PTA is the metallurgical bond between the coating and the substrate. Another advantage is that the powder is usually completely melted during the deposition, and coatings with low porosity levels can be achieved.[1]

The deposition of intermetallic materials with PTA hardfacing on selected base alloys can result in an attractive combination of properties. For example, the production of intermetallic matrix composite (IMC) coatings with reinforcement constituents, as carbides and borides, or the *in-situ* formation of NiAl on alloyed substrates, such as stainless steels, are very attractive. In the other hand, the formation of these alloys by PTA on alloyed substrates are not completely understood.

This work presents a step toward the development of NiAl coatings, and addressed the *in-situ* formation of NiAl with chromium carbide reinforcement through the deposition of mixtures of Ni, Al and carbide powders on an AISI 304 stainless steel plate. The results show that NiAl coatings with Cr_7C_3 reinforcements can be produced by *in-situ* reactions during depositions. Furthermore, PTA hardfacing is able to produce high-temperature and wear resistance coatings for various applications.

2 EXPERIMENTAL PROCEDURE

NiAl coatings were processed by plasma transferred arc hardfacing on an AISI 304 stainless steel plate. The PTA equipment used in this study was a Starweld™ 300M manufactured by Deloro Stellite and the deposition parameters are shown in Table 1. Two current intensities were used and argon was the plasma, shield and carrier gas.

Table 1. PTA deposition parameters

Arc current	(A)	100 150
Plasma gas flow	(l.min^{-1})	2
Shield gas flow		15
Carrier gas flow		0,8
Travel speed	(mm.min^{-1})	100
Torch Stand off	(mm)	12

The mass composition of powders mixtures are given in Table 2. These mixtures were prepared using commercial powders with 75-150 µm (Ni and Al powders) or 15-100 µm (carbide powder) particle size range and homogenized for an hour at 40 rev.min^{-1}. These powder mixtures always present the Ni-25Al wt% stoichiometry and carbide powders were mixed together with the Ni-Al powders. Before depositions, powders were dried at 70 ºC for 24 hours. As expected, mixtures presented different densities resulting in different feed rates (but were constant in volume) as shown in Table 2. The AISI 304 100x50x10 mm plates were cleaned before the deposition with an emery wheel to remove oxides from the surfaces. These plates were not preheated and, after the deposition, coatings were air cooled to room-temperature.

Table 2. Nominal chemical compositions and feed rates for the powder mixtures

Alloy number	Ni	Al	Carbide powder	Feed rate (g.min^{-1})
	Weight percent (wt%.)			
0	75	25	-	6.82
1	63.75	21.25	15	7.14
2	52.50	17.50	30	7.13
3	41.25	13.75	45	7.53

The chemical compositions of the commercial carbides powder and of the AISI 304 stainless steel plate are shown in Table 3.

Table 3. Nominal chemical compositions of the carbide powder and of the AISI 304 stainless steel plate

	Weight percent (%wt.)						
	Fe	Ni	Cr	Al	Cr$_{23}$C$_6$	Mn	Si
Substrate	bal	8-10,5	18-20	-	-	≤2	≤1
Carbides powder	-	9.44	-	-	bal	-	-

Coatings were cut at transverse sections and prepared using standard procedures. Specimens were etched in a solution of 20% HCl - C$_2$H$_5$OH (ethyl alcohol) and the microstructure of the beads was investigated using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction analysis (XRD). Semi-quantitative chemical analysis performed by EDS were done on transverse sections. Moreover, microhardness profiles measurements were carried out in a Shimadzu HVM-2 tester using 300 g load. XRD analysis were performed using Cu K$_\alpha$ radiation on a polished top surface of coatings.

Dilution (d) of the deposited mixtures with the substrate was determined by the Fe ratio according Eq. 1, where $Fe_{coating}$ is the Fe content measured by EDS, Fe_{powder} is the Fe content of the powder mixtures and $Fe_{substrate}$ is the Fe content of the substrate.

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$$d\ (\%) = \frac{Fe_{coating} - Fe_{powder}}{Fe_{substrate}} \cdot 100$$

Equation 1

3 RESULTS AND DISCUSSION

During the deposition, a black soot layer was formed over and around the coatings which was cleaned with an iron brush. In a previous study on processed *in-situ* with elemental powders by PTA, Almeida et al.[15] reported that this soot is associated with the interaction between the plasma arc and the powder mixture, which results in the "burning" of some powder particles. It was also mentioned that this fact can result in the loss of elements during deposition and, consequently, deviations from the expected chemical composition. In this study, the layer of soot became larger when the carbide content increases. This behavior is associated with the particle size range of the carbide powder, which is smaller than Ni and Al powders and consequently, easily get "burned". According to Xibao and Hua,[16] the small particles are heated more easily than large ones for the same processing parameters, and the small particles can also be completely evaporated.

Visual inspection revealed transverse cracks in the coatings with higher carbide content (30 and 45 wt%) processed with 100 A. There are three reasons for the formation of these cracks: 1) the stress state imposed by the strong coat/plate bond; 2) the lower energy input of the 100 A than that of 150 A and 3) the carbide precipitation. The first one occurs during cooling because of the difference between the total contraction of the processed coating and that of the substrate, if a strong bond does not exist, coatings can delaminate from the substrate as reported by Fan et al.[1] The second reason results from the temperature gradient between coating and substrate immediately after the deposition. Considering the 100 A current, less thermal energy was transferred to the substrate and the temperature gradient is higher than on coatings processed with 150 A. Finally, the carbide precipitation can also contribute to the crack development, because of its high hardness and low toughness, and coatings were not able to support the stress state imposed.

X-rays diffraction patterns (Fig. 1) revealed that Ni reacts with Al to produce NiAl and that carbide particles precipitate as Cr_7C_3 for both current intensities.
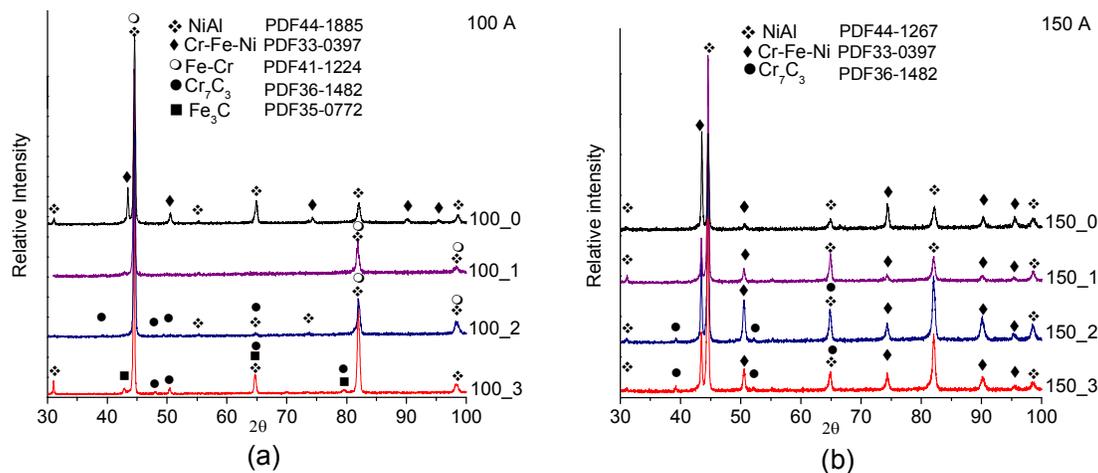

Figure 1. X-rays diffraction patterns for specimens deposited with (a) 100A and (b) 150A.

The $Cr_{23}C_6$ was melted and dissolved during deposition and Cr_7C_3 precipitates during cooling. Despite $Cr_{23}C_6$ has lower free formation energy (-396 kJ.mol-1) than Cr7C3 (-143 kJ.mol-1),[17] it was not identified in the XRD patterns.

The main phases identified in the coatings were the Ni aluminide, with excess of Ni for both currents intensities. When carbides were added the dissociated $Cr_{23}C_6$ precipitates in the form of Cr_7C_3. As observed by Hirota et al.,[18] the formation of phases with higher free formation energies, like Fe_3C and Cr_7C_3 was not understood.

Microstructures as observed in the transverse cross-sections of the coatings are shown in Fig. 2 for 100A current. The coating processed from the alloy number 0 presented a dendritic microstructure with NiAl dendrites and interdendritic Cr-Fe-Ni. When 15% of the carbides were added, the deposits became Cr-richer, due to the melting and dissolution of these carbides, resulting in a refined microstructure (alloy number 1). According to Cotton et al.,[6] Cr causes the grain refinement in Ni-rich NiAl alloys.

The alloy number 2 resulted in coatings with a NiAl matrix with Fe-Cr spherical precipitates and Fe-Cr and Cr_7C_3 interdendritic. The "composite" morphology at the interdendritic region suggests an eutectic solidification. These observations suggested that a NiAl/Fe-Cr pseudo-binary system may exist, as already reported for NiAl and Cr.[6] This can also be extrapolated for the NiAl/Cr-Fe-Ni pseudo-binary since Fe-Cr and Cr-Fe-Ni are similar. In Fig. 2d, the microstructure of the coating processed with 45% of carbide powder is characterized by NiAl dendrites, coarse interdendritic Fe-Cr and carbides. This interdendritic network consists in a large amount of Cr_7C_3 and little Fe_3C and Fe-Cr.
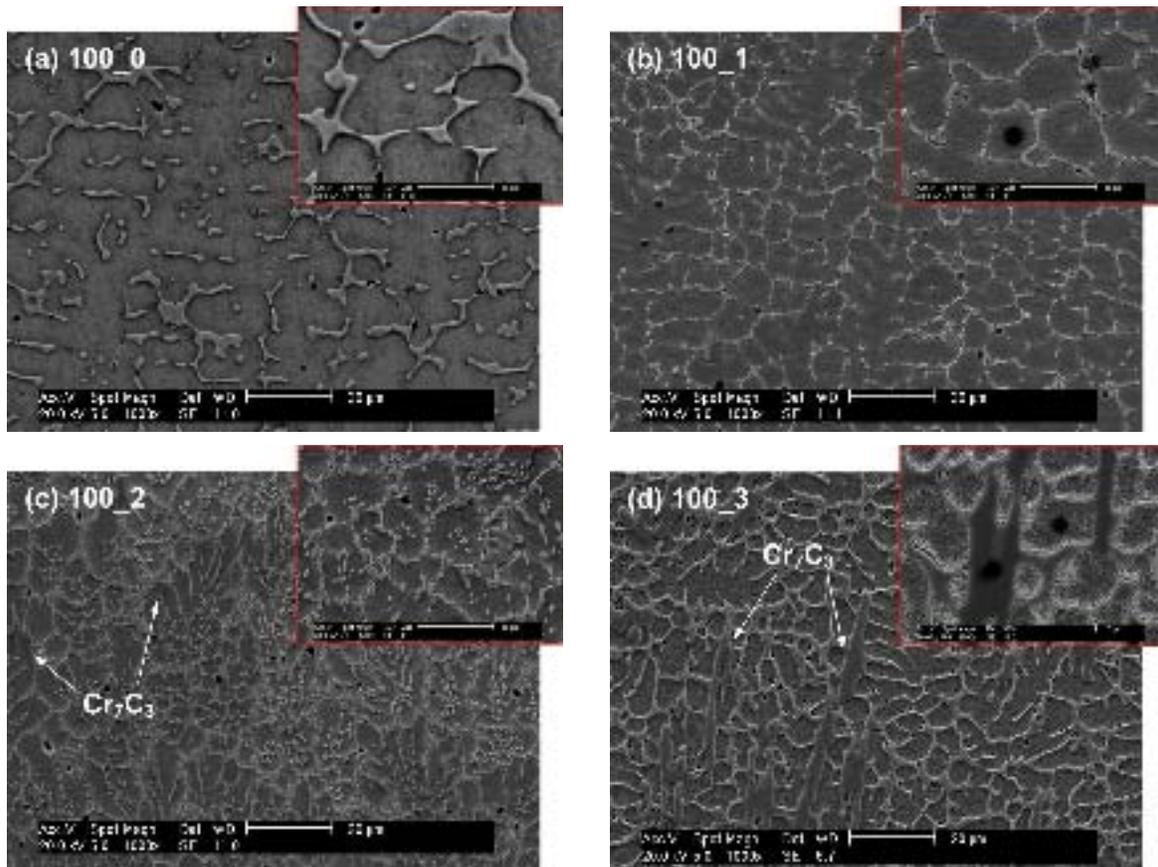

Figure 2. SEM micrographs of the coating processed with 100A.

A detailed analysis of the microstructure of the coating processed with alloy 3, Fig. 3, shows that the interdendritic region phase has eutectic characteristics and supports the NiAl/Cr-Fe-Ni pseudo-binary system.
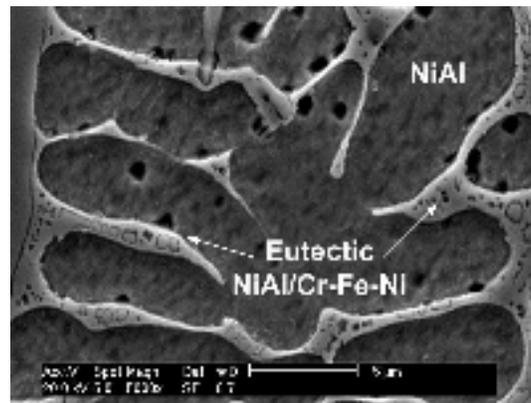

Figure 3. SEM micrograph of the coating processed with alloy number 3.

Transverse cross-section microstructures of coatings are shown in Fig. 4 for the 150 A current. Alloy number 0 resulted in coarse dendrites of Cr-Fe-Ni with about 50 wt% Fe and interdendritic NiAl. Considering the NiAl/Cr-Fe-Ni pseudo-binary system this is a hypereutectic microstructure. Its microstructure, typically hypereutectic, reinforces the idea that these alloys can follow a NiAl/Cr-Fe-Ni quasi-binary phase diagram.
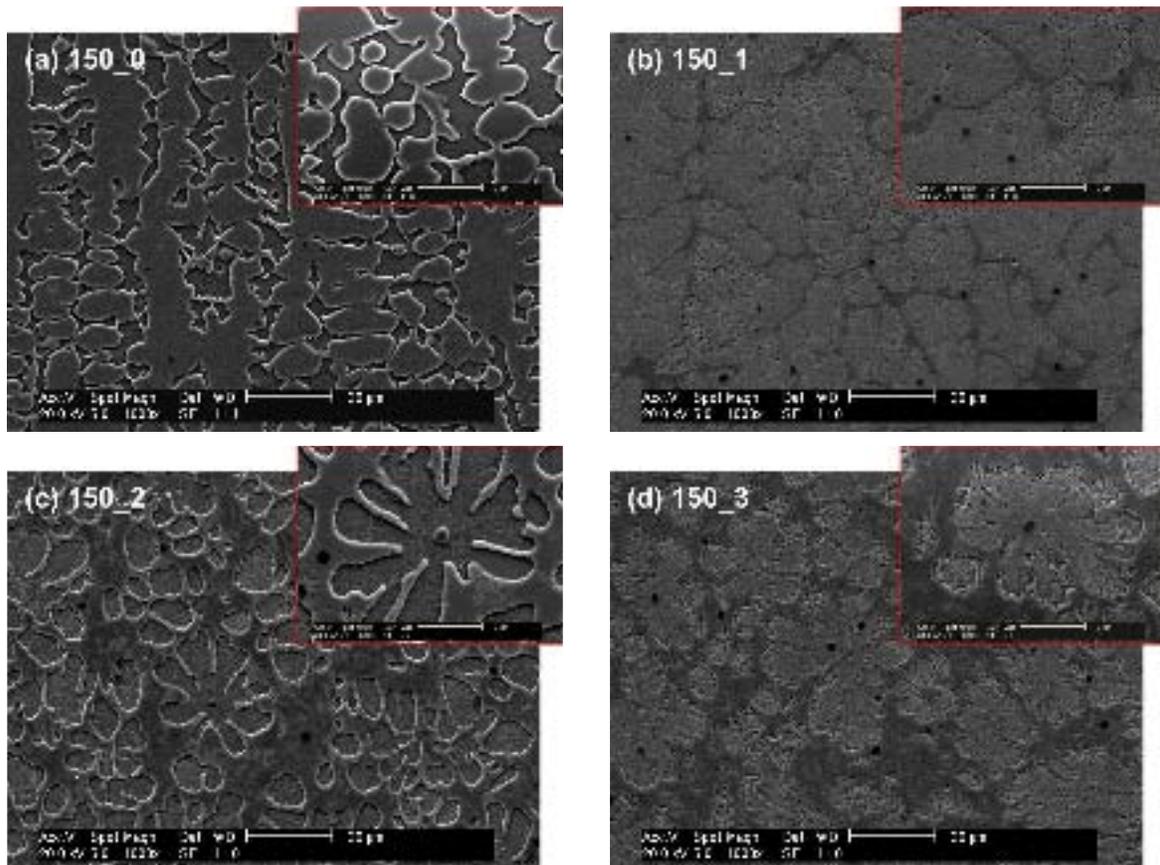

Figure 4. SEM micrographs of the coating processed with 150A.

Semi-quantitative EDS analysis identified a strong solubility in the NiAl interdendritic with 34.81 at% Fe and 9.70 at% Cr. Cotton et al.[6] reported that Cr has a limited solubility (about 1 at%) in Ni-50 at% Al at lower temperatures and this solubility increases for lower Al percentages. However, α-Cr precipitates were found in Ni-rich NiAl with Cr content of 2 at% by Fischer et al.,[19] Therefore, the solubility of 9.7 at% Cr in NiAl is very unlikely, and a very fine distribution of precipitates might be present. The presence of carbides in the deposited powder mixture alters the solidification, and more nucleation sites, due to partial melted carbides, contributed to a refined microstructure (Fig. 4b, 4c and 4d).

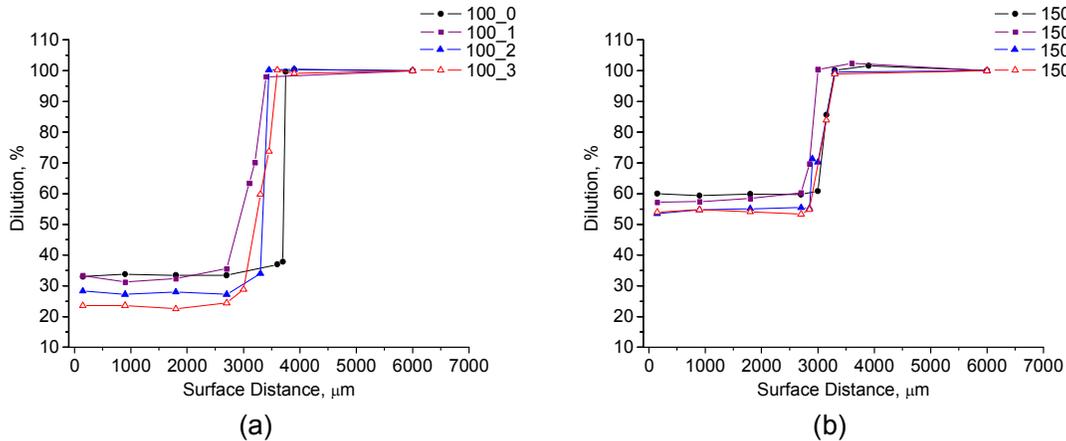Fig. 5 shows the dilution of coatings processed with 100 A and 150A.

Figure 5. Dilution measurements for beads deposited with (a) 100 A and (b) 150 A.

It is observed that the dilution increases with the current and it results from the highest energy input of the 150A current. For each current, the dilution decreased with the carbide content. Increasing carbide content requires more energy to melt the powder going through the arc.[14]

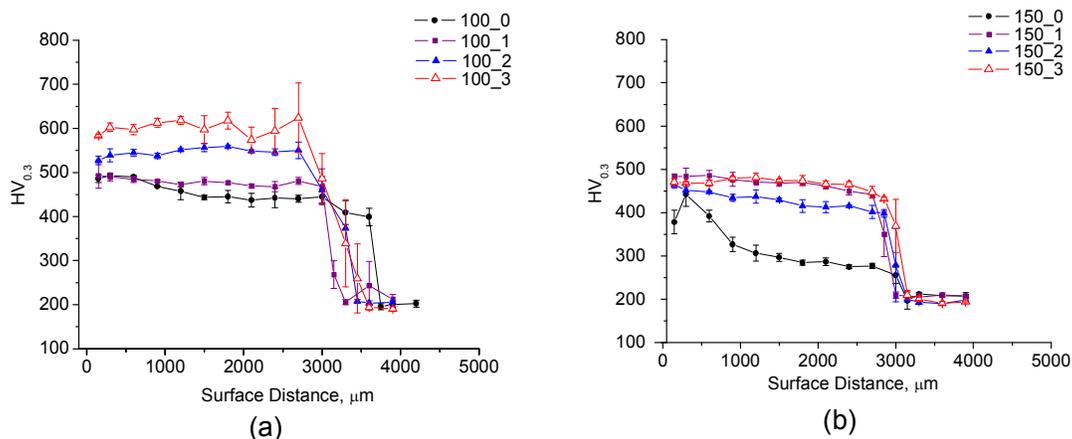Hardness profiles of the deposited coatings are shown in Fig. 6 for coatings processed with 100 A and 150A.

Figure 6. Microhardness profiles for the specimens deposited with (a) 100A and (b) 150A.

Coating hardness increased with the amount of carbides in the deposited powder mixture. Although carbides were not identified in coatings processed with the mixture containing 15 wt% carbides, the observed structure refinement can account for the

measured hardness increase. Larger amounts of carbides (30 and 45 wt%) in the powder mixtures caused the precipitation of the carbides, which together with the observed refinement of the structure (Fig. 2 and Fig. 4) explain the hardness increase.

4 SUMMARY

The present study presents advances toward the development of coatings that can withstand severe conditions of temperature and wear. The influence of various elements simultaneously diffusing from the substrate and the effect of carbide additions were qualified. Our results show that it is possible to produce high-temperature wear performance coatings by *in-situ* reactions during PTA surfacing. However, further studies will be done to clearly understand the solidification behavior of NiAl when high amounts of alloying elements are presented in the weld pool. Moreover, quality of coatings improvements changing processing parameters and enhance in NiAl and carbide formations can be made optimizing both chemical composition and processing parameters.

For the testing conditions evaluated in this study, major contributions are:

• PTA hardfacing is able to produce NiAl coatings reinforced with Cr_7C_3 for high-temperature applications.

• The microstructure developed in the process coatings can be described by a pseudo-binary NiAl/Cr-Fe-Ni phase diagram.

• Deposition current changed the microstructure development of coatings because the variation of the energy input, which results in different dilutions.

• The interaction of the powder mixture with the plasma arc resulted in coatings with a dilution that depended on the chemical composition of the deposited mixture.

• Hardness of coatings has a strong dependence on the amount of precipitated carbides and NiAl intermetallic formed. Furthermore, small variations in hardness were also attributed to microstructures refinement.

Acknowledgements

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