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Kinetic and morphologic study of the pack-aluminization of a series of refractory alloys

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Abstract. — Five refractory alloys, Fe-20Cr-20Ni, Fe-20Cr-36Ni, Fe-20Cr-45Ni, Fe-20Cr-60Ni and Ni-20Cr, were submitted to pack aluminization at 850 °C for different durations in a NaF-activated pack. After a short period to achieve steady state, the coating kinetics were shown to be linear. The rate of aluminization was the same for the four alloys containing iron (about $1 \text{ mg.cm}^{-2}.\text{h}^{-1}$) and notably higher ($1.8 \text{ mg.cm}^{-2}.\text{h}^{-1}$) in the case of the Ni-20Cr alloy. The nature of the formed products and the morphology of the layers were shown to depend on the alloy composition. The most important feature was the presence of external FeAl_3 on the four Fe-containing alloys, whereas a mixture of Ni_2Al_3 + NiAl was observed on the Ni-20Cr alloy. Kinetic experiments and thermodynamic calculations allowed a derivation of the value of the Al-activity at the gas-substrate interface. The mechanisms involved in the aluminization were shown to depend on the Al-concentration in the pack, on gaseous diffusion for low Al concentration and on interface reaction for high Al concentration.

1. Introduction.

Pack-aluminization is a powerful technique to produce surface alloys with high resistance to thermal oxidation. Due to the importance of the coating composition, adherence and morphology, many studies have been devoted in the past to these topics [1-7]. In this paper, we focus on the kinetics of aluminization, particularly on its variation with substrate composition and aluminium concentration in the pack.

2. Experimental.

A series of five refractory alloys (Gilphy from Imphy S.A.) was chosen for this study. These alloys exhibit roughly the same Cr-content (16-24%) with different Ni:Fe ratios. The amounts of the major elements are presented in table I. The minor elements are Mn (150-300 ppm), Al (200 ppm) and Ce (50-80 ppm). Carbon is 30 ppm.

Coupons were cut in these alloys with the average dimensions $1.5 \times 1.5 \text{ cm}$. The thickness of the foils was between 0.5 and 1 mm. After careful cleaning and weighting, these coupons were embedded vertically in the powdered aluminizing pack constituents consisting of:

Al : 40 wt%; Al_2O_3 : 55 wt%; NaF : 5 wt%.

Table I. — *Average compositions (wt.%) of the different alloys.*

	Fe	Ni	Cr	Si
Gilphy 20	bal.	19.5	24	1.6
Gilphy 36	bal.	36.5	18.5	2
Gilphy 45	bal.	45.5	23	2
Gilphy 60	bal.	60	16	1.3
Gilphy 80	0.05	bal.	20	1.4

After pumping down to 1×10^{-3} mbar, the apparatus was filled with helium at the atmospheric pressure. The pack was subsequently heated to 1123 K where the reaction took place for 3 to 15 hours. Then, the pack was cooled and the coupons gently brushed and weighed. Classical examination techniques (visual, XRD, optical and scanning electron microscopy, EDX) were used to assess the nature, composition and morphology of the coatings.

3. Results.

3.1 KINETICS. — As shown in figure 1, the kinetic curves are linear in the 3 h-15 h time range. The linear rate constants obtained (k_1) are reported in table II.

Fig. 1. — Gravimetric curve of aluminization at 850 °C of G20 alloy in the Al-rich pack (40 wt.Al%).

The four alloys containing iron exhibited the same value of the linear constant ($\sim 1 \text{ mg.cm}^{-2}.\text{h}^{-1}$), whereas the nickel-base alloy aluminizes approximately two times more rapidly. Before 3 h of cementation, the transient period corresponds probably to the achievement of steady-state conditions.

Table II. — *Linear rate constants for aluminization at 1123 K for the different alloys.*

Alloy	G20	G36	G45	G60	G80
k_l ($\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$)	1.07	0.94	1.06	0.97	1.80

A series of experiments was done with alloy G20 in a pack containing only 10 wt% Al. For such conditions, the rate law of aluminization is parabolic, as shown in figure 2, with a parabolic rate constant $k_p = 13 \text{ mg}^2\cdot\text{cm}^{-4}\cdot\text{h}^{-1}$.

Fig. 2. — Gravimetric curve of aluminization at 850 °C of G20 alloy in the Al-poor pack (10 wt%Al%).

3.2 NATURE AND MORPHOLOGY OF THE COATINGS. — Microscopic examinations shows that the aluminized coatings exhibited two major layers. In the case of iron-containing steels, a third (minor) layer appears in contact with the substrate. Table III summarizes the observations.

Figures 3 to 5 present three different morphologies corresponding to the G20/G36, G45/G60 and G80 alloys, respectively.

4. Discussion.

4.1 GROWTH MECHANISMS OF THE SCALES. — Due to the high Al-activity in the pack, aluminium is the major diffusing species in the growth process. The measured amounts of Ni and Cr in the monophasic FeAl_3 external scales are in good agreement with those calculated

Table III. — *Nature of the different sublayers observed after pack aluminization of the Gilphy alloys. When biphasic, the first compound cited is the major one. Atomic percentages.*

Alloy	layer 1	layer 2	layer 3
G20	Compound(s) FeAl_3	Fe_2Al_5 + little Ni_2Al_3	Fe
	Solid solution Ni $\sim 5\%$ Cr $\sim 5\%$	Ni 5-10% Cr 5-10%	Cr
G36	Compound(s) FeAl_3	$\text{Fe}_2\text{Al}_5 + \text{Ni}_2\text{Al}_3$	Fe
	Solid solution Ni $\sim 5\%$ Cr $\sim 5\%$	Cr $\sim 8\%$	Cr
G45	Compound(s) FeAl_3	$\text{Ni}_2\text{Al}_3 + \text{NiAl}$	Fe
	Solid solution Ni $\sim 10\%$ Cr $\sim 5\%$	Cr $\sim 15\%$ Fe $\sim 13\%$	Cr
G60	Compound(s) FeAl_3	$\text{Ni}_2\text{Al}_3 + \text{NiAl}$	Fe
	Solid solution Ni $\sim 20\%$ Cr $\sim 5\%$	Fe $\sim 10\%$ Cr $\sim 8\%$	Cr
G80	Compound(s) $\text{Ni}_2\text{Al}_3 + \text{NiAl}$	$\text{NiAl} + \text{Ni}_2\text{Al}_3$	
	Solid solution Cr $\sim 5\%$	Cr $\sim 10\%$	

assuming no diffusion of these elements. However, the presence of the internal Fe-Cr sublayer shows the ability of nickel to preferentially leave the alloy, but the small thickness of this layer indicates a low Ni-diffusivity.

If the presence of a $\text{Fe}_2\text{Al}_5 + \text{Ni}_2\text{Al}_3$ mixture in the middle of the coatings grown on G20 and G36 alloys is not in contradiction with thermodynamics, the $\text{Ni}_2\text{Al}_3/\text{NiAl}$ biphasic layer observed on G45, G60 and G80 alloys results from a non equilibrium process. At the temperature used, rather low for aluminization of Ni-containing materials, grain boundary diffusion may play a role and be more rapid than the $\text{Ni}_2\text{Al}_3 \rightarrow \text{NiAl}$ transformation. Ni_2Al_3 domains can therefore be embedded in NiAl, as experimentally observed.

4.2 THERMODYNAMICS. — Pack and substrate equilibrium calculations were performed with the Solgasmix program [8] to determine the partial pressures in the pack and in contact with the aluminized alloys.

Fig. 3.

Fig. 4.

Fig. 3. — Cross-section of aluminized G36 alloy.
 Fig. 4. — Cross-section of aluminized G45 alloy.

Fig. 5. — Cross-section of aluminized G80 alloy.

4.2.1 Pack equilibrium. — Table IV shows that the major gaseous aluminium fluoride in the pack at 850 °C is $[\text{AlF}]$, followed by $[\text{AlF}_3]$. The other Al-F species are considered to be negligible in the following. Due to the rather low total pressure of the reactive gases, helium remains the major species in the gas ($P_{\text{He}} \sim 1$ bar).

Table IV. — *Partial pressures of the aluminium fluorides in equilibrium with the pack at 850 °C*

Gaseous species	$[\text{AlF}_3]$	$[\text{AlF}_2]$	$[\text{AlF}]$	$[\text{Al}_2\text{F}_6]$
Partial pressure (bar)	1.252×10^{-4}	4.949×10^{-5}	2.817×10^{-3}	8.021×10^{-7}

4.2.2 Substrate equilibrium. — For the G80 alloy, the formation, in the external part of the coating, of the mixture $\text{NiAl-Ni}_2\text{Al}_3$ imposes $a_{\text{Ni}} = 1.08 \times 10^{-3}$ and $a_{\text{Al}} = 1.06 \times 10^{-2}$. For these conditions, the $[\text{AlF}_x]$ pressures are given in table V; iron fluorides are negligible.

Table V. — *Partial pressures of the aluminium fluorides in equilibrium at 850 °C with aluminized G80 alloy ($\text{NiAl} + \text{Ni}_2\text{Al}_3$).*

Gaseous species	$[\text{AlF}_3]$	$[\text{AlF}_2]$	$[\text{AlF}]$	$[\text{Al}_2\text{F}_6]$
Partial pressure (bar)	2.394×10^{-4}	1.673×10^{-5}	1.683×10^{-4}	2.934×10^{-6}

In the case of G20 and G60 alloys, monophase FeAl_3 is formed in the external part of the scale and the $[\text{AlF}_x]$ pressures can be given only in function of a_{Fe} or a_{Al} in table VI. Under $a_{\text{Al}} \sim 0.6$, solid AlF_3 appears, leading to constant $[\text{AlF}_3]$ and $[\text{Al}_2\text{F}_6]$ pressures. Iron fluorides are again also negligible.

Tables IV, V and VI show that for all alloys, $[\text{AlF}]$ is formed in the pack and consumed on the substrate. On the contrary, $[\text{AlF}_3]$ is formed on the substrate and consumed in the pack. The transport reaction is therefore:

its displacement depending on Al activity.

4.3 KINETICS. — As the rate law for aluminization for alloy G20 changed with decreasing Al-content in the pack, we assume that gas transport across the Al-depleted zone of the pack contributes mainly to the kinetics. The participation of the diffusion in the solid state is thought to be much smaller. If not, lowering the Al-content of the pack, would not change the rate law.

Using the model published by Levine and Caves [5], the parabolic rate constant measured for the G20 alloy can be related to the $[\text{AlF}]$ pressure difference between the pack and the substrate by the relation:

$$k_p = \frac{4}{3} \frac{\varepsilon}{\tau} D_{\text{AlF}} \frac{\Delta p_{\text{AlF}}}{RT} C_{\text{Al}} M_{\text{Al}}$$

ε and τ are the porosity and tortuosity of the pack, D_{AlF} is the AlF/He interdiffusion coefficient, C_{Al} is the Al concentration in the pack and M_{Al} is the atomic mass of Al.

The following values were used:

$k_p = 13 \text{ mg}^2 \cdot \text{cm}^{-4} \cdot \text{h}^{-1}$, $\varepsilon = 0.6$, $\tau = 4$, $D_{\text{AlF}} = 5.12 \text{ cm}^2 \cdot \text{s}^{-1}$, $C_{\text{Al}} = 113 \text{ kg} \cdot \text{m}^{-3}$ to calculate $\Delta p_{\text{AlF}} = 1.1 \times 10^{-4} \text{ bar}$

The same calculation was made with AlF_3 , leading to:

$$\Delta p_{\text{AlF}_3} = 4.4 \times 10^{-5} \text{ bar}$$

Table VI. — *Equilibrium partial pressures of the aluminium fluorides at 850 °C for aluminized alloys (FeAl₃) for different Al (or Fe) activities - (For $a_{Al} < 0.113$, lower Fe aluminides appear).*

gaseous species a_{Al} a_{Fe}	[AlF ₃]	[AlF ₂]	[AlF]	[Al ₂ F ₆]
0.113 2.22.10 ⁻²	2.394.10 ⁻⁴	3.691.10 ⁻⁵	8.197.10 ⁻⁴	2.934.10 ⁻⁶
0.398 5.15.10 ⁻⁴	2.394.10 ⁻⁴	5.607.10 ⁻⁵	1.891.10 ⁻³	2.934.10 ⁻⁶
0.546 1.99.10 ⁻⁴	2.394.10 ⁻⁴	6.231.10 ⁻⁵	2.336.10 ⁻³	2.934.10 ⁻⁶
0.650 1.18.10 ⁻⁴	1.428.10 ⁻⁴	4.680.10 ⁻⁵	2.210.10 ⁻³	1.044.10 ⁻⁶
0.815 5.98.10 ⁻⁵	1.337.10 ⁻⁴	4.831.10 ⁻⁵	2.513.10 ⁻³	9.156.10 ⁻⁷
0.960 3.65.10 ⁻⁵	1.271.10 ⁻⁴	4.931.10 ⁻⁵	2.756.10 ⁻³	8.264.10 ⁻⁷
1 2.99.10 ⁻⁵	1.252.10 ⁻⁴	4.949.10 ⁻⁵	2.817.10 ⁻³	8.021.10 ⁻⁷

and verification of the mass balance relation:

$$\Delta p_{AlF_3} \times D_{AlF_3} = \frac{1}{3} (\Delta p_{AlF} \times D_{AlF})$$

From the values of Δp_i , the substrate pressures can be calculated and the corresponding aluminium activity derived from table VI. The results are:

$$\begin{aligned} P_{AlF}(\text{substrate}) &= 2.71 \times 10^{-3} \text{ bar} \\ a_{Al}(\text{substrate}) &= 0.93 \end{aligned}$$

For packs containing more aluminium, where the observed rate laws are linear, it is generally assumed that the thickness of the Al-depleted pack zone remains constant.

The thickness y of Al-depleted pack zone can be derived from the expression of the linear rate constant k_l (Fick's law):

$$k_l = \frac{2}{3} \frac{\varepsilon}{\tau} D_{\text{AlF}} M_{\text{Al}} \frac{\Delta p_{\text{AlF}}}{yRT}$$

For G80 alloy, where Δp_{AlF} is fixed, or for G20 to G60 alloys using the same Al activity as in low packs, the values of y are too small to have any significant physical meaning ($y \sim 10^{-12}$ m). The reasons for this fact can be:

- underestimation of the $\frac{\varepsilon}{\tau}$ factor;
- departure from equilibrium of the AlF disproportionation reaction on the substrate, leading to lower and higher values of p_{AlF} and p_{AlF_3} respectively.

This last supposition may explain why the rate of aluminization is only about 2 times faster for G80 compared to the other alloys although Δp_{AlF} is ~ 20 times higher.

Rate control by solid state diffusion through the solid product(s) formed has not to be taken into account, as it would lead to parabolic kinetics.

5. Conclusions.

Aluminization of FeNiCr refractory alloys proceeds by slow transport of [AlF] from the pack to the substrate (and counterdiffusion for [AlF₃]). For packs containing low amounts of Al, the Al-depleted layer, where diffusion takes place, increases in function on time, leading to parabolic kinetics. For packs containing large amounts of Al, the thickness of this layer remains constant and linear kinetics are observed. A surface-controlled step must participate to the kinetics to account for the calculated thickness of the Al-depleted layer.

Further experiments are needed, in this complicated field, particularly with different total pressures, or different Al-activities in the packs.

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