MICROSTRUCTURAL STABILITY OF NICKEL ALUMINIDE COATINGS PROCESSED BY PTA WITH DIFFERENT CONTENTS OF ALUMINUM

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ABSTRACT
This study analyzes the microstructural stability of nickel aluminide coatings processed by PTA using a mixture of elemental powders (nickel, aluminium, chromium carbide and iron boride), varying the aluminum content. Deposition on AISI316L steel plates was carried out with current of 130A. The stability was evaluated using isothermal exposure at temperatures up to 1000 °C for intervals up to 72h in an air furnace. Scanning electron microscopy analysis showed precipitations of Cr-rich phases, which did not alter significantly the as-deposited hardness.

Keywords: plasma transferred arc; nickel aluminides; microstructural stability.

ESTABILIDADE MICROESTRUTURAL DE REVESTIMENTOS DE ALUMINETOS DE NÍQUEL PROCESSADOS POR PTA COM DIFERENTES TEORES DE ALUMÍNIO

RESUMEN
Este estudo analisa a estabilidade microestrutural de revestimentos de aluminetos de níquel processados por PTA utilizando uma mistura de pós elementares (níquel, alumínio, carbeto de cromo e boreto de ferro), variando o teor de alumínio. As deposições sobre chapas de aço AISI316L foram conduzidas com corrente de 130A. A estabilidade foi avaliada usando exposição isotérmica a 1000 °C por intervalos de até 72h em forno ao ar. Análise em microscopia eletrônica de varredura mostrou precipitações de fases ricas em Cr, o que não alterou significativamente a dureza dos revestimentos como depositados.

Palavras chaves: plasma de arco transferido; aluminetos de níquel; estabilidade microestrutural.

INTRODUCTION

Nickel aluminides have been extensively used to manufacture components exposed to high temperature environments [1].

To improve their performance against other industrial aspects, such as wear resistance, different alloying elements have been added, particularly those that form carbides [2-4]. The understanding of the metallurgy of nickel aluminides is complex when alloying elements are incorporated. There are different intermetallics and carbides that can precipitate, and their morphology and distribution having a direct influence in the coating performance.

Plasma transferred arc (PTA) is a process that allows designing coatings, especially for those compositions that presents poor weldability as mentioned by Almeida et al. [5]. Solidification rate is governed by the processing parameters and by the alloy formed during the processing. These parameters have a large influence on the final chemical composition of coatings as a consequence of the interaction with substrate (dilution), that is a characteristic of weld coatings, but in the case of aluminides dilution is known to be relatively high [5, 6].

A previous study [6] of microstructural stability of nickel aluminides processed by plasma transferred arc (PTA) using powder mixtures with nominal compositions of an atomized powder alloy [7] was carried out by Benegra et al. [6]. The use of 100 A as deposition current resulted on

an unsound coating, resulting in a material with transverse cracks. It follows that the use of a higher deposition current is preferred, and some changes in chemical composition allow maintaining the mechanical properties at high temperatures during longer times of exposure.

Considering the above mentioned facts, the present investigation compares the previously published results of nickel aluminide coating processed by PTA with a different powder mixture, which differs in the aluminum content, and characterizes them with respect to their microstructural stabilities.

MATERIALS AND METHODS

Elementary powder mixtures of Ni, Al, Cr, chromium carbide and iron boride were prepared to process the coatings. Two mixtures of powders were prepared with nominal compositions varying aluminum content. The one with lower Al contente named L-Al (nominal composition: 10% Cr, 15% Al, 8% chromium carbide, 0.1% iron boride and Ni balance), and the other with the higher Al content, named H-Al (10% Cr, 20% Al, 8% chromium carbide, 0.1% iron boride and Ni balance).

Plasma transferred arc (PTA) hardfacing on 316 L stainless steel substrate plate (100 mm X 80 mm X 7 mm) used with a deposition current of 130 A. Processing parameters were identical to those used in the previous study [6]. The powders with a grain size range of 90-180 micrometers were mixed for 1 hour in a Y-mixer. Subsequently, the powder mixture was dried at 100 °C for 48 hours to avoid agglutinations. Argon of 99.995% purity is used as the plasma, protection and transport gas.

Dilution level was determined at the cross-sections of the coatings, considering the insignificant amounts of iron in the elemental powders. In this way, an evaluation of Fe content was made using energy diffraction X-ray spectroscopy (EDS) in a central area of the coating and the substrate, and dilution level is equivalent to the ratio

$\%Fe_{final} / \%Fe_{substrate}$.

The specimens were isothermally exposed to 600, 800 and 1000 °C in an air furnace for 1, 6, 24 and 72 hours to evaluate their microstructural stabilities. For each test condition, i.e., a combination between temperature and time, a single sample was used, which means that 12 samples were tested.

The samples were cut and polished at top surface for X-Ray Diffraction (XRD) analysis, using CuKα radiation. The morphology and local chemical composition (EDS) of precipitated phases were analyzed using scanning electron microscope (SEM). For global analysis an area of 8 mm$_2$ was used, while for each constituent punctual areas were selected.

Hardness evaluation of coatings was carried out on Vickers hardness test equipment with a load of 49 N and the average values correspond to a series of 5 measurements.

RESULTS AND DISCUSSION

As-deposited coatings

Table 1 shows the chemical compositions of the as-deposited coatings. One can note that elements content in the L-Al and H-Al coatings are similar after deposition, and that the differences in the aluminum content in the deposited powder mixtures were reduced to a 10%. This fact is caused by the dilution (~40%), in which the elements of substrate are incorporated in the coating, particularly iron and chromium.

Local chemical composition assessed by EDS showed no significant differences between L-Al and H-Al specimens, considering dendritic and interdentritic regions, as presented in Table 2. For both coatings richer Cr and Fe interdentritic region can be identified.

Table 1. As-deposited chemical composition (EDS) obtained for 8 mm^2 area (% mass).

	L-Al	*H-Al*
Al	18.8	20.4
Si	1.13	0.79
Mo	0.48	0.35
Cr	13.2	12.9
Mn	0.92	0.99
Fe	25.3	26.1
Ni	40.3	38.5

Table 2. Chemical composition (EDS) of dendritic and interdendritic regions for L-Al and H-Al coatings (% mass).

% mass	L-Al		H-Al	
	Dendritic (β)	Interdendritic	Dendritic (β)	Interdendritic
Al	24.8	12.3	28.1	11.2
Cr	7.8	**16.0**	7.8	**19.0**
Fe	18.7	**31.3**	19.1	**34.7**
Ni	46.8	38.6	43.3	32.9

The hardness of as-deposited coatings is 299 HV for L-Al and 328HV for H-Al. The H-Al coating presents a higher volume fraction of dendritic phase, composed by the intermetallic β−NiAl (Fig. 1). Although in a previous investigation [6] the interdendritic region was identified as either a solid solution (γ) or the γ'-Ni₃Al intermetallic phase, in this study evidences corroborate with the hypothesis that this region is a solid solution. A higher corrosion resistance of an intermetallic phase is expected which goes against the experimental evidences of the corrosion after electrochemical attack [6]. Further, a detailed chemical analysis by EDS and XRD of thermal exposed specimen that are shown later in the current investigation will not support the possibility of existence of an intermetallic as a second phase constituent.

For two-phase nickel aluminides alloy, a higher volumes fraction of β phase is able to promote an increase in strength at room temperature [2]. Previous study [6] shows that the L-Al coatings presented carbides in the as-deposited condition.

Considering a hardening effect due to the presence of either chromium carbide or NiAl constituent, a possible compensation effect might explain the similar values of hardness.

Microstructural stability
Figure 2 shows the hardness variation after exposure to temperature.

As a general observation, the coating with higher aluminum content is harder than that with the lower content regardless of the testing conditions. It is an important fact, considering that in both coatings no cracks were observed, different from the previous study [6] with L-Al coating processed under 100 A. The observed trends in hardness variation with exposure time were similar for both coatings, i.e., for a same temperature, when a coating harden or soften, the other repeat the same tendency along the time.
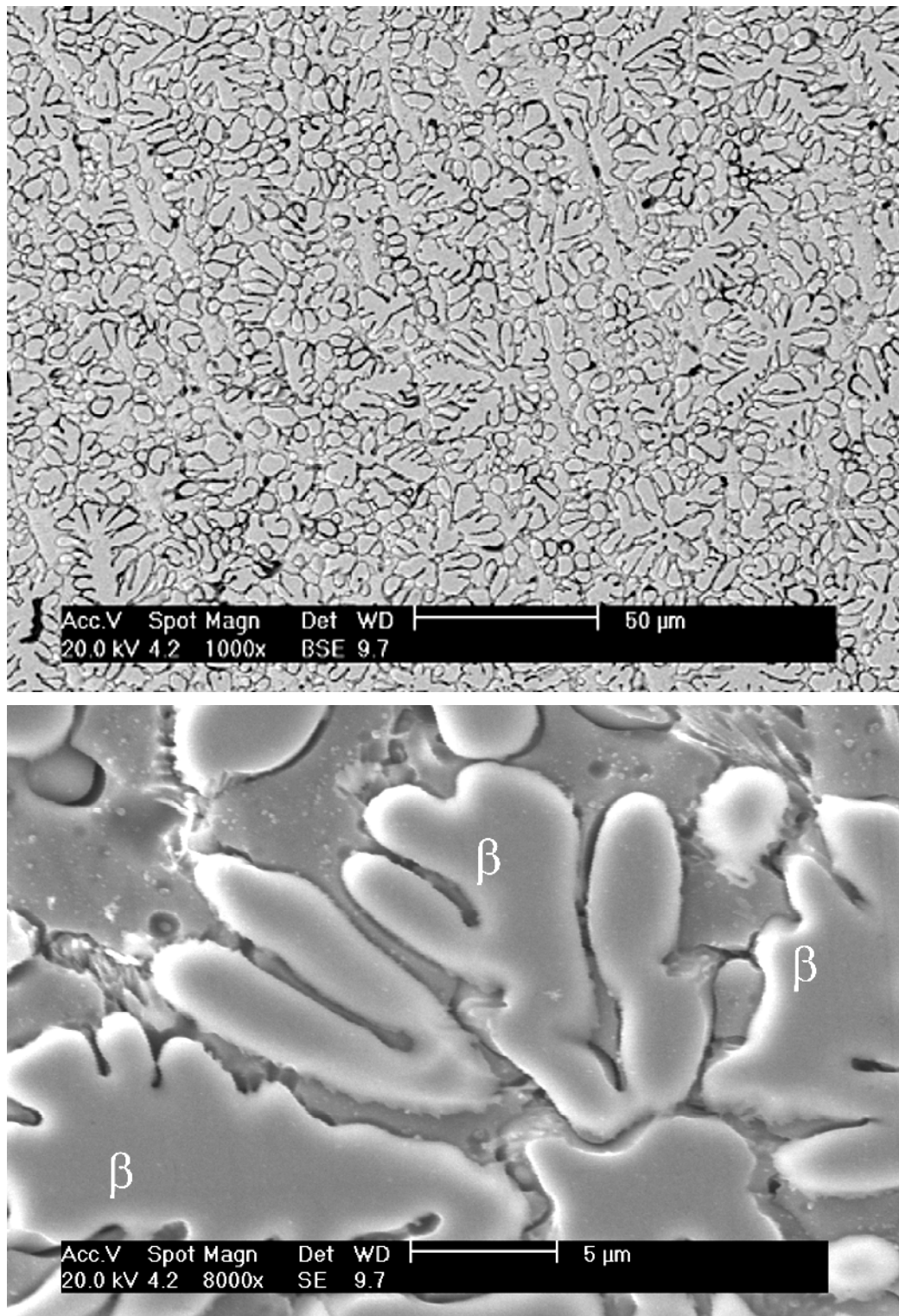
Fig. 1. (a) Microstructure of as-deposited H-Al nickel aluminide coating. (b) Zoom of image (a), showing a large volume fraction of β phase.
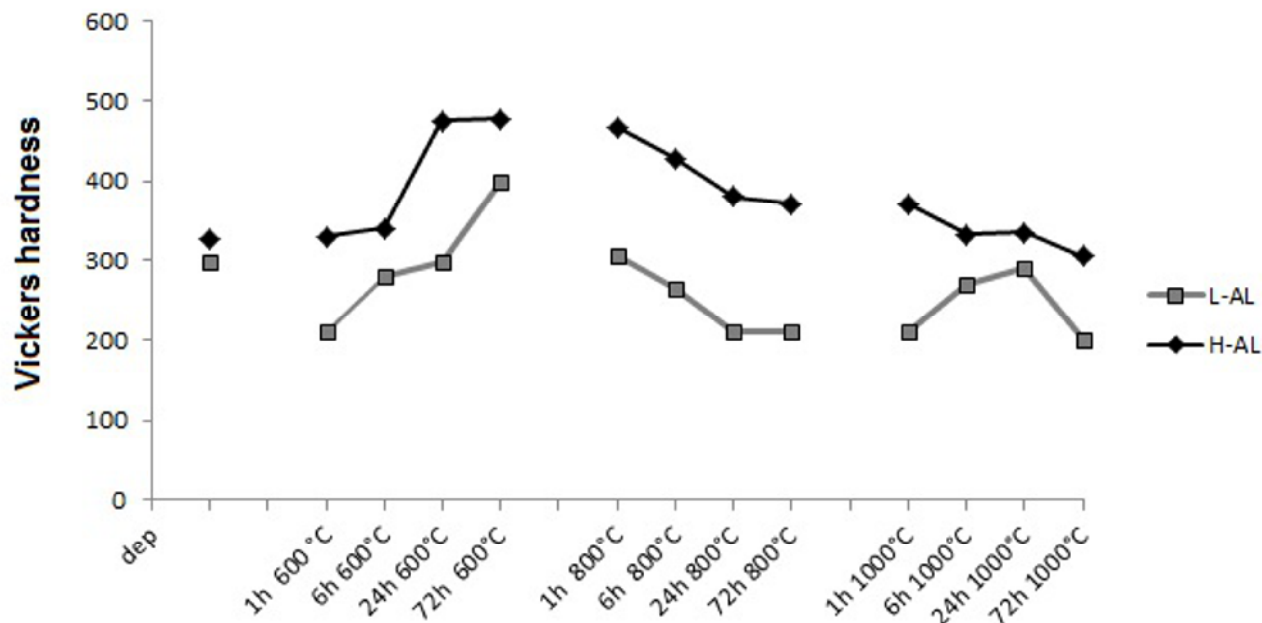
Fig. 2. Hardness variations of L-Al and H-Al coatings deposited by PTA with different isothermal exposure conditions.

The observed variations in hardness are dependent on the microstructural changes. Fig. 3 presents selected microstructures to illustrate this behavior.

Comparing figs. 3a and 3b a more refined microstructure of L-Al coating after thermal exposure to 600 ºC for 6 h is observed. Nonetheless, the H-Al is harder than L-Al coating, suggesting that this was not the main factor contributing to the coating hardness.

Exposure to increasing temperature figs. 3c and 3d, revealed the presence of a precipitate. It is revealed in a relatively low volume fraction at 800 ºC (Fig. 3c) and finally, at 1000 ºC, it coarsens and appeared to have spread into whole microstructure (Fig. 3d). In fig. 3d, it is

possible to observe that some precipitates were pulled out during the metallographic preparation (grinding step). Since this occurrence influences the EDS analysis, samples exposed to 1000 ºC for a reduced time, 6h, were used in subsequent analysis.

A detailed analysis of the precipitates observed following exposure at 600 ºC and at 1000 ºC was carried out (Fig. 4) shows the precipitate at the interface and its composition. Considering the precipitate local chemical composition and the hardness after thermal exposure (~500 HV), the most probable constituents in this case are either carbide or sigma phase, as stated for L-Al coating.
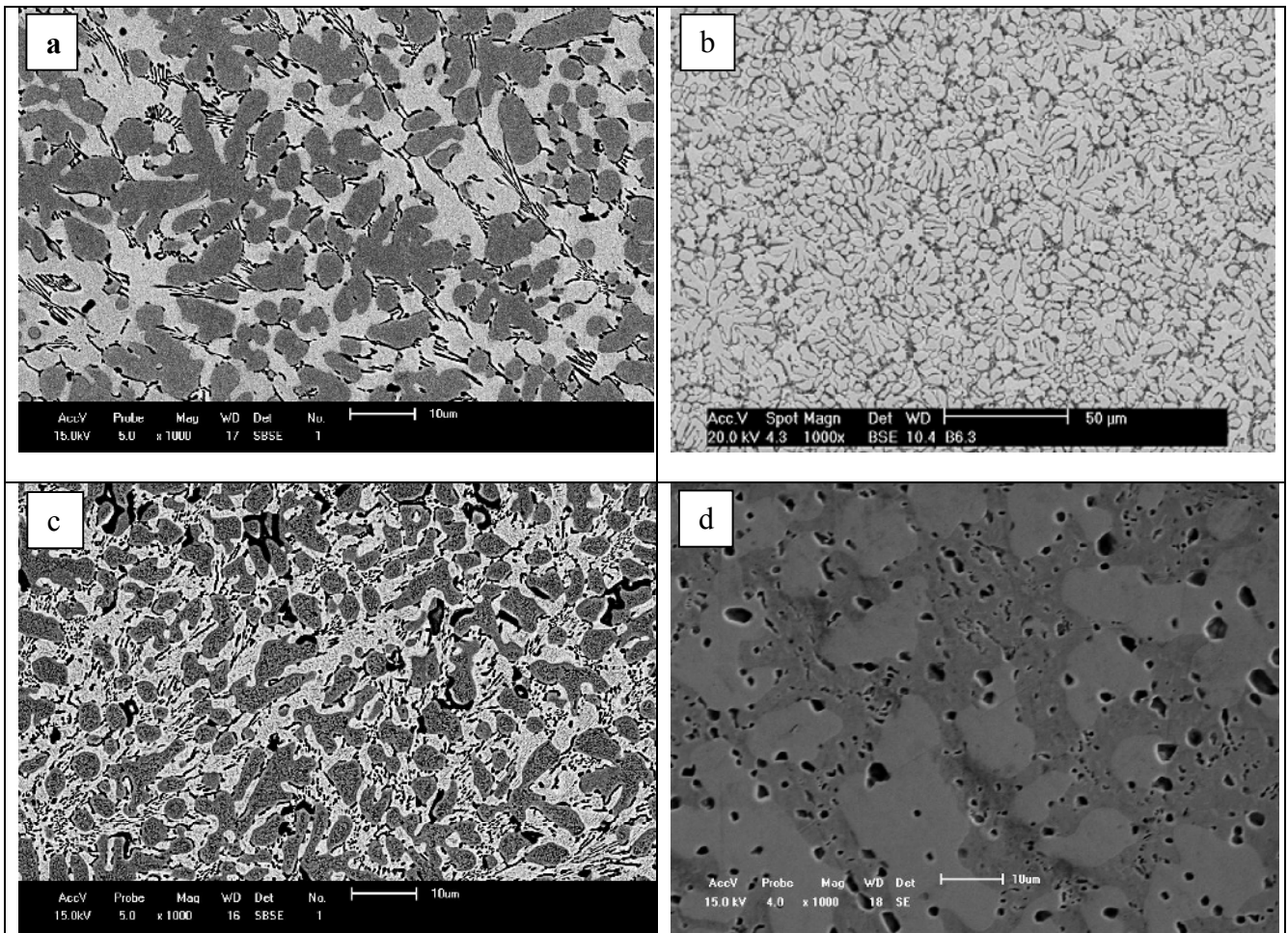
Fig. 3. Microstructures of nickel aluminides PTA coatings revealed in SEM: (a) H-Al submitted to 600 ºC for 6 h; (b) L-Al submitted to 600 ºC for 6 h; (c) H-Al submitted to 800 ºC for 72 h; and (d) H-Al submitted to 1000 ºC for 24 h.

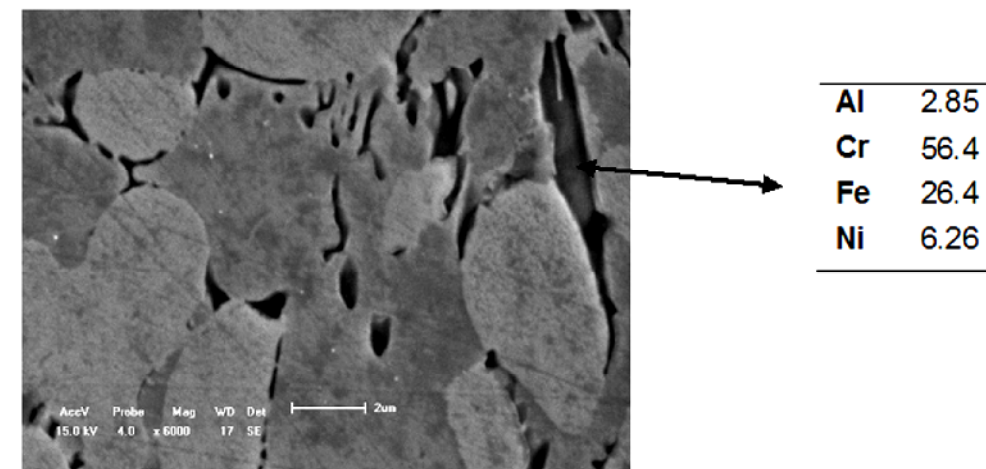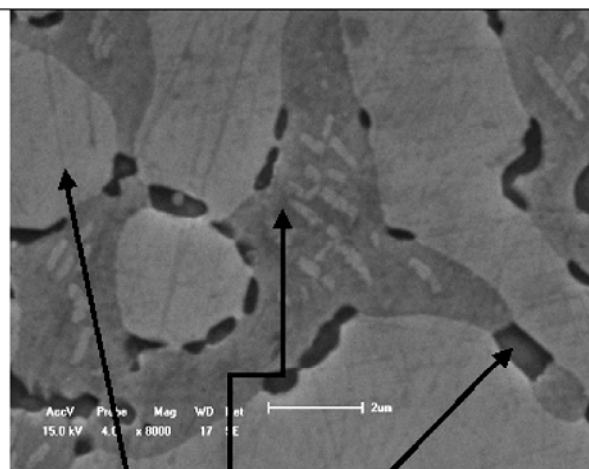| Al | 2.85 |
Cr	56.4
Fe	26.4
Ni	6.26

Fig. 4. EDS analysis (% at.) of a precipitate observed in H-Al coating after thermal exposure at 600 ºC for 72 h.

The detailed analysis of the microstructure and of main elements of the H-Al coating after exposure at 1000 ºC

for 6 h is shown in fig. 5.

	A	B	C
Al	30.8	7.41	10.3
Cr	3.65	26.0	44.7
Fe	10.9	39.2	16.7
Ni	52.9	24.8	22.9

Fig. 5. EDS analysis (% at.) on three different regions of microstructure of H-Al coating after thermal exposure at 1000 ºC for 6 h.

Figure 5 shows that the Cr-rich precipitates are located at the interface of the β-NiAl phase. For a longer time of exposure, the residual chromium content in all coating is enough to increase the volume fraction of these precipitates, as observed in Fig. 3d.

Similar microstructure to the one described in Fig. 4 was observed by García Barriocanal et al. [8] after annealing at temperatures between 750 and 1100 ºC for different times. According to these researchers, the precipitation of

Cr-rich phases is favored by the low solubility of Cr in γ'-Ni_3Al and β-NiAl.

In region B, there was a large increase in the iron content, as opposed to that measured in β-NiAl (region A). These microstructural changes led to a decrease of the volume fraction of β-NiAl. After exposure at 1000 ºC for 6 h, X-Ray diffraction is not able to detect the volume fraction of Cr-rich precipitates, but an increase in the volume fraction of austenite phase was observed (Fig. 6).
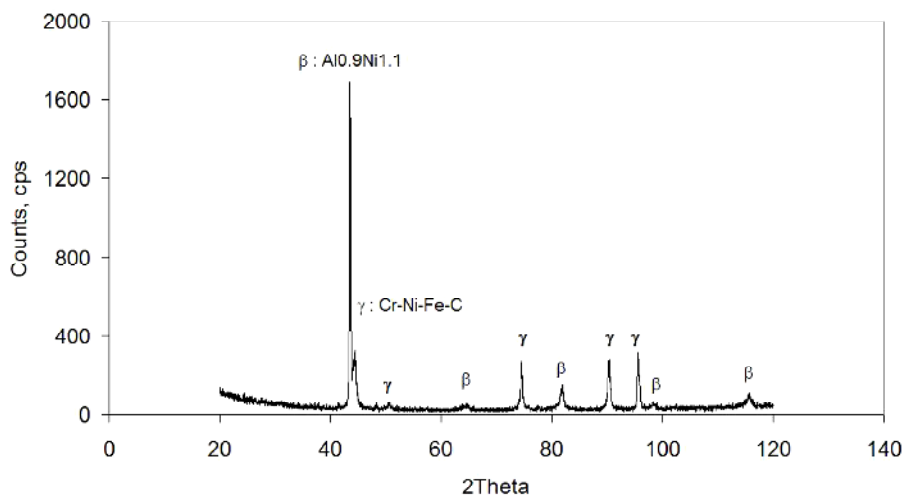

Fig. 6. XRD spectrum of H-Al coating after thermal exposure at 1000 ºC for 6 h.

Results indicate that the major contribution to hardness is given by the β-NiAl. The increase in the volume fraction of highly alloyed austenite by itself can not account for the coating hardness reduction. Also the presence of the Cr-rich precipitate does not seem to be sufficient to increase or maintain the measured hardness, suggesting that it could be a low hardness phase. It could be the Chi-phase, as reported by Fischer et al. [9], because this Cr-rich phase can contain larger contents of aluminum (> 10% at.). The hypothesis that a relatively soft precipitate occurred in H-Al coating is put forward which is a very different reasoning of a previous investigation for L-Al ones.

CONCLUSIONS

Based on the abovementioned results, the following conclusions can be put forward:

- In two-phase nickel aluminide coatings (β + γ) the aluminum content affected the amount of intermetallic β-NiAl constituent, and this effect contributed to different responses to thermal exposure,

- In coatings with high aluminum content a formation of a relatively soft Cr-rich precipitate was detected after thermal exposure, and

- The studied coatings have a low microstructural stability although their hardness values were equivalent of that reported for as-deposited condition.

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