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## PACK ALUMINIZATION PROCESS OF HEAT RESISTANT FeCrAl AND NiCr ALLOYS

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**Abstract:** Pack aluminization process is one of the possible production methods to improve oxidation resistance at high temperatures of various types of metallic materials. It is a chemo-thermal process where products are embedded in the powder mixture, consisting of Al powder, halide activator  $\text{NH}_4\text{Cl}$ , and inert diluent  $\text{Al}_2\text{O}_3$  powder, and annealed at high temperature. This exposure to high temperature causes the Al diffusion into the base material and formation of the aluminide surface layer. During the component service at elevated temperatures, the oxidation resistance is obtained due to the constant formation of an aluminium oxide film that forms on the aluminide surface layer and acts as an oxygen impermeable barrier. In the present study, FeCrAl and the NiCr heat resistant alloys in the form of 1 mm thick sheet were aluminized at various process parameters. The effect of time, temperature, concentration of aluminium and halide activator in the powder mixture as well as the influence of furnace atmosphere on coating formation mechanism, mass gain and the thickness of the aluminide diffusion layer was evaluated by scanning electron microscopy, X-ray photoelectron spectroscopy and micro hardness analytic techniques. Isothermal exposure tests at 1200 °C for 24h in air were conducted and compared with untreated samples for high temperature oxidation resistance estimation.

**Keywords:** Aluminizing, heat resistant alloys, FeCrAl, NiCr, high temperature oxidation

### INTRODUCTION

Aluminizing is a widely used process to protect materials, particularly metals and alloys against high temperature oxidation and hot corrosion attack. In this process the metal to be coated is placed in a powder pack consisting essentially of the coating element source such as pure aluminium or aluminium alloy (Cr-Al), an activator such as halide salts  $\text{AlF}_3$ ,  $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{F}$  and an inert filler material, usually alumina [1]. The process is carried out at atmospheric pressure in flowing hydrogen or in an inert atmosphere at a temperature between 700 °C and 1150 °C. The aluminizing process can be divided into three steps: (a) gaseous diffusion, (b) surface reaction and (c) solid diffusion. At the coating temperature halide activator reacts with the metal elements in the powder pack and form a series of metal halide vapour species with characteristic partial pressure distribution that is determined by their thermodynamic stability in a particular powder pack. The coating is formed via reduction reaction of metal halide vapours at the substrate surface and subsequent solid state diffusion between metal elements and substrate [2,3].

The thermodynamics and kinetics of the aluminizing process are defined by the pack components and operating conditions like temperature, time and atmosphere [4]. Two critical issues for the application of aluminide coating have been identified: (i) loss of Al from the coating into the substrate which limits coating lifetime, (ii) the difference in thermal expansion coefficient (CTE) between aluminide

coating and the substrate, which can cause mechanical damage (cracks) to the coating [5].

### EXPERIMENTAL PROCEDURE

The substrate alloys used in this study were a commercial ferritic alloy Fe-Cr-Al (Kanthal AF) and a commercial austenitic alloy Ni-Cr (Microthal 80); the composition is listed in Table 1.

Table 1. Chemical composition of the coated alloys in wt.%.

Alloy	Ni	Cr	Fe	Mn	Si	Al	Ti
Kanthal AF	0.4	21.0	Bal.	0.2	0.2	5.5	1.0
Microthal 80	Bal.	20.0	1.0	0.5	1.3	-	-

Flat coupons (20 x 10 x 0.7 mm) were ultrasonically cleaned in an alcohol, dried and immediately embedded in a powder pack, which consist of the deposition element (Al), an activator ( $\text{NH}_4\text{Cl}$ ) and an inert filler ( $\text{Al}_2\text{O}_3$ ), and semi-sealed in alumina crucible. The crucible is heat treated in a tube furnace under an Ar-5% $\text{H}_2$  atmosphere. Process parameters of the aluminizing process are process time, process temperature and the powder pack. The coating time was varied from 0.5 to 2.5 hours and the process temperature from 670°C to 750°C. The heating rate was 10°C/min and the cooling rate from the process temperature to 200 °C was 5 °C/min. The Al to  $\text{NH}_4\text{Cl}$  mass ratio in the powder mixture was 3 (21 wt.% Al, 7 wt.%  $\text{NH}_4\text{Cl}$ , 72 wt.%  $\text{Al}_2\text{O}_3$ ) for all aluminizing experiments. Coated specimens were cleaned with a brush and then put into ultrasonic bath and cleaned in an alcohol.

Cross sections of samples for microstructure observations were prepared by standard metallographic preparation by

grinding and polishing. Optical microscope AXIO CSM 700 and scanning electron microscope Jeol JSM 5610 with energy dispersive X-ray spectroscopy (EDS) were used for the microstructure observations.

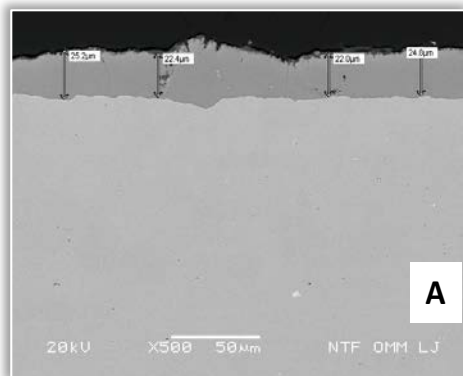
The phase constitution of the as deposited coatings was examined by X-ray diffraction (XRD), using Cu K $\alpha$  radiation. The oxidation resistance of the samples was investigated under isothermal conditions by thermobalance Netzsch STA 429 at 1200 °C, 24 h in a laboratory air atmosphere. Samples were heated at a rate of 20 K/min, followed by cooling at the rate 20 K/min.

## RESULTS AND DISCUSSION

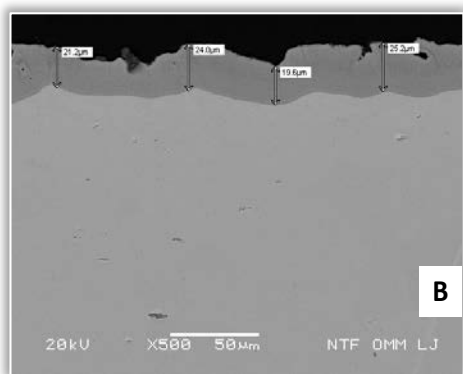
### Coating thickness as a function of time and temperature

Aluminium was successfully deposited onto Fe-Cr-Al and Ni-Cr alloy in the form of 0.7 mm sheet through the halide activated aluminizing process at different coating temperature and time. The coatings show some irregularities and a small pore size but are free of cracks. The number of irregularities in coatings increases with coating temperature. After aluminizing, coating thickness measurements were performed at various sites.

Figure 1 shows the SEM cross sections of aluminide coatings on Fe-Cr-Al and Ni-Cr alloy deposited at 670 °C for 1.5h and Figure 2 aluminide coatings on both alloys deposited at 730 °C for 1.5 h. The aluminide coating is thicker in the case of Fe-Cr-Al alloy because of a higher diffusion rate of Al in Fe-Cr-Al alloy, especially at higher temperature.

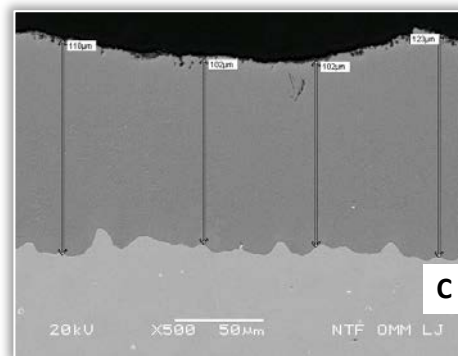


(A)

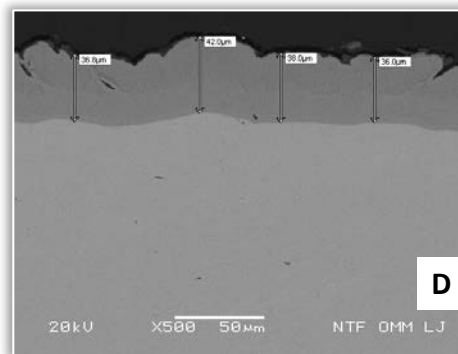


(B)

Figure 1. SEM image of FeCrAl (A) and NiCr alloy (B) aluminized at 670°C, 1.5 h



(C)



(D)

Figure 2. SEM image of FeCrAl (C) and NiCr alloy (D) aluminized at 730°C, 1.5 h

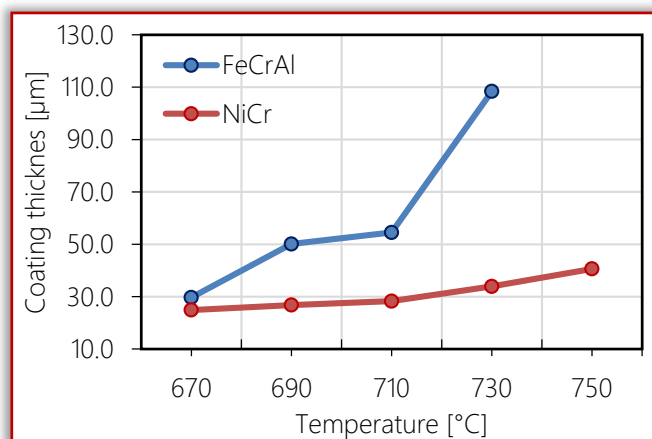


Figure 3. The average aluminide coating thickness as a function of aluminizing temperature at a constant annealing time 1.5 h

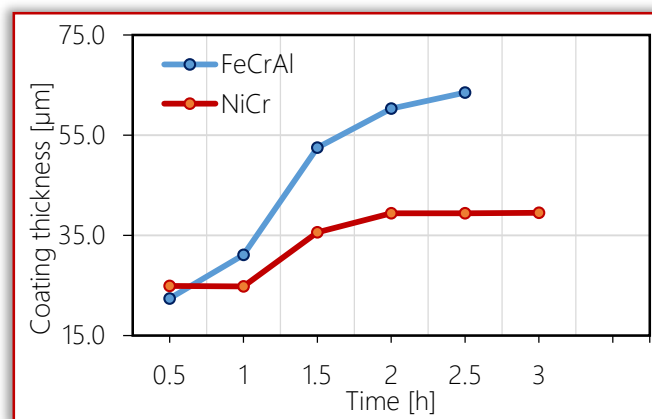


Figure 4. The average aluminide coating thickness as a function of time at a constant temperature 690 °C

Figure 3 shows the average coating thickness as a function of coating temperature at constant time. The data points for each coating temperature demonstrate that as the coating temperature is increased, the coating thickness increased. With an increase in aluminizing temperature from 670 °C to 730 °C at constant coating time 1.5 h, the coating thickness is increased threefold for Fe-Cr-Al alloy and thirty percent for Ni-Cr alloy. Figure 4 shows the average coating thickness as a function of coating time at constant temperature 690 °C. The thickness of the coating increase with time from 0.5 to 3 h for both alloys. Increase in thickness was much higher for Fe-Cr-Al alloy.

### Scanning Electron Microscopy (SEM/EDS)

Chemical analysis of coating and substrate subsurface were performed by energy dispersive spectroscopy (SEM-EDS). Figure 5 shows the representative sample subjected to the coating temperature of 730 °C for 1.5h for the Fe-Cr-Al alloy and Figure 6 for the Ni-Cr alloy. Coating thickness ranged from 100 to 120 μm for Fe-Cr-Al alloy and 30 to 45 μm for Ni-Cr alloy.

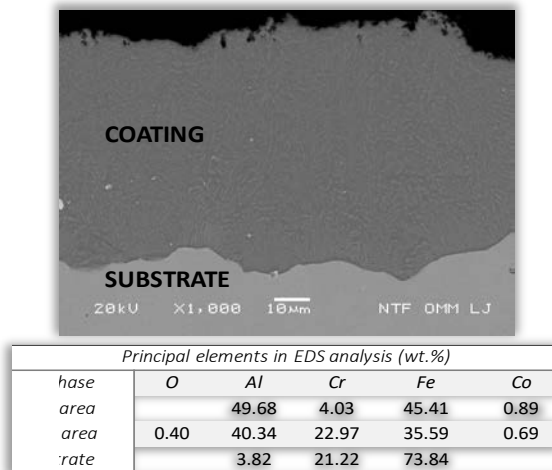


Figure 5. SEM-EDX analysis of Fe-Cr-Al coated at 730 °C for 1.5 h

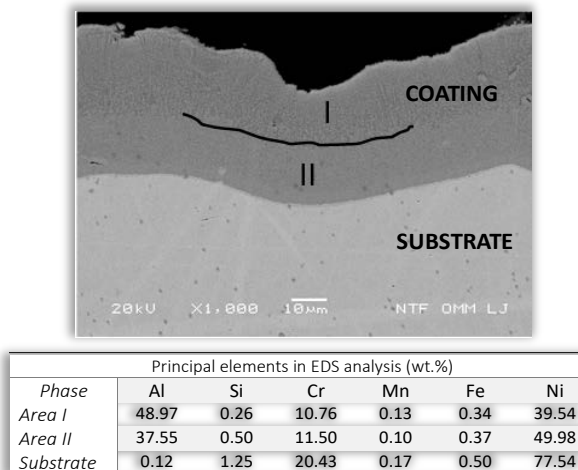


Figure 6. SEM-EDX analysis of NiCr coated at 730 °C for 1.5 h. The coating on Fe-Cr-Al alloy is a dual phase mixture with dark and light areas. EDS analysis show that the dark phase is rich in aluminium and contain iron and a small amount of chromium. The light phase contains a smaller percentage of aluminium and iron, and a larger percentage of chromium. It

is evident that Fe-Cr-Al alloy forms a number of different phases. The formation of these phases depends on the diffusion of aluminium through the coating in direction to the substrate. The aluminium content increased in the direction to coating surface and the content of chromium and iron decreased.

On the other hand, aluminized layer on Ni-Cr alloy consists of two layers: the darker top layer (Area I), rich on aluminium, chromium and nickel and lighter subsurface layer (Area II), which contains smaller percentage of aluminium and a higher percentage of nickel and chromium. The average coating thickness is 35 μm, thickness of top layer is 15 μm followed by a sub layer of about 20 μm.

### X-ray diffraction

X-ray diffraction (XRD) was used for phase identification of coatings. From these study it was established that for the coating time 1,5h at 730°C, the surface of the coated Fe-Cr-Al alloys consists mainly from α- Al<sub>3</sub>Fe<sub>5</sub>, β- Al<sub>5</sub>Fe<sub>2</sub>, γ- AlFe<sub>3</sub> (see Figure 7a). According to the phase diagram Fe-Cr the iron forms a number of different intermetallic compounds such as: FeAl<sub>3</sub>, Fe<sub>2</sub>Al<sub>5</sub>, FeAl<sub>2</sub>, FeAl, Fe<sub>3</sub>Al, as well α-Al and α-Fe. Based on the intensity of the scattered X-rays the largest content has Al<sub>3</sub>Fe<sub>2</sub> phase.

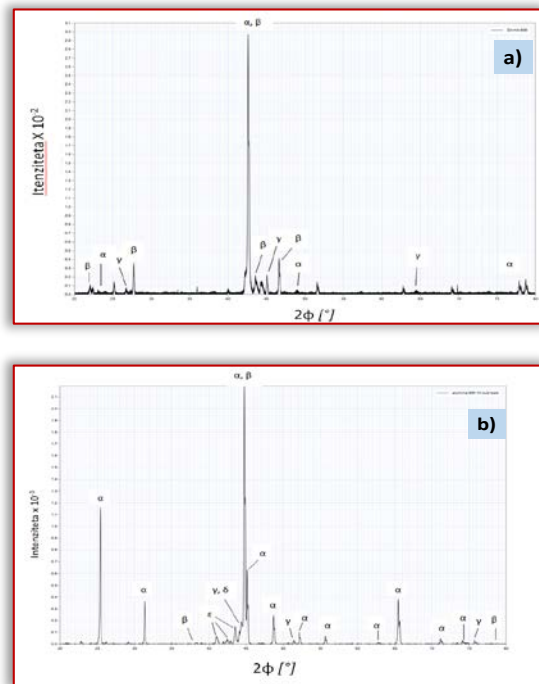


Figure 7. XRD patterns of the aluminizing coating on Fe-Cr-Al substrate a) and NiCr substrate b)

Aluminized coating of Ni-Cr alloy comprises the following phases: α- Al<sub>3</sub>Ni<sub>2</sub>, β- Al, γ- Ni, δ- Cr, ε- Al<sub>3</sub>Ni (see Figure 7 b), with the largest proportion of the Al<sub>3</sub>Ni<sub>2</sub> phase. From the results of XRD and SEM analysis, it can be concluded, that the upper layer (I) is comprised mainly of Al<sub>3</sub>Ni phase, and the layer (II) of Al<sub>3</sub>Ni<sub>2</sub> phase, with continuously increased proportion of other phases according to the Al-Ni phase diagram. This finding is in a good agreement with [6]. They found out that Al<sub>3</sub>N<sub>2</sub> is the major phase because of a very high diffusivity of Al<sub>3</sub>Ni<sub>2</sub>.

## Oxidation test

The effectiveness of the aluminizing process was evaluated by the oxidation testing of the commercial Fe-Cr-Al 0.7 mm thick sheet in comparison with aluminized Fe-Cr-Al samples under isothermal conditions (thermo-balance Netzsch STA 429) at constant temperature of 1200 °C/24 h in a laboratory air atmosphere. Samples were heated and cooled at the same rate of 20 K/min. The results are presented by the relative mass gain versus time (Figure 8). According to the measurements, the initial oxidation rate of as received commercial Fe-Cr-Al sheets is higher than for aluminized Fe-Cr-Al samples (first 24 h). Because of short time of isothermal temperature exposure, further longer tests would be needed to determine whether or not the increased Al alloy content prolong the life time of the Kanthal AF sheet at 1200 °C [7].

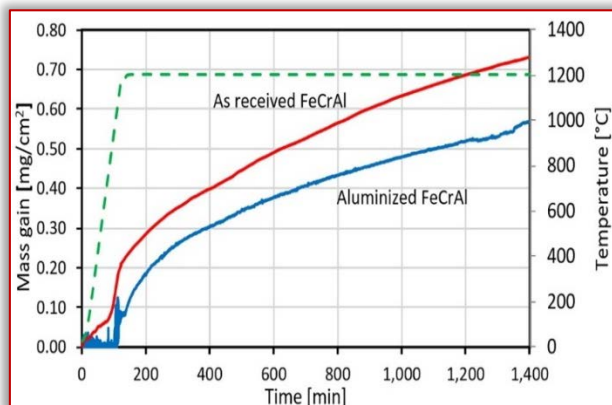


Figure 8. Relative mass gain as a function of oxidation time in air at 1200°C (heating rate 20 K/min)

## CONCLUSIONS

Within the work it was successfully prepared homogeneous aluminized layer on ferritic Kanthal AF (Fe-Cr-Al) and on austenitic Microthal 80 (Ni-Cr) with sufficient aluminium reservoir, which should enable the formation of protective alumina scale in oxidizing conditions.

The effect of Al activity in powder pack on the coating kinetics and structure was studied at several coating temperatures in the range from 650 to 750 °C for 0.5 to 2.5 hours. Samples in the form of sheet were uniformly aluminized at various times and temperatures. The dependence of coating thickness from temperature and time at constant powder pack was evaluated.

The coating is free of cracks with some imperfections like pores or porous area. According to SEM/EDS analyses of Fe-Cr-Al alloy aluminium content decreased from the coating surface to the substrate material, the content of chromium and iron increases. Aluminized layer on Fe-Cr-Al alloy contains intermetallic phases  $Al_8Fe_5$ ,  $Al_5Fe_2$  and  $AlFe_3$ .

Analyses of the aluminized layer on Microthal 80 (Ni-Cr) alloy showed that aluminized layer consists of two layers. The upper layer, with higher percent of aluminium and the lower layer, with smaller percentage of aluminium and a higher percentage of nickel and chromium. The upper layer is

comprised mainly of  $Al_3Ni$  phase, and the lower layer of  $Al_3Ni_2$  phase, with continuously increased proportion of other phases in direction of the substrate alloy. The thickness of the layers increases with aluminizing time and temperature. Coating thickness is increased faster in Fe-Cr-Al alloy because of significantly higher diffusion rate of aluminium in KANTHAL AF alloy than in Microthal 80 alloy [8].

## Note

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## References

- [1] Mévrel, C., Duret, R., Pichoir, P. (1986). Pack cementation processes. *Material Science and Technology*, Vol. 2, Issue 3, pp. 201-206.
- [2] Gupta, B. K., Sarkhel, A. K., Seigle, L. L. (1976). On the kinetics of pack cementation. *Thin solid films*, Vol. 39, pp. 313-320.
- [3] Xiang, Z. D.J. S. Burnell-Gray, S., Datta, P. K. (2001). Aluminide coating formation on nickel-base super alloys by pack cementation process. *Surface & Coatings technology*, Vol. 36, Issue 23, pp. 5673-5682.
- [4] Zhang, Y. (2008). Formation of aluminide coatings on the Fe-based alloys by chemical vapour deposition. *Surface & Coatings technology*, Vol. 202, pp. 3830-3849.
- [5] Kung, S. C., Rapp R. A. (1987). Fundamental study of aluminization of iron by pack cementation at 900°C. *Surface and coatings technology*, Vol. 32, pp. 41-56.
- [6] Seigle, L. L. (1982) Kinetics of formation and microstructure of aluminide coatings on Ni-Cr alloys, *Thin Solid Films*, Vol. 95, 1982, pp. 47-56.
- [7] Bennett, M.J., Nicholls, J.R., Simms, N.J., Naumenko, D., Quadackers, W.J., Kochubey, V., Fordham, R., Bachorczyk, R., Goossens, D., Hattendorf, H., Smith, A.B., Britton, D. (2005). Lifetime extension of FeCrAlRE alloys in air: Potential roles of an enhanced Al-reservoir and surface pre-treatment. *Materials and Corrosion*, Vol. 56, Issue 12, pp. 854-866.
- [8] Goward, G. W., Boone, D. H. (1971). Mechanisms of Formation of diffusion Aluminide Coatings on Nickel-Base Superalloys. *Oxidation of Metals*, Vol. 3, No. 5, pp. 475-495.



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