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PROCESSING OF NiAl INTERMETALLIC COATINGS MODIFIED WITH Fe AND Cr

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Abstract. *NiAl aluminide intermetallic coatings are used in many industries mainly for their resistance to high temperature environments. Performance associated with their ordered crystal structure, low density and the ability to form a continuous and adherent protective film of alumina. Different alloying elements have been studied to enhance the competitiveness of NiAl. Carbides such as WC or elements such as Fe and Cr have been shown to increase hardness, improving the tribological behavior of NiAl alloys. The aim of the present work is to understand how these alloying elements affect the microstructure and mechanical properties of NiAl intermetallic coatings processed by in-situ synthesis during Plasma Transferred Arc (PTA) processing. Alloying elements were added both by the interaction with the stainless steel substrate (Cr and Fe) and the addition of 1wt% of carbides (W and C) to the Ni+Al powder mixture. The strong interaction with the substrate caused dual phase coatings of β-NiAl and γ-FeNi phases in agreement with predictions based on the ternary Ni-Al-Fe alloy system. W carbides in the elemental powder mixture induced a greater dilution with the substrate favoring the increase in Fe and Cr content. Changes in composition of coatings resulted in an increase in the austenite phase and the presence of point defects in the NiAl crystalline structure, which brought a significant increase in hardness.*

Keywords: *Coatings, aluminides, Plasma Transferred Arc, alloying elements, intermetallics.*

1. INTRODUCTION

Nickel aluminides, NiAl, are intermetallic compounds that have been widely studied due to the interest of the automotive, energy, manufacturing and particularly the aerospace industry. This attention is a consequence of the high melting temperature (1638 °C), chemical resistance to a variety of environments, fatigue resistance, attractive modulus of elasticity, together with low density (5.9 $g.cm^{-3}$) and competitive cost of raw materials (Miracle and Darolia, 2000). The ordered phase β-NiAl, has been considered for high temperature structural applications (operating at 500 °C or higher), for example, monocrystalline NiAl for the blades of gas engines or as a fine matrix of reinforced engine nozzles, which operate above 1000 ºC (Meetham and Van De Voorde, 2000). The high resistance to isothermal oxidation makes NiAl ideal for protecting superalloys or as thermal barrier coatings (TBC) (Yan *et al*., 2014). NiAl aluminide can operate at temperatures higher than those currently accepted for Ni based superalloys parts, and allowing for more efficient engines. However, low toughness at room temperature as well as low strength and creep resistance in high temperature often compromise the competitiveness of unalloyed NiAl. Different elements have been studied to overcome those problems and enhance the competitiveness of NiAl. A variety of elements such as Fe and Cr have shown to induce an increase in hardness, improving the tribological behavior of NiAl matrix. The addition of Fe and Cr, in solid solution with NiAl, impacts the density of point defects in the crystal lattice, such as vacancies or anti-sites, which have a strong impact in the hardness of the aluminide (Pike *et al*., 1997).

In the present work, Plasma Transferred Arc (PTA) technique is used in order to process NiAl intermetallic coatings on stainless steel substrates, which have been demonstrated to be an effective method in the development of high temperature aluminide coatings by *in-situ* synthesis, during the deposition of elemental Ni and Al powder mixtures with predefined composition (Almeida *et al*., 2011; Brunetti *et al*., 2014).

PTA is a hardfacing process that consists of a plasma arc produced between a tungsten electrode and a substrate, which heats a gas (Argon) that passes through the torch, causing it to expand and flow at high speed through the lower orifice. The powder mixtures are fed and quickly heated and melted. Afterwards, they make contact with the molten surface of the substrate (this area is usually called melt pool), where the melted particles mix with the substrate material in the liquid state (dilution), forming a coating after solidification, which is metallurgically bonded to the substrate (Deuis et. al., 1998). The synthesis of elemental powders starts in the plasma arc where the particles are in the liquid state, by interdiffusion, and continues in the melt pool until the coating is completely solidified and cooled (Abreu-Castillo, 2019). This process can be applied to manufacture single-layer coatings and also multi-layer depositions which are associated to Additive Manufacturing (AM) technology (Bueno, 2019).

As PTA processing results in metallurgical bonding (welding) between the coating and the substrate, the alloying elements (Fe and Cr) were added to the coating by controlling the dilution with the substrate elements (mainly Fe and Cr). The dilution is controlled through two different mechanisms:

a) The deposition current: the higher the deposition current, the greater the heat imput which induces to higher dilution levels (Brunetti *et al.*, 2014).
b) The addition of a small quantity (1 wt.%) of W carbides to the Ni+Al powder mixture, which tend to retain energy due to its low thermal conductivity, increasing the dilution (D'Oliveira *et al.*, 2008).

The resulting coatings were characterized in order to confirm the formation *in-situ* of phase β-NiAl and other phases associated the dilution and to observe the effects of the addition Fe and Cr on the microstructure and mechanical properties by comparing the coatings processed with and without WC and also with different deposition currents.

This research is part of an ongoing investigation on the effect of elements and compounds (Fe, Cr and W carbides) on the microstructure and mechanical resistance of NiAl intermetallic coatings deposited by PTA. Further advances should include a better understanding of the microstructure/performance relationship that improves tribological behavior of coatings, while maintaining resistance to oxidation.

2. MATERIALS AND PROCESSING

Powder mixtures with two compositions were prepared:

- **Ni + Al powder mixture:** 80 wt.% Ni – 20 wt.% Al, using Ni and Al elemental powders with irregular-shaped particles with 75 - 150 μm and 99,9 % purity.
- **Ni + Al + WC-Co powder mixture:** same composition Ni+Al poder mixture, with 1 wt.%WC-Co (88%WC - 12%Co, irregular-shaped particles with average size ~ 35 μm).

The mixtures were deposited by Plasma Transferred Arc on AISI 304 austenitic stainless steel plates (150 mm x 100 mm x 10 mm), preheated at 200 ºC to better control the cooling rate and avoid cracks. Single layer coatings of 100 mm long were processed on a Starweld 300 PTA Welding System equipment. Deposition parameters (Table 1) were kept constant, except for the deposition current, which was set to 100 A and 120 A. Each set of coatings is identified according to their composition: NiAl coatings (processed from Ni + Al powder mixture) and NiAl-WC coatings (processed from Ni + Al + WC-Co powder mixture).

Table 1. Deposition parameters

Parameter	
Plasma gas flow	2.0 l/min
Gas flow protection	15.0 l/min
Powder flow gas	1.0 l/min
Powder feed rate	6.0 g/min
Torch distance	10 mm
Deposition speed	100 mm/min
Deposition current	100, 120 A

Analysis of phases was performed by X-ray diffraction (Shimadzu XRD7000 diffractometer with Cu kα radiation, λ=0.15406 nm) on the cross section of the coatings. Scanning electron microscopy (SEM) (TESCAN VEGA3 LMU microscope) was used to characterize the microstructure on the cross section of the coatings. Microhardness tests were carried out with a Vickers penetrator (Shimadzu HMV-equipment), using normal force of 0.3 kgf, also on the cross section of the coatings.

The dilution of the coating with the substrate was assessed by the iron content incorporated in the coatings, using chemical analysis by energy dispersive spectroscopy (EDS). This procedure refers to the ratio between the variation in Fe content due to deposition (Fe coating minus Fe powder mixture) and iron content in the substrate (Fe substrate), Equation (1). The composition of coatings, including Fe coating, was determined at the cross section of the coatings, using Dispersive Energy Spectroscopy (EDS), over an area of 80 mm² with a DSS detector, coupled to the scanning electron microscope.

$$\text{Dilution (\%)} = \frac{Fe\ coating\ - Fe\ powder\ mixture}{Fe\ substrate} \quad (1)$$

3. RESULTS AND DISCUSSION

Continuous coatings were obtained, without porosity or cracks. The cross sections of the coating are shown in Figure 1. The highly exothermic nature of the NiAl synthesis reaction accounts for the relatively high dilution values shown in Figure 2 (Almeida *et al.*, 2011; Noebe *et al.*, 1996). Figure 2 also shows that regardless of the deposition current used, NiAl-WC coatings had a greater dilution, behavior associated with the low thermal conductivity of the carbides, which retain heat energy that is released by conduction and radiation when the metal is molten, melting a larger volume of the substrate (D 'Oliveira *et al.*, 2008). The higher dilution associated with the addition of WC led to an increase in Fe and Cr content in the coatings, for both deposition current, as shown in figure 3.

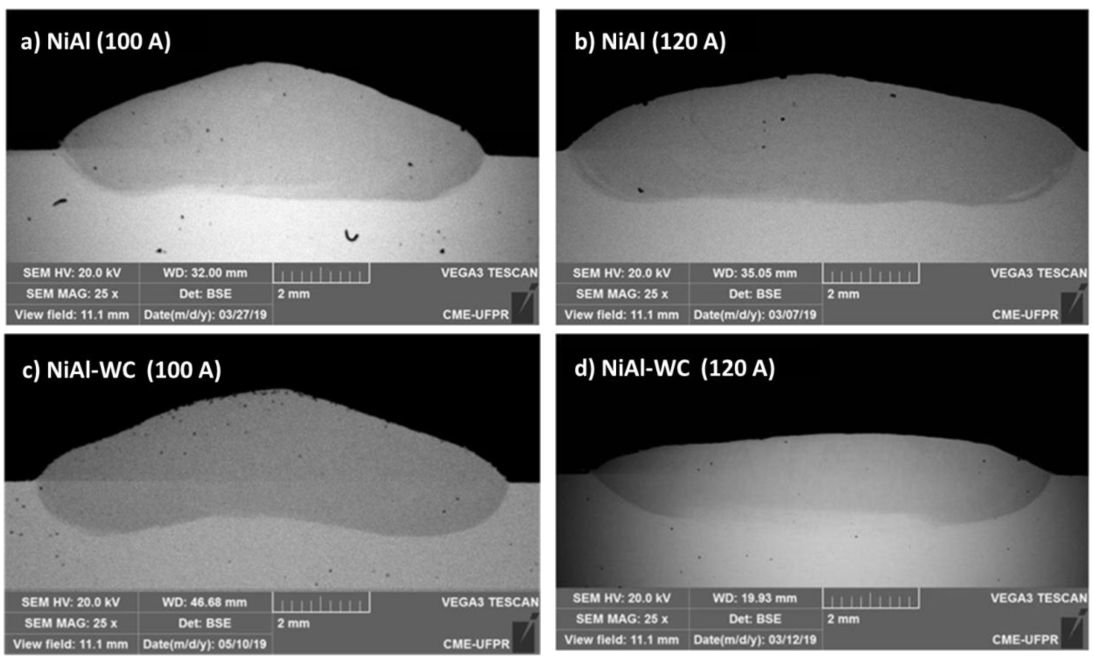

Figure 1. Transversal section of the coatings.

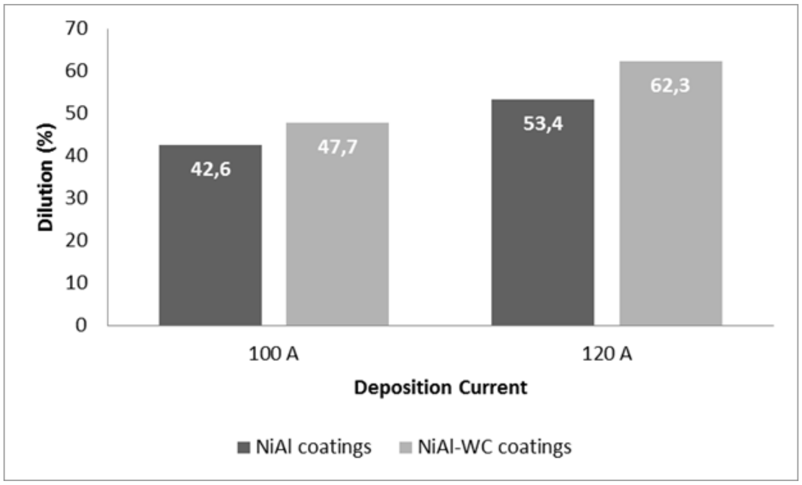

Figure 2. Percentage of dilution of the coatings.

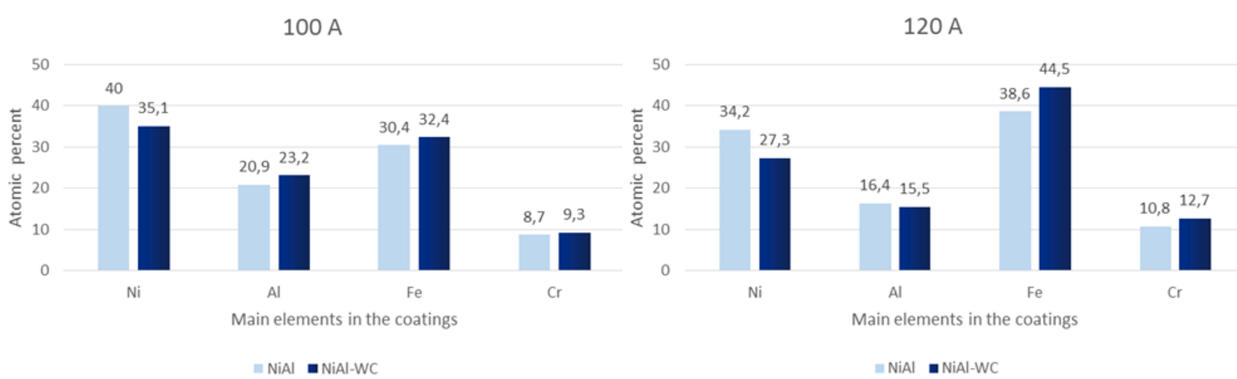

Figure 3. Chemical composition of the coatings, processed with deposition current: a) 100 A; b) 120 A.

The chemical composition of coatings, a consequence of the powder mixture and the selected deposition current account for the phases formed in the coatings. Figure 4 shows the XRD analysis, confirming the *in-situ* synthesis of the β-NiAl phase (Al0.9Ni1.1) in coatings processed with both powder mixtures (NiAl and NiAl-WC) and deposition currents (100 A and 120 A). The presence of the Ni-rich aluminide compound could be attributed to the high availability of nickel in the synthesis, coming from the austenitic substrate which is incorporated due to its high solubility in NiAl, causing the occurrence of point defects, typical of off-stoichiometric compositions. It is of relevance that the addition of WC particles in the powder mixture did not affect the synthesis. WC peaks were not detected confirming that neither precipitation nor segregation of these elements occurred. WC particles were melted during the deposition, hence, W and C atoms are incorporated in the phases that compose the coatings. In NiAl lattice, the maximum solubility W varies between 0.01 and 1 at.% (Alekseeva, 2011; Milenkovic *et al.*, 1993) and carbon might form a solid solution with NiAl as an interstitial element (George & Liu, 1990) inducing lattice distortion.

The presence of γ-FeNi austenitic phase is a result of the iron content coming from the substrate that also impacts the aluminide compound. Fe can substitute for Ni or Al in the NiAl crystal structure, as observed by the shift in the main peak of the intermetallic complex aluminides such as Al [Ni, Fe] (Fe substituting Al) and [Fe, Al] Ni (Fe substituting Ni) are expected for Fe content above 25 at.% Fe (Almeida, 2011). No Iron aluminides were identified in the coatings, which could be associated with the higher Fe aluminides enthalpy of formation in comparison with NiAl enthalpy of formation (Brunetti *et al.*, 2014).

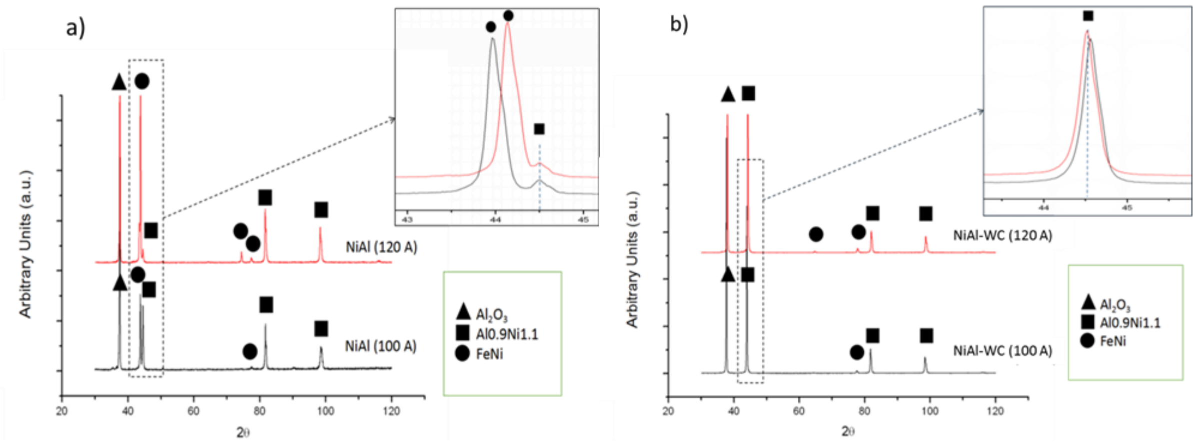

Figure 4. X-Ray diffraction of the NiAl coatings: a) without the addition of WC; b) with WC.

Iron and Chromium content were not only responsible for the phases formed in the coatings, but also for the mechanical behavior, Figure 5. For both deposition current tested, NiAl-WC coatings exhibited an increase in hardness compared to NiAl coatings. Coatings processed with 100 A, exhibit an increase on the average hardness from 365.2 HV to 490.8 HV (+ 34%), while in coatings processed with 120 A, the average hardness increase 19%, from 406.3 HV to 485.6 HV due to the addition of WC and a higher dilution. The increase in Fe and Cr content may be related to an increase in the concentration of vacancies and anti-sites, as these elements act as solid solution strengtheners that lead to the formation of crystalline imperfections in the ordered structure of the aluminide.

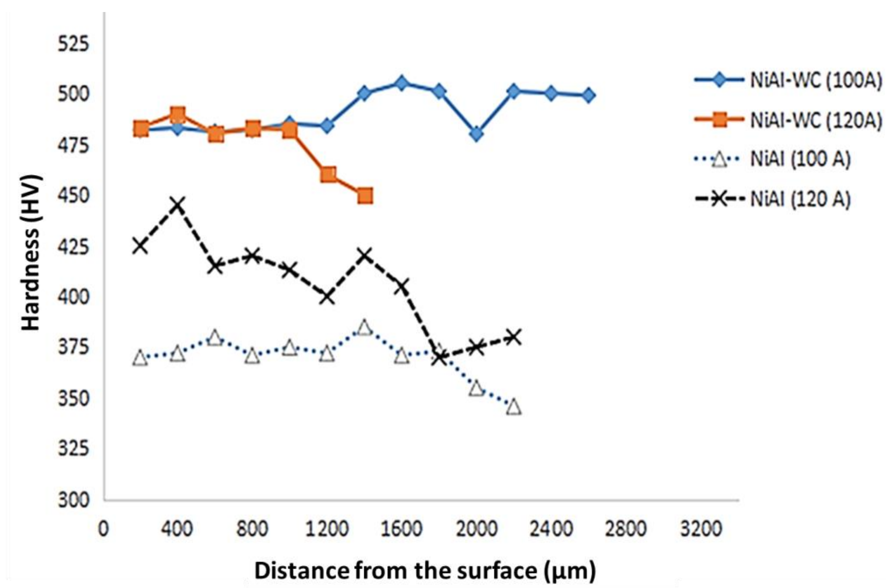

Figure 5. Microhardness profile of the coatings

Brunetti *et al.*, (2014) studied the impact of Fe in NiAl coatings and pointed out that small amounts of Fe, due to low deposition current of 70, 80 and 90 A, resulted in the presence of anti-sites in both sublattices. Higher deposition currents, 100, 110 and 120 A, resulted not only in the presence of anti-sites but also vacancies in the Ni sublattice. According to Pike (1997), the concentration of each of these defects impacts hardness differently: Vacancies have a stronger hardening effect than anti-sites and the addition of Fe progressively can change the stoichiometry of NiAl, promoting the formation of these defects. The further away from stoichiometry (Ni/Al=1), the higher the hardness seems to be (Munroe *et al.*, 2002). Point defects present in non-stoichiometric NiAl impact differently the properties depending on the alloying element that is present (Miracle and Darolia, 2000).

The role of Chromium in the hardening process must also be studied because it is the second most abundant element in AISI 304 substrates (approximately 18 wt.% Cr). Chromium can act as a strengthener: through solid solution strengthening or precipitation. The solubility of Cr in stoichiometry NiAl is limited, between 1 and 10 at.%, hence, amounts of Cr beyond the solubility limit might lead to a fine α-Cr phase precipitates. For the conditions used in the present work, α-Cr precipitates were not detected, as confirmed by Figure 4, which means that all chromium was incorporated in the NiAl matrix as a solid solution. This behavior can be associated with the Ni-rich β-NiAl composition that tends to dissolve more Cr, since Cr solubility increases as Aluminum content decreases (Cotton, 1993). The hardening effect of Chromium in NiAl is known to have its minimum values for stoichiometric composition and increases as off-stoichiometric compositions are processed. This behavior is due to the presence of point defects (Vacancies or anti-sites). The preference of Cr atoms for the Aluminum sublattice, leads to the presence of Ni Vacancies that have strong hardening effects (Cotton, 1993).

Tungsten is frequently used and studied as a precipitation strengthener in different superalloys, but the information available in literature referring to its solid solution effects are still very limited and would require further studies for a better understanding of the role W plays on the coating hardness increase (Milenkovic *et al.*, 1993). Carbon provides strength to NiAl matrix in the form of solid solution as an interstitial element, which could have participated in the increased hardness of the coatings (George and Liu, 1990).

4. CONCLUSION

Under the processing conditions used for the analysis of Fe and Cr alloying elements in NiAl coatings processed in situ, it is possible to conclude the following:

a) The highly exothermic synthesis of β-NiAl is responsible for the high levels of dilution with the substrate, leading to the inclusion of large amounts of Fe and Cr in coatings, hence, the formation of austenitic γ-FeNi.

c) The addition of tungsten carbide particles in the powder mixture did not compromise the synthesis of β-NiAl intermetallic phase (Al0.9Ni1.1) and led to higher temperatures in the melt pool due to their low thermal conductivity, further increasing dilution ,of the coatings with the substrate.

d) The increase in dilution, whether by the deposition current or by the addition of carbides, caused an increasing in Fe and Cr content coming from the austenitic stainless steel. The solubility of these elements in the β-NiAl crystal lattice causes the formation of point defects (vacancies and anti-sites). These point defects in NiAl matrix had strong hardening effects on the coatings.

5. ACKNOWLEDGMENTS

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