OXIDE EVOLUTION AFTER ISOTHERMAL OXIDATION OF Ni AND Ni-Cr ALUMINIZED SURFACE

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Abstract. *Aluminization is a diffusive process for surface enrichment with aluminum. It aims at forming a protective oxide layer which protects the substrate against oxidation and that is powered by an inter-diffusion layer consisting of Nickel Aluminides. The aluminizing procedures include two steps: (1) thermochemical pack cementation treatment for diffusion of Al and formation of aluminides, (2) pre-oxidation stage to form an alpha alumina layer. The latter depends on the composition of the substrate and pack cementation parameters that can compromise the development of a stable oxide layer. This work is part of an ongoing project and it aims to characterize the oxides formed on the aluminized surface of Ni-50Cr-2Nb alloy and a Ni based alloy after isothermal oxidation. Specimens were aluminized at 950ºC for 6h in and controlled atmosphere furnace and pre-oxidized in an air furnace at 1100ºC for 1h. 8 hours isothermal oxidation tests were carried out at 700, 825, 950, 1075 and 1200ºC. Vickers microhardness profiles and laser confocal microscopy characterized the transverse cross section of aluminized samples. Oxides were characterized by low angle X-ray diffraction (XRD), and Raman spectroscopy. Aluminized samples exhibit a layer of beta-Ni and also Cr aluminides. After pre-oxidation at 1100ºC, a more complex set of oxides were identified including alumina Ni oxide, Cr2O3 oxide and the NiCr2O4 spinel. Differences in chemical composition seems to be directly influence the ability to form a film of alpha-Al2O3 during the isothermal oxidation, which reinforces the idea that some characteristics of these surfaces (phases formed and the Al layer thickness aluminized) may make them more or less susceptible to oxidation.*

Keywords: *Aluminization, Oxidation, Nickel Alloys*

1. INTRODUCTION

One of the challenges associated with the durability of mechanical components is oxidation. In order to protect against oxidation and thus the in-service performance, coatings can be applied by various techniques. Aluminizing is a thermochemical treatment during which the surface of the component is enriched in Al and an alumina layer is formed. The procedure involves a two-step operation where the first step refers to the cementation step and the second step refers to the oxidation of the surfaces; the latter guarantees that a stable and adherent alpha alumina layer is formed (YUAN *et al.*, 2010). Different aluminizing techniques are available among which pack cementation (pack aluminizing) is a very competitive procedure, given its low cost and versatility of applications (CHOUX *et al.*, 2007). Several researches have been dedicated to study whereby the influence of aluminization parameters under the formation of subsequent aluminized layer (GOWARD, 1998). In recent work Rafiee *et al.* (2010) conducted a study of the influence of temperature and aluminum concentration during aluminizing for nickel-based superalloy IN738LC. The results indicate the existence of two distinct mechanisms of diffusion for these different temperatures (850ºC and 1050ºC) conditions. As a consequence of the diffused layer thickness is dependent on these parameters tested, as expected.

Extensive studies have also been devoted to the research of the development of alumina films (GONZÁLEZ-CARRASCO *et al.*, 1999). Prescott and Graham (1991) presented a review relating to the formation of alpha alumina in alloys of Fe, Co and Ni at elevated working temperatures. In this work, emphasis is placed on the proposed mechanisms of scale growth based on observations of scale morphologies and microstructures, inert-marker experiments and the distribution of oxygen isotope tracers within thermally-grown oxides. Choux *et al.* (2007) performed isothermal and cyclic oxidation (temperatures of 900°C, duration 100 hours) of pure nickel. Their data show a diffusion layer and two other intermediate layers with very specific concentration distributions. Studies isothermal and cyclic oxidation were also developed by Tolpygo and Clarke (1998) for a Fe-Cr-Al. Among the causes for separation of the surface oxide of the base metal in isothermal oxidation at 1000°C can be associated with the presence of impurities or, more commonly, the resulting stresses at the contact surface metal-oxide. In cyclic oxidation conditions are reached the extreme case of complete peeling of the oxide.

Despite all the work previously published studies related to the oxidation of aluminized alloys remains an issue of great interest due to its influence on the lifetime of components used in high temperatures (LEYENS *et al.*, 1995). This work assessed the evolution of oxide film formed on aluminized Ni alloys after isothermal oxidation.

2. MATERIALS AND PROCEDURES

Two Ni based alloys with different Cr content, identified as Ni gamma prime and NiCr2Nb alloy, were processed by pack aluminizing. Chemical composition of the alloys is shown in Tab.1 and Tab.2.

Table 1 – Chemical composition of the Alloy identifies as Ni gamma prime

Ni	Bal	Al	2,80-3,20	Zr	0,03-0,10	Ti	4,80-5,20	Ta	0,10	Nb	0,10
Cr	13,70-14,30	Fe	0,35	Hf	0,10	Mo	3,70-4,30	Si	0,10	Cu	0,10
Co	9,00-10,00	C	0,19	V	0,10	W	3,70-4,30	Mn	0,10	B	0,01-0,02

Table 2 – Chemical composition of the alloy identified as NiCr2Nb

Ni	47,67	Cr	48,68	Nb	1,65	Fe	0,82	Si	0,76	Al	0,31	Co	0,12

The alloys were processed using above the pack procedures where samples (5 mm x 7 mm x 2 mm) rest on a grip above the pack avoiding direct contact with the pack mixture. Pack aluminizing parameters were set constant according to the parameters on Tab. 3.

Table 3 – Processing parameters used for pack cementation and subsequent surface pre-oxidation

Pack mixture	Source: 20%Al; Halide activator: 3%NH_4Cl; Inert powder: 77%Al_2O_3
Cementation Temperature	Argon furnace: 950°C
Cementation time	Argon furnace: 6h
Pre-Oxidation	Air furnace: 1h at 1100°C

Surfaces were characterized by XRD, chemical composition analyzed by XR spectroscopy, Laser confocal microscopy and Scanning Electron microscopy.

In order to evaluate the oxidation behavior tests were performed as summarized in the Tab.4.

Table 4 – Processing parameters used for isothermal oxidation tests

Oxidation Temperature	Air furnace: 700-1200ºC
Oxidation Time	Air furnace: 8h

The Ni alloys were placed inside individual non-sealed porcelain crucibles in a furnace and heated to temperature at 20°C/min. The cooling was performed in the furnace down to 150°C. The effect of oxidation was evaluated by mass variation on a precision balance. Additional analyzes were performed by Raman spectroscopy.

3. RESULTS AND DISCUSSION

3.1 Pack Cementation

The impact of the chemical composition of the Ni based alloy on the response to pack aluminizing is summarized in Fig. 1 for data acquired immediately after pack cementation and before pre-oxidation. The Ni gamma prime alloy, which had more alloying elements, exhibited a richer Al surface compared to that measured on the surface of NiCr2Nb alloy. However the opposite trend is observed regarding the aluminized surface thickness; thinner layers were observed in Ni gamma prime than NiCr2Nb alloy, suggesting that the latter has more diffusion paths that facilitate the diffusion of Al into the material.

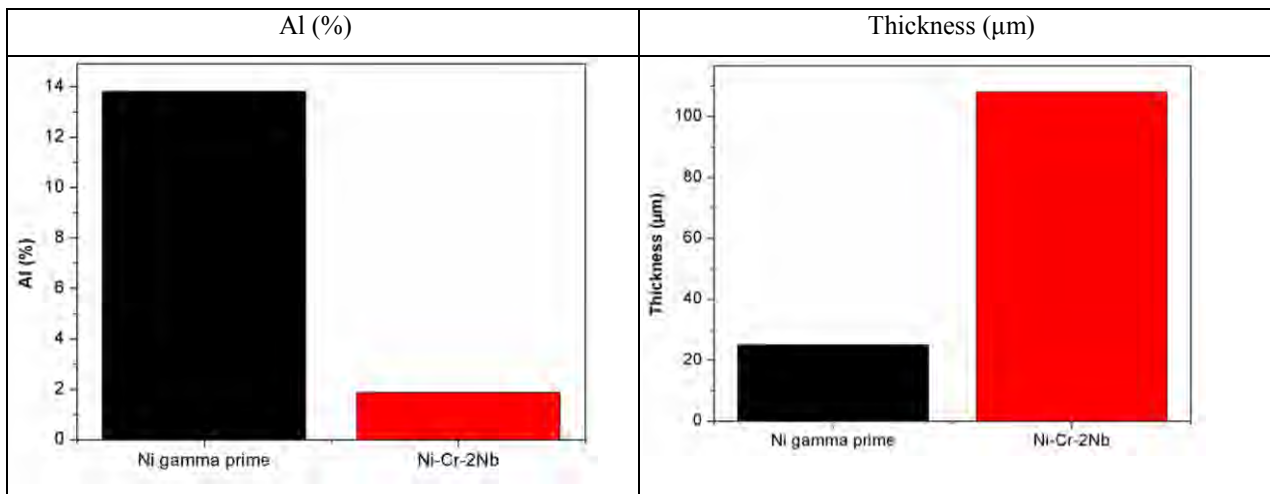| Al (%)	Thickness (μm)

Figure 1. Effect of cementation time and temperature on the aluminized surface measured by the thickness and composition of the diffusion layer.

X-ray diffraction, Fig.2, confirmed that the interaction of the Al with the different substrates used has influenced constitution of the diffusion layer: (a) Ni gamma prime alloy: NiAl, Ni_3Al, Ni_2Al_3 (main phases), and Cr aluminides; (b) NiCr2Nb alloy: more complex set of phases besides of Ni (Ni_3Al, Ni_2Al_3) and Cr (Cr_2Al_{13}, Cr_5Al_8) aluminides, the spinel $NiCr_2O_4$ were also identified.
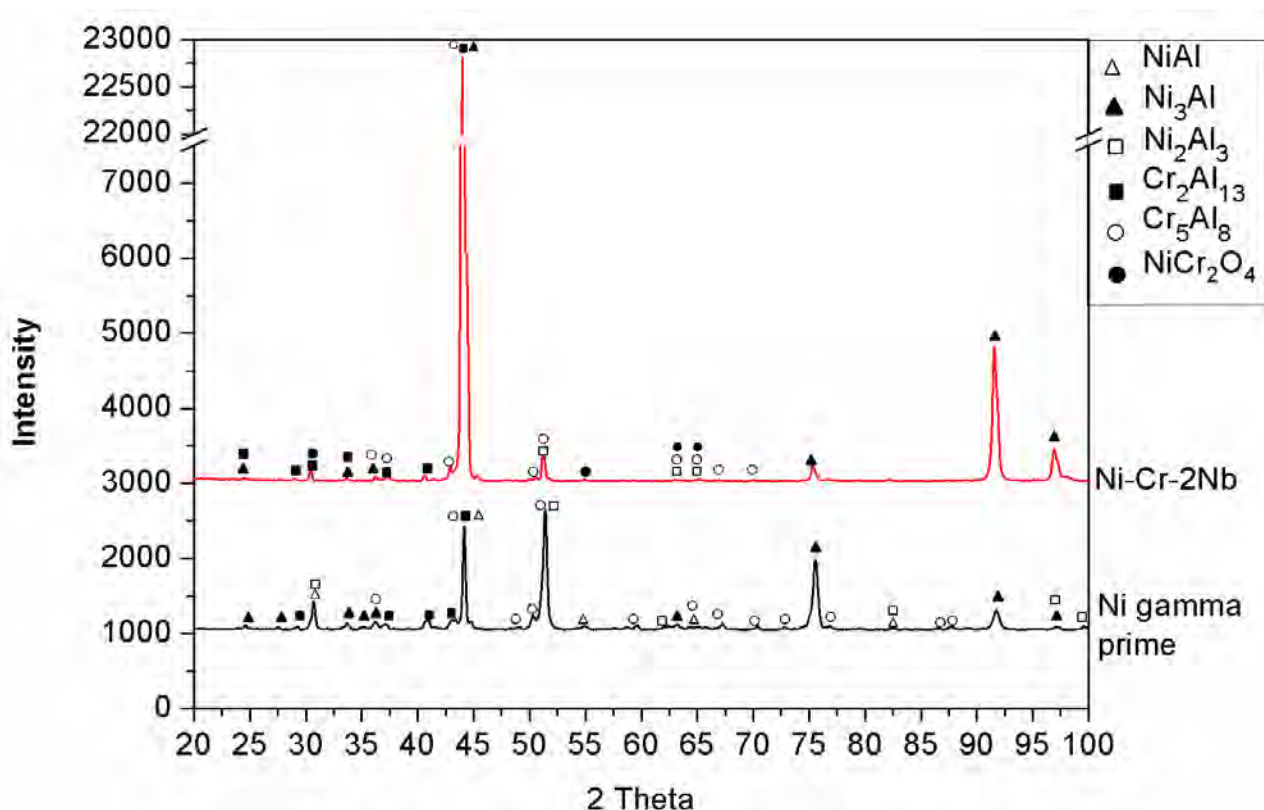
Figure 2. Compounds formed in the diffusion layer for both Ni based alloys processed with increasing cementation time

Detailed analysis of the oxide layer formed before and after pre-oxidation gives further information on the influence of the chemical composition of the substrate, Fig.3 and Fig.4. Results of low angle X-ray diffraction showed that a complex set of oxides was identified before pre-oxidation for both alloys.
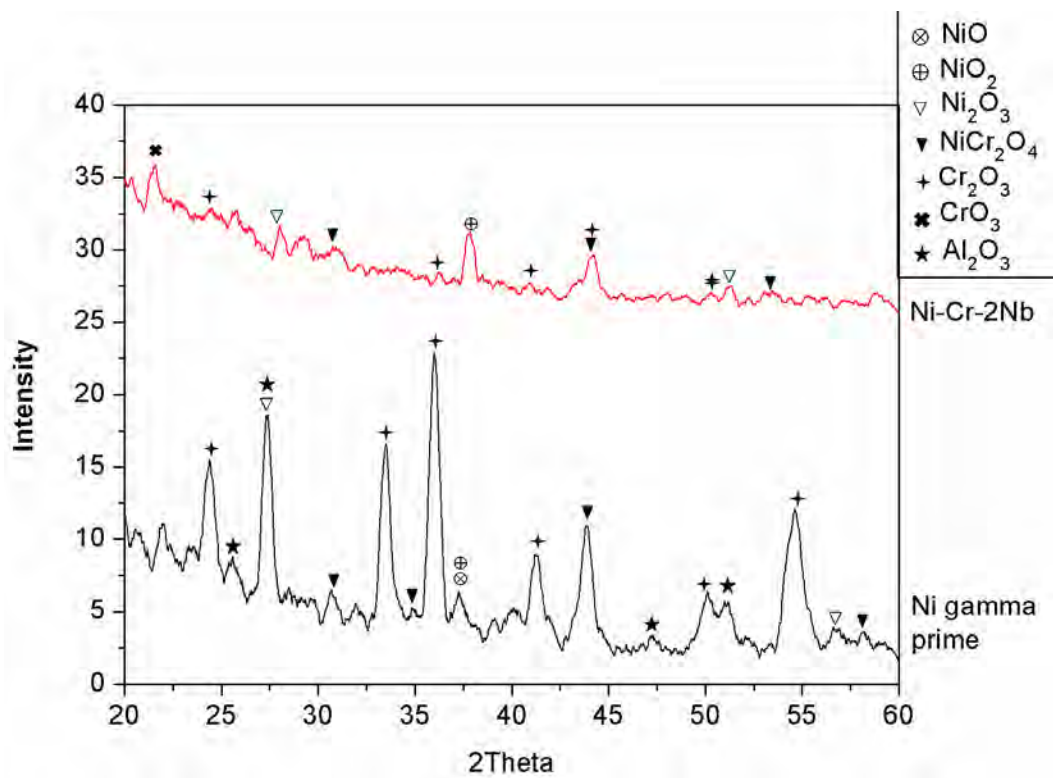
Figure 3 – Oxides formed at the surface after pack cementation, identified by low angle X-ray diffraction
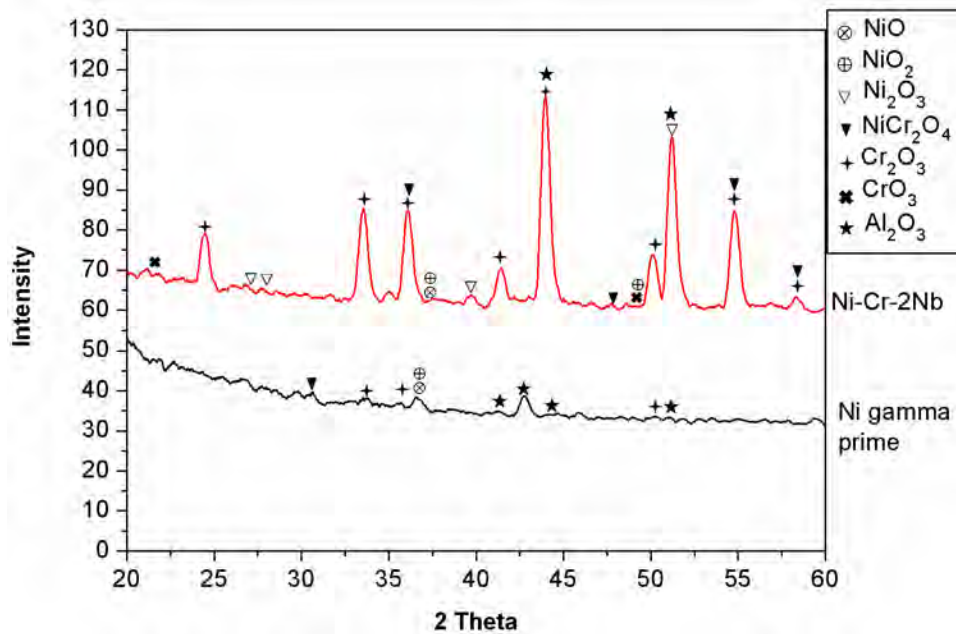

Figure 4 – Oxides formed at the surface after pack cementation and after pre-oxidation step, identified by low angle X-ray diffraction

Pre-oxidation temperature was selected to favor the formation of the stable and adherent alpha alumina. After pre-oxidation, although both alloys show peaks of alumina differences could be observed. For the Ni gamma prime alloy there is a decrease on the intensities of the peaks of other oxides, suggesting a trend for the alumina film to develop and overlapping other oxides, in accordance to its thermodynamic stability. A different response to the pre-oxidation step was identified on NiCr2Nb alloy the presence of a complex set of oxides is identified, in particular Alumina and Chromia. It suggests that exposing these surfaces to oxidation environments would cause the non-uniform

development/growth of the oxide film which my lead to cracks initiation or spalling of the oxide film. Alpha alumina as confirmed by Raman spectroscopy on both Ni based alloys after the pre-oxidation stage.

3.2 Oxidation

Raman Spectroscopy revealed that under the pre-oxidation temperature range specimen has α-Alumina. However, as revealed by XRD the presence of other oxides might influence on the oxidation behavior.

Figure 5 shows the variation of weight during exposition under temperature oxidation tests. Results show that the aluminized Ni gamma prime alloy has a stable oxidation behavior within the temperature range tested. The mass loss after oxidation at $700^{o}C$ does not change for the higher temperatures tested suggesting that a stable film of oxide with a very low growth rate was formed. A very different behavior with a strong dependence on the oxidation temperature was identified for the pack aluminized NiCr2Nb alloy. At the lower temperature test, $700^{o}C$ mass loss was identified and at the higher temperature tested a significant mass gain was measured. At the lower end of the temperature range tested stress induced by the different oxides can cause the oxide film to break. However, the significant mass gain at $1200^{o}C$ suggests that the alumina film is still growing. This behavior might be associated with vaporization of certain oxides or to spalling due to the competitive growth of different oxides that exposes the pack aluminized surface to air inducing the formation of more oxide.
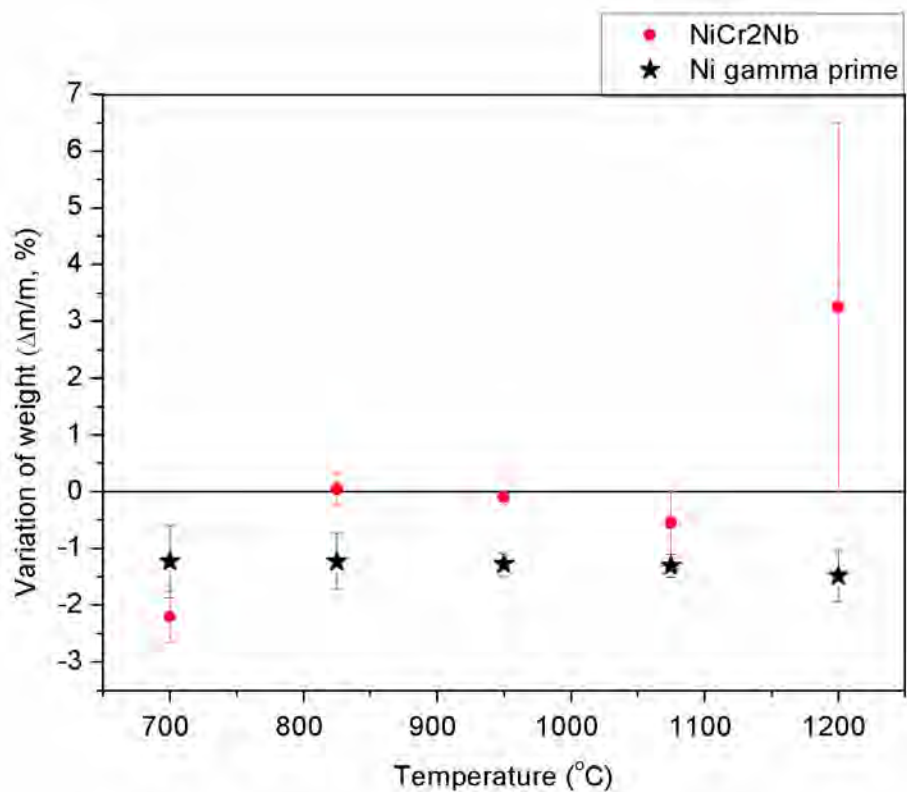

Figure 5 – Variation of weight with increasing temperature oxidation (time oxidation = 8 h)

4. CONCLUSIONS

As expected, the substrate influences the morphology and thickness of the diffused layer, as well as its phases and composition, after pack cementation (GOWARD, 1998). The Ni gamma prime alloy, which had more alloying elements, exhibited thinner layers and richer Al surface than NiCr2Nb alloy, suggesting that the latter has more diffusion paths that facilitate the diffusion of Al into the material. The main phases formed on the Ni gamma prime were Ni aluminide ($NiAl$, Ni_3Al, Ni_2Al_3), beyond Cr aluminides; while for NiCr2Nb alloy besides of Ni (Ni_3Al, Ni_2Al_3) and Cr (Cr_2Al_{13}, Cr_5Al_8) aluminides, the spinel $NiCr_2O_4$ were also identified.

The substrate also influences the oxides formed after pack cementation and after pre-oxidation. After pre-oxidation, although both alloys show peaks of alumina, for the Ni gamma prime alloy the results suggest there is a trend for the alumina film to develop and overlapping other oxides, whilst on NiCr2Nb alloy the presence of a complex set of oxides is identified, in particular Alumina and Chromia.

Differences in behavior of oxidation for both alloys, measured by variation of weight at the temperature of oxidation range, indicate that the formation and growth of the oxide film is also strongly influenced by layer aluminide and scale oxide the previously formed. The NiCr2Nb alloy was more sensitive test conditions than Ni gamma prime, which may indicate the formation of discontinuous film of alumina.

Additional studies will be conducted regarding the thermodynamic of growth of oxide.

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