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Simultaneous chromizing-aluminizing of nickel and nickel-base alloys by halide-activated pack cementation

Ravi, Vilupanur Alwar, Ph.D.

The Ohio State University, 1988
SIMULTANEOUS CHROMIZING-ALUMINIZING OF NICKEL
AND NICKEL-BASE ALLOYS BY
HALIDE-ACTIVATED PACK CEMENTATION

DISSertation

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

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1988

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To Sundari Periamma - a saga of sorrow and sacrifice.
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These people shall always be a pleasant part of my life.
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Polymers                                J. Lee

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ABSTRACT

A method for simultaneously chromizing-aluminizing Ni and Ni-base alloys via halide-activated pack cementation is described. Equilibrium partial pressures of the gaseous species in halide-activated cementation packs have been determined with the computer program SOLGASMIX. The effect of the activator and the composition of the masteralloy on the coating process has been predicted. The activities of Al and Cr have been incorporated into the calculations and the results indicate that codeposition of Al and Cr is possible using NaCl, CrCl$_2$ or NH$_4$Cl as activators and Al–Cr masteralloys with composition between 90 w/o and 97.5 w/o Cr.

The thermodynamic predictions were used as guidelines in choosing pack chemistries to attain the desired corrosion-resistant coating composition of 18-30 a/o Cr - 5-10 a/o Al in Ni-base alloys. Chromous chloride (CrCl$_2$) activated packs with a 90 a/o Cr - 10 a/o Al masteralloy provided a coating composition of 32 a/o Cr - 5 a/o Al on pure Ni substrates. Ni-20 w/o Cr, Rene 80 and IN 600 substrates have also been coated using a CrCl$_2$-activated pack containing 90 a/o Cr - 10 a/o Al masteralloy to obtain Cr-rich coatings containing Al.

Diffusion profiles for Cr and Al into Ni, coated under different conditions, have been obtained. A finite element program which predicts diffusion profiles for a given surface concentration was developed and evaluated, using diffusion coefficients from literature. Very good agreement between predicted and experimental profiles were obtained.
Low temperature hot corrosion tests of the coated Rene 80 coupons show excellent corrosion protection for exposure times up to 16 hours at a temperature of 730 °C. Coating degradation at some points is observed at the end of 72 hours of corrosion testing. The morphology of the corrosive attack and the extent of the damage is comparable to the commercial General Electric Codep coating.
INTRODUCTION

In marine, utility and aircraft turbine environments, sodium sulfate, which forms from sulfur impurity in the fuel and sodium from ingested seawater aerosol, may condense on the turbine blades and vanes. Although pure sodium sulfate melts at 884\(^\circ\) C, it may form a low-melting eutectic (565\(^\circ\) C) with the nickel sulfate corrosion product on the turbine blade surface. A catastrophic form of corrosion occurs beneath these thin, fused salt films at the temperatures of turbine operation (600-750\(^\circ\) C). This form of corrosion is called low temperature or type II hot corrosion [1-3].

Certain coatings between the corrosive salt film and the substrate alloy provide resistance to low temperature hot corrosion by forming a protective oxide film. Coatings containing aluminum, chromium and silicon are effective against oxidation and hot corrosion by forming protective \(\text{Al}_2\text{O}_3\), \(\text{Cr}_2\text{O}_3\) and \(\text{SiO}_2\) scales. Figure 1 [4] is an oxide map of the \(\text{Ni-Cr-Al}\) system at 1273 K showing steady state oxide scales formed for given alloy compositions, as well as the position of commercially used superalloys [5].

When exposed to oxidizing environments, coatings containing 25-30 a/o Cr and 10-15 a/o Al, form a \(\text{Cr}_2\text{O}_3\) scale initially. The \(\text{Cr}_2\text{O}_3\) prevents the oxidation of \(\text{Ni}\) to \(\text{NiO}\) while lowering the partial pressure of oxygen at the oxide-substrate interface so that internal oxidation of \(\text{Al}\) is avoided. Subsequently, \(\text{Al}\) reacts with the transient \(\text{Cr}_2\text{O}_3\) to form the more stable \(\alpha-\text{Al}_2\text{O}_3\) phase, which is isomorphic with \(\alpha-\text{Cr}_2\text{O}_3\). Eventually, the \(\text{Cr}\) is substituted by \(\text{Al}\) to form \(\text{Al}_2\text{O}_3\), which exhibits a much lower growth rate at steady state.
Figure 1. Oxide map of the Ni-Cr-Al system showing the position of commercially used superalloys [4]
than $Cr_2O_3$. To be protective, the oxide scales should be non-porous and not spall during service.

High temperature protective coatings are applied by several methods as shown in Table 1 [6]. Overlay coatings, in which the diffusion of the coating element into the substrate is minimal, may require subsequent heat treatment to achieve interdiffusion. Of the surface modified processes, pack cementation is used extensively for applying aluminide coatings because it is

- economical, since no elaborate equipment or post heat-treatment is required
- versatile, because a variety of alloys of complex geometries can be coated by various constituents.

Pack cementation is an internally generated chemical vapor deposition process carried out in a closed container at elevated temperatures (usually near 1000° C) under an inert or reducing atmosphere. A 'pack' usually consists of the substrate(s) to be coated and powders of an inert filler, a masteralloy rich in the element(s) to be deposited and an activator salt. The activator salt reacts with the masteralloy to generate volatile metallic halides which diffuse through the porous filler material (usually alumina) to the substrate surface. At the substrate surface, the metallic halide vapors participate in one or more of several possible reactions [7]:

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<table>
<thead>
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<th>Surface Modified Coatings</th>
</tr>
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<tbody>
<tr>
<td>{deposition with minimal interdiffusion of coating with substrate}</td>
<td>{modification of chemical composition and/or microstructure of substrate}</td>
</tr>
<tr>
<td>Hot spraying</td>
<td>Pack cementation</td>
</tr>
<tr>
<td>-Flame spraying</td>
<td>Slurry cementation</td>
</tr>
<tr>
<td>-Plasma spraying</td>
<td>Metalliding</td>
</tr>
<tr>
<td>-Detonation coating</td>
<td>Hot dipping</td>
</tr>
<tr>
<td>Chemical vapor deposition</td>
<td>Surface alloying</td>
</tr>
<tr>
<td>Physical vapor deposition</td>
<td>-Ion implantation</td>
</tr>
<tr>
<td>-Thermal evaporation</td>
<td>-Laser surface alloying</td>
</tr>
<tr>
<td>-Ion sputtering</td>
<td></td>
</tr>
<tr>
<td>-Ion plating</td>
<td></td>
</tr>
</tbody>
</table>


Disproportionation

$$2 \text{AlCl} (v) = \text{AlCl}_2 (v) + \text{Al}$$  (0.1)

$$3 \text{CrCl}_2 (v) = 2 \text{CrCl}_3 (v) + \text{Cr}$$  (0.2)

Precipitation (of activator salt)

$$\text{AlCl} (v) + \text{Na} (v) = \text{Al} + \text{NaCl} (l)$$  (0.3)

$$\text{CrCl}_2 (v) + 2 \text{Na} (v) = \text{Cr} + 2 \text{NaCl} (l)$$  (0.4)

Reactions with environment/substrate

$$\text{AlCl} (v) + \text{H}_2 (g) = \text{HCl} (g) + \text{Al}$$  (0.5)

$$\text{CrCl}_2 (v) + \text{Fe} (s) = \text{Cr} + \text{FeCl}_2 (v)$$  (0.6)

All of the above reactions result in the deposition and the subsequent solid-state diffusion of the desired coating element into the substrate.

The coating process is generally carried out in an inert or reducing atmosphere. Flowing argon is commonly used as an inert shroud, while hydrogen or hydrogen mixed with argon could be used as a reducing atmosphere to aid in the coating kinetics as in reaction (0.5).

The substrate may also play a role in the cementation process. If an iron or an iron-base alloy is coated, the substrate can undergo a displacement reaction as in (0.6) because the partial pressures of the iron halides are significant [8]. But, if a Ni-base alloy substrate is used, reactions of the substrate with the halide environment are not significant since the partial pressures of the nickel halides are comparatively small [8].
Current commercial practice almost always involves the deposition of single elements (Al, Cr or Si) to form coatings [9-13]. However, combinations of two of these elements are frequently advantageous in providing enhanced corrosion and oxidation resistance, e.g., Cr plus Al or Cr plus Si. Currently, two-step coating procedures have been adopted to incorporate Cr and Al sequentially into the substrate [9,14]. The resulting structure has complex concentration profiles consisting of an inner Cr-rich zone and an outer Al-rich zone, which is not optimum for either corrosion resistance or mechanical properties. A single step chromizing-aluminizing coating of substrates would be cheaper and simpler, and the more uniform composition gradients of the coatings obtained should provide effective oxidation/hot corrosion resistance.

Restall [9] and Walsh [15] have stressed that simultaneous deposition of Al and Cr is generally not possible because of the considerable difference in the thermodynamic stabilities of the volatile halides of the Al and Cr. However, Rapp, Wang and Weisert [16] have developed procedures for the codeposition of Al and Cr simultaneously into iron-base alloys to achieve ‘Kanthal-like’ surface compositions on pure iron and Fe–2½ Cr–1 Mo substrates by suitably adjusting pack chemistries. Because of the controversy and considerable difficulty associated with the codeposition process, there is a need for the systematic study of the feasibility of such a process, and its demonstration in Ni-base alloys.
The objective of this thesis is three-fold:

1. To evaluate the thermodynamics and kinetics of the simultaneous chromizing-aluminizing process for Ni and Ni-base alloys,

2. On the basis of the thermodynamic analysis, to engineer pack chemistries to obtain the desired chromium-aluminum surface composition, and

3. To evaluate the performance of such coatings in low temperature hot corrosion environments.
1.1 PACK ALUMINIZING

Van Aller [17] invented the process of pack cementation aluminizing ("calorizing") in 1911. Iron or copper pieces were heated to 450°C in a mixture of powders of aluminum, ammonium chloride and graphite (inert filler) in revolving drums. After removal from the drums, the pieces were heat-treated at approximately 700°C. Gilson [18] used aluminum oxide instead of graphite as an inert filler material.

The early application of pack aluminizing of iron and copper was used for the coating of power plant steam condenser tubes. Currently, more than 90% of all coated airfoils for aircraft gas turbines are coated by pack cementation processes [19].

1.1.1 Structure of Aluminide Coatings on Nickel and Nickel-base Alloys

Aluminum and nickel form a series of intermetallic compounds - $Al_3Ni$, $Al_3Ni_2$, $NiAl$ ($\beta$) and $AlNi_3$ ($\gamma'$) at 1000°C (Fig. 2) [20]. A summary of the invariant reactions in the $Al-Ni$ system and the crystal structure data for the $Al-Ni$ system are presented in Table 2.

Goward and Boone [21], Pichoir [22], and Goward and Cannon [19] have classified the structures formed during pack aluminization of $Ni$ and $Ni$-base alloys based on the activity in the pack. However, the distinction between low and high activity packs is not thermodynamically precise. The 'high' and 'low' activities demarcate two distinct, coated
Figure 2. The Al-Ni equilibrium diagram [20].
TABLE 2. Invariant reactions and crystal structure data for the Al-Ni system

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Composition at. % Al</th>
<th>Temperature °C</th>
<th>Reaction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L=(Ni)+AlNi_3 )</td>
<td>25 20.2 26</td>
<td>1385</td>
<td>Eutectic</td>
</tr>
<tr>
<td>( L+AlNi=AlNi_3 )</td>
<td>25.5 30.8 26.25</td>
<td>1395</td>
<td>Peritectic</td>
</tr>
<tr>
<td>( AlNi+AlNi_3=Al_3Ni_5 )</td>
<td>39.5 27 34</td>
<td>700</td>
<td>Peritectoid</td>
</tr>
<tr>
<td>( L+AlNi=Al_3Ni_2 )</td>
<td>73.1 58 60</td>
<td>1133</td>
<td>Peritectic</td>
</tr>
<tr>
<td>( L+Al_3Ni_2=Al_3Ni )</td>
<td>85 63.2 75</td>
<td>854</td>
<td>Peritectic</td>
</tr>
<tr>
<td>( L=Al_3Ni+(Al) )</td>
<td>97.3 75 99.89</td>
<td>639.9</td>
<td>Eutectic</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition at. % Al</th>
<th>Strukturbericht designation</th>
<th>Prototype</th>
</tr>
</thead>
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<td>(Ni)</td>
<td>0 to 21.2</td>
<td>( A1 )</td>
<td>( Cu )</td>
</tr>
<tr>
<td>AlNi_3</td>
<td>24 to 27</td>
<td>( L1_2 )</td>
<td>( AuCu_3 )</td>
</tr>
<tr>
<td>Al_3Ni_5</td>
<td>32 to 36</td>
<td>...</td>
<td>( Ga_3Pt_5 )</td>
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<tr>
<td>AlNi</td>
<td>30.8 to 58</td>
<td>( B2 )</td>
<td>( CsCl )</td>
</tr>
<tr>
<td>Al_3Ni_2</td>
<td>59.5 to 63.2</td>
<td>( D5_{13} )</td>
<td>( Al_3Ni_2 )</td>
</tr>
<tr>
<td>Al_3Ni</td>
<td>75</td>
<td>( D0_{11} )</td>
<td>( CFe_3 )</td>
</tr>
<tr>
<td>(Al)</td>
<td>99.89 to 100</td>
<td>( A1 )</td>
<td>( Cu )</td>
</tr>
</tbody>
</table>
microstructures. Figure 3 shows the microstructure of an outward-diffusion type aluminide coating on Udimet 700 formed by a low aluminum activity process. Figure 4 shows the microstructure of an inward-diffusion type aluminide coating on Udimet 700 formed by a high aluminum activity process [21]. The high $Al$ activity packs contain unalloyed aluminum as the source while low $Al$ activity packs contain $Ni_2Al_3$ powder.

Shankar and Seigle [23] have shown that the structures in Figs. 3 and 4 are limiting cases and that a range of intermediate structures exist due to the variation of the interdiffusion coefficient ($D$) in the $\beta$-$NiAl$ phase of the $Al$-$Ni$ system (Table 3 and Fig. 5). Nickel diffusion dominates in the low-$Al$ $NiAl$ phases with $D_{Ni}/D_{Al} = 3 - 3.5$ and $Al$ becomes the dominant diffusing element in the high-$Al$ $NiAl$ phase ($D_{Ni}/D_{Al} \leq 0.10$). The transition in the dominant diffusing species is sharp and occurs close to the stoichiometric $NiAl$ composition.

Pichoir, in an excellent review [22], has discussed the modes of formation of aluminide coatings. The two limiting structures obtained by Goward and Boone have been rationalized as:

1. Preferential diffusion of nickel to form $NiAl$ at 1000$^\circ$C in a single aluminizing cycle (outward grown, low $Al$ activity pack),

2. Preferential diffusion of aluminum into nickel to form $Ni_2Al_3$ when aluminized between 700 - 850$^\circ$C and subsequent transformation to $NiAl$ when diffusion annealed at 1000$^\circ$C (inward grown, high $Al$ activity pack).
Figure 3. Microstructure and phase identities of outward diffusion type aluminide coating on Udiment 700 formed by a low-aluminum activity process. × 1000. [21]
Figure 4. Microstructure and phase identities of inward diffusion type aluminide coating on Udimet 700 formed by a high-aluminum activity process followed by heat treatment for 4 hours at 1975°F. x 1000 [21].
TABLE 3. Interdiffusion coefficients in the Al-Ni system at 1000° C [23]

<table>
<thead>
<tr>
<th>Atom % Al</th>
<th>Phase</th>
<th>$\bar{D}$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>$\gamma$</td>
<td>$2.2 \times 10^{-11}$</td>
</tr>
<tr>
<td>14</td>
<td>$\gamma$</td>
<td>$4.9 \times 10^{-11}$</td>
</tr>
<tr>
<td>25</td>
<td>$\gamma$ ($Ni_3Al$)</td>
<td>$6.3 \times 10^{-11}$</td>
</tr>
<tr>
<td>50</td>
<td>$\beta$ ($NiAl$)</td>
<td>$6.2 \times 10^{-10}$</td>
</tr>
<tr>
<td>60</td>
<td>$\delta$ ($Ni_2Al_3$)</td>
<td>$2.6 \times 10^{-7}$ (average of four values in Table V of [23])</td>
</tr>
</tbody>
</table>
Figure 5. Variation of D with composition in the nickel rich phases of the Al-Ni system (1000° and 1100° C) [23].
Type I (Low Al Activity) Coating [22]

A schematic of the structures which can be classified as type I coatings are shown in Fig. 6 [22]. Markers placed on the surface of a pure Ni-substrate coated in a low-Al activity pack are located within the Ni-substrate after the coating treatment. Kirkendall porosity is observed near the Ni–NiAl interface (Fig. 6a). Powders of the inert filler are observed throughout the coating. Pack aluminization of Ni results in the formation of a β-NiAl phase with practically no Ni$_3$Al (γ') phase formation, in contradiction to the Al–Ni equilibrium diagram. This observation is also in contradiction with the results of Janssen [24]. Janssen annealed Ni-NiAl diffusion couples for 25 hours at different temperatures in the range 1000 - 1300 °C and found that an Ni$_3$Al layer did form. He also made the important observation that grain boundary diffusion accounts for about 65 % of the Ni$_3$Al layer thickness after a 25-hour anneal. This also explains the irregular morphology of the Ni$_3$Al layer at 1000° C. However, in an earlier work, when Janssen and Rieck [25] annealed a Ni–NiAl diffusion couple at 1000° C for 5 hours, no Ni$_3$Al layer was observed. This was attributed to the formation of porosity which limits the supply of Ni and lowers the growth rate of Ni$_3$Al. Additionally, in this earlier work, stoichiometric NiAl was used while in Janssen’s work [24], Ni-rich NiAl, which has higher growth rates of Ni$_3$Al, was used. Therefore, this may account for Pichoir’s interpretation of the formation of NiAl on Ni substrates without intermediate Ni$_3$Al in low Al-activity packs.
Figure 6. Aluminization by the low-activity process
(a) pure Ni ($e_1$ is formed first, then $e_2$, $e_3$, etc.)
(b) Ni-base superalloy (first $e_1$ and $e'_1$ form simultaneously, then $e_0$ and $e'_0$,...etc)
(c) structure of coated Ni-base superalloy. [22]
Figures 6b and 6c depict the sequence of changes occurring in a Ni-base superalloy when coated in a low Al activity pack. Once again, Ni diffuses outward faster than inward Al diffusion through the β-NiAl layer. However, due to outward Ni diffusion and the attendant Ni-depletion from the substrate alloy, elements in the substrate which have no significant solubility in NiAl form precipitates beneath the initial substrate surface (Figs. 6b and 6c). A two zone coating is formed, with the NiAl formed by outward diffusion of Ni constituting the external zone and an internal NiAl zone is formed as a result of Ni-denudation from the alloy. The internal zone contains precipitates of alloying elements with low solubility in NiAl. Kirkendall voids are not generally observed (see Fig. 3). For the same coating thickness, there is less Ni transport in the superalloy than in pure Ni [22]. Inclusions from the pack are found in the external zone of the coating.

Type II (High Al Activity) Coating [22]

Figure 7 shows a schematic of the process for forming inwardly growing coatings produced in high Al activity packs on pure Ni and Ni-base superalloys. The following characteristics are observed:

1. Markers placed on the surface of the substrates remain on the outer surface indicating that the coating grows by the inward diffusion of Al.

Since this is a high Al-activity pack, Ni$_2$Al$_3$ forms first and subsequently, NiAl and Ni$_3$Al layers are expected to form in accordance with the Al-Ni equilibrium diagram. Janssen and Rieck [25] annealed a Ni-Ni$_2$Al$_3$ diffusion couple for 32 hours at 1000° C and found that a thin (4 μm) Ni$_3$Al layer and a relatively thick (140 μm)
Figure 7. Aluminization by the high-Al activity process
(a) pure Ni (e₁ forms first, then e₂, e₃, etc.) (b) Ni-base superalloy (e₁ forms first, then e₂, e₃, etc.). [22]
$NiAl$ layer. However, Pichoir's schematic of the aluminization of $Ni$ in a high Al-activity process indicates that $Ni_2Al_3$ alone forms (Fig. 7a).

2. No Kirkendall voids or porosities are observed (see also Fig. 4).

3. No filler material is embedded in the coating.

Elements in the superalloys with limited solubility in $Ni_2Al_3$ form precipitates. MC-type carbides, if present in the substrate, remain embedded in the $Ni_2Al_3$ layer.

Diffusion annealing of the coatings on pure $Ni$ and $Ni$-base superalloys results in structures of the type shown in Figs. 8a and 8b. In Fig. 8a, the $Ni_2Al_3$ layer is completely transformed into a $NiAl$ layer by outward diffusion of $Ni$. In Fig. 8b, diffusion annealing of the superalloy results in an outer zone containing precipitates, a central precipitate-free zone and an inner zone with precipitates similar to the inner zone of low activity Al packs.

Thus, the major difference between low and high activity Al packs is the existence of an outer zone with precipitates for high Al activity packs.

1.1.2 Thermodynamics of Pack Aluminizing

In a $NaCl$ activated aluminizing pack containing pure aluminum as the source, the following equilibria pertain:

**Pack - gas equilibria**

The activator reacts with the source alloy to produce volatile metallic halides in the reaction:

$$Al \ (l) + NaCl \ (l) = AlCl \ (v) + Na \ (v)$$ (1.1)

$AlCl_2 \ (v)$ and $AlCl_3 \ (v)$ are also formed in the pack.
Figure 8. High-activity process followed by diffusion annealing (a) pure Ni (b) Ni-base superalloy [22].
Substrate - gas equilibria

The most important reaction occurring on the substrate surface is the disproportionation of the metal halide vapors $\text{AlCl}$ or $\text{AlCl}_2$:

$$2\text{AlCl} \ (v) = \text{AlCl}_2 \ (v) + \text{Al}_{\text{Ni}} \ (1.2)$$

Direct transfer of $\text{Al}$ by forming $\text{Al} \ (v)$ occurs only to a very small extent. Displacement reactions with the substrate such as

$$\text{Ni} + 2\text{AlCl} \ (v) = \text{NiCl}_2 \ (v) + 2\text{Al}_{\text{Ni}} \ (1.3)$$

do not occur because of reasons explained below.

The standard Gibbs energies of formation of the $\text{Al}$ halides are significantly more negative than those for the $\text{Ni}$ halides. This is shown in Fig. 9 which is an Ellingham diagram for the volatile $\text{Ni}$ and $\text{Al}$ chlorides constructed with data from Pankratz [26]. Figure 10 shows the partial pressures of $\text{Al}$ and $\text{Ni}$ halides in a $\text{NaCl}$ activated pack containing a pure $\text{Al}$ source and a $\text{Ni}$ substrate. For these calculations, performed by the author, the $\text{Al}$ chlorides are assumed to be in equilibrium with pure liquid $\text{Al}$ and the $\text{Ni}$ chlorides with pure solid $\text{Ni}$. Therefore, if pure $\text{Al}$ is used as the source for aluminizing pure $\text{Ni}$, the $\text{NiCl}$ and $\text{NiCl}_2$ partial pressures are significantly lower than the partial pressures of $\text{AlCl}$, $\text{AlCl}_2$ and $\text{AlCl}_3$ so that the $\text{Ni}$ does not participate in interchange reactions with the aluminum chloride vapors.

In the example calculation above, aluminizing of $\text{Ni}$ is treated for a pure $\text{Al}$ pack with the thermodynamic activity of $\text{Al}$ equal to 1. While the activity of $\text{Al}$ is unity in the pack, it is reduced considerably at the $\text{Ni}$ surface due to the formation of an aluminum-depleted zone.
Figure 9. Standard Gibbs energies of formation of gaseous Ni and Al chlorides.
Figure 10. Plot of log partial pressure vs temperature for aluminizing pure Ni in a NaCl-activated pack.
adjacent to the Ni surface [27]. This initial observation of Brill-Edwards and Epner [27] has been confirmed by Levine and Caves [28] and Seigle [7]. Walsh [15] has proposed that as free Al metal adjacent to the substrate is consumed, the activity of Al is still unity. Aluminum depleted vapors returning to the pack from the substrate would react with the Al adjacent to the substrate and completely consume it before Al further away is reacted. Levine and Caves proposed that the Al activity on the Ni substrate surface is as low as 0.01. Figure 11 shows the activity of Al as a function of the atom fraction of Al in binary Ni–Al alloys at 1000°C [29]. The Al content of the Ni–Al alloy corresponding to an activity of Al of 0.01 (log $a_{\text{Al}} = -2$) is in the high Al end of the $\beta$–NiAl field which is consistent with the microstructural observations of Goward and Boone [21] and Pichoir [22] described earlier.

Walsh, however, correctly pointed out that the pack cementation process is quite complex and involves a series of steps:

a. Reactions in the pack.

b. Gas phase diffusion through the pack.

c. Reactions at the surface to deposit the coating element, involving adsorption, dissociation and surface diffusion.

To fully understand the coating process, the kinetics of the process must be studied in conjunction with the thermodynamics.
Figure 11. The activity of aluminum in solid Ni-Al alloys at 1000°C. [29]
1.1.3 Kinetics of the Pack Aluminizing Process

Several models for the aluminizing of Ni and Fe base alloys have been proposed [28,30-34]. All of them are based on the existence of a depletion zone.

Levine and Caves (L-C) [28] proposed a kinetic model of pack aluminizing based on the assumption of local thermodynamic equilibrium at both the pack-gas and the substrate-gas interfaces. They also assumed that the transport of gases through the pack was purely diffusional. Instantaneous fluxes of the species to and from the substrate were calculated under conditions of one atmosphere total pressure and an activity of Al equal to 0.01 at the substrate surface. Figure 12 [28] shows the Levine-Caves model for NaX and NH₄X activated packs where (X = F, Cl, Br or I). The diffusion direction for each species in the depletion zone is obtained by computing the instantaneous fluxes. Then, depending on the temperature and the choice of X, certain gradients (e.g. $P_{AlX_3}$, $P_{AlX_2X_6}$) will be opposite to those shown schematically. Figure 12a is a simplified model in which the formation of liquid NaX is neglected. Figure 12b is more complete since the liquid NaX film on the substrate is taken into account while computing fluxes. Figure 12c is a complete model for NH₄X activated packs. The direction of the diffusion of Al₃X₂, Al₃X₃ and Al₂X₆ depends on X. In NH₄F activated packs, AlF and AlF₂ diffuse inward while AlF₃ and Al₂F₆ diffuse outward. In NH₄Cl, NH₄Br and NH₄I activated packs, AlX alone diffuses inward. In all cases, for the NH₄X and NaX activated packs, aluminum deposition is primarily done by AlX. The NaX (I) condensation on the substrate surface aids in Al deposition since there is no requirement for halogen removal by the diffusion of AlX₂ and AlX₃ away from the substrate surface.
According to the Levine-Caves model for pack aluminization, we can use pure Al as the source and NaX or NH4X as activators [28].
The Levine-Caves model was applied to the aluminizing of the IN 100 superalloy. Loss of alloying elements during the coating treatment, especially Cr, had to be considered. The Ni and Cr can be removed from the surface either in the metal vapor form or by forming volatile halides. Levine and Caves considered the loss of Ni and Cr only by forming a metal vapor. The Ni flux leaving the substrate is negligible while the Cr flux is about 1% of the Al weight gain. The loss of Ni by forming a halide would also be negligible as pointed out earlier, but the loss of Cr by forming Cr halides could make Cr loss somewhat higher than 1% used by Levine and Caves. However, this model is comprehensive and provides an adequate description of the pack aluminizing of superalloys.

Kandasamy, Seigle and Pennisi (K-S-P) [30] point out that in a NaX or AlF₃ activated pack, condensation of activator as NaX (l) or AlF₃ (s) on the substrate results in a net flux of activator from the pack to the specimen. Therefore, in addition to an Al-depleted zone, an activator-depleted zone forms adjacent to the substrate. If the amounts of activator and Al were stoichiometrically comparable, the activator and Al depletion zones would coincide. However, the amount of activator used in pack aluminizing is much less than Al and the activator-depleted zone is wider than the Al-depleted zone (Fig. 13). Kandasamy, Seigle and Pennisi have shown that it is possible to maintain a minor difference in total pressure between the pack-gas interface and the substrate-gas interface.

Nciri and Vandenbulcke (N-V) [31] modified the L-C and K-S-P models by including bulk flow of the vapors as an additional feature. This flow occurs due to the difference in the
Figure 13. The Kandasamy-Seigle-Pennisi model with mixed aluminum transport through activator and activator + Al depleted zones.
number of moles of gas involved in reactions at the interfaces. However, no difference in total pressure was allowed as in the K-S-P model.

More recently, Wang and Seigle (W-S) [32] have developed a more complete model taking into account the total pressure differential (K-S model) as well as the viscous flow of the halide vapors through the porous pack (N-V model) (Fig. 14). Aluminum transport rate constants and partial pressure values (for $NH_4Cl$ and $AlF_3$ activated packs) have been calculated. The values obtained fall between those obtained by the N-V and the L-C models which represent limiting cases for packs with zero resistance to viscous flow (large particle size of pack powders) and infinite resistance to viscous flow (small particle size).

Kung and Rapp [33] studied the aluminizing of iron through a fixed porous barrier (ceramic felt wrapping) and proposed a model based on the following assumptions: local equilibrium at the pack-gas and substrate-gas interfaces, rate control by diffusion of gases through a porous barrier surrounding the substrate in series with solid-state diffusion and condensation of activators such as $NaCl$ (l) and $AlF_3$ (s) on the specimen surface.

Figures 15 and 16 indicate the direction of fluxes of the species involved. Kung and Rapp did not consider a total pressure difference between the pack-gas interface and the substrate-gas interface, but viscous flow was considered. Good agreement between theoretical and experimental values for rates of Al gain were obtained for $NaCl$-activated packs.

Akeuzue and Stringer [34], in a very recent paper, have determined the surface Al concentration based on the formation of a liquid Al-enriched layer of variable Al composition on an iron substrate ($Fe$) (Fig. 17). The two new features of this model are:
Figure 14. The Wang-Seigle model for Al transport incorporating diffusional flux and viscous flow in the depleted zone. [32]
Figure 15. The Kung-Rapp model for transport in a NaCl-activated pack with an Fe-Al alloy source and with the depletion zone corresponding to the thickness of the alumina wrapping [33].
Figure 16. The Kung-Rapp model for transport in a $\text{AlF}_3$-activated pack containing an $\text{Fe-AL}$ alloy as the source. The thickness of the depleted zone corresponds to the thickness of the alumina wrapping [33]
Figure 17. The Akuezue-Stringer model for aluminization of pure iron. [34]
1. Formation of a thin liquid metal layer of almost constant thickness on the substrate allows an Al flux balance to be set up.

2. The concentration of Al at the transition boundary layer, M, is given by the solidus composition of the Fe–Al equilibrium diagram.

The Akeuzue-Stringer prediction of surface Al concentration agrees reasonably well with the experimentally obtained values.

1.2 PACK CHROMIZING

Kelly invented the process of pack chromizing of steels in 1923 [35]. Chromized coatings were found to be highly resistant to aqueous corrosion and the initial application was in improving the surface stability of steam turbine blades. Chromium coatings were used later for gas turbine blades and vanes for hot corrosion protection [19].

1.2.1 Structure of Chromium Coatings

Figure 18 shows the Ni-Cr equilibrium diagram [36]. At 1000° C, the maximum solubility of Cr in γ-Ni is 41 w/o Cr (44 w/o Cr) and the maximum solubility of Ni in α-Cr is 5.9 w/o Ni (5.3 w/o Ni). A eutectic reaction occurs at 1345° C at a Cr composition of 56 w/o Cr. A peritectoid decomposition of γ+α to γ' (the ordered Ni$_2$Cr phase) occurs at 590° C. Metastable δ and σ phases have been reported. δ-Cr with a primitive cubic structure containing 8 atoms per unit cell was observed only under special conditions such as evaporation of Cr particles at very low pressures. A metastable σ phase at about 71.8 w/o Cr is thought to exist below 600° C. Table 4 [17] gives crystal structure data for the Ni–Cr system.
Figure 18. The binary Ni-Cr equilibrium diagram [17]

TABLE 4. Crystal structure data for the Ni-Cr system [17]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition at. % Cr</th>
<th>Strukturbericht designation</th>
<th>Prototype</th>
</tr>
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<td>(Ni)</td>
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<td>Cu</td>
</tr>
<tr>
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<td>...</td>
<td>MoPt&lt;sub&gt;2&lt;/sub&gt;</td>
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<tr>
<td>(Cr)</td>
<td>68 to 100</td>
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<td>W</td>
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<td>Metastable phases</td>
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<td>D&lt;sub&gt;8&lt;/sub&gt;</td>
<td>σCrFe</td>
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<td>δ</td>
<td>100</td>
<td>A15</td>
<td>Cr&lt;sub&gt;3&lt;/sub&gt;Si</td>
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</tbody>
</table>
Figure 19 shows a typical chromium coating on a nickel-base superalloy coated in a pack containing chromium, ammonium chloride and alumina. The coating is a $\gamma$–Ni–Cr solid solution with discontinuous $\alpha$–Cr in the outer layer. The dark phase is $Al_2O_3$ particles attributed by Goward [19] to internal oxidation of $Al$ in the substrate. Goward further points out that Baldi [37] and Brill-Edwards [38] have prevented this by adding $Al$ to the chromium source in the pack. Baldi [37] preheated a mixture of $Ni$, $Co$, $Cr$ and $Al$ powders in a pack containing $NH_4Cl$, $MgCl_2$ and $Al_2O_3$ to approximately 1040° C and held it there for 20 hours. The pack was cooled and substrates introduced before reheating to 1040° C in a $H_2$ atmosphere. Since Baldi did not use a $H_2$ environment during pretreatment, it is probable that most of the $Al$ was oxidized to $Al_2O_3$ while some of the $Al$ probably alloyed with the $Co$, $Ni$ and $Cr$ powders. Subsequently, since the coating operation was performed in a $H_2$ atmosphere, the $Al$ in the substrate was internally oxidized and since the pack contains virtually no $Al$, chromizing without internal-oxidation results. Brill-Edwards [38] performed the coating treatment in air with $Cr$ and $Al$ present in the pack. The $Al$ in the pack therefore functions as an oxygen getter and permits the $Cr$ coating to be applied without internal oxidation. In the author's opinion, the results of both patents could have been achieved without using $Al$, $Ni$ or $Co$ in the pack. An inert or reducing atmosphere would have been effective in preventing internal oxidation of $Al$ in the substrate. These patterns indicate an incomplete understanding of the fundamental aspects of pack cementation coating processes.

Literature on the structure and properties of chromium coatings for $Ni$-base superalloys is sparse. Samuel and Lockington [39] and Drewett [40] presented structural and kinetic data
Figure 19. Chromium diffusion coating formed by pack cementation [3]
for chromide coatings on steel, but these are anticipated to be quite different for Ni-base alloys.

1.2.2 Thermodynamics of Pack Chromizing

Hoar and Croom [41] analyzed the thermodynamics of chromizing. The incorporation of Cr into substrates was achieved by one or more of the following reactions.

i. Displacement reactions:

\[
CrCl_2 (v) + Fe (s) = FeCl_2 (v) + Cr
\]  
(1.4)

ii. Reduction of halide vapor (in a reducing \( H_2 \) atmosphere):

\[
CrCl_2 (v) + H_2 (g) = 2HCl (g) + Cr
\]  
(1.5)

iii. Thermal decomposition of halide vapor

\[
CrCl_2 (v) = Cr + Cl_2 (g)
\]  
(1.6)

Displacement reactions are important only if the substrate element forms volatile halide vapors of appreciable partial pressure (e.g., \( Fe \)). Figure 20 is an Ellingham diagram for \( Ni \) and Cr chlorides showing standard Gibbs energies of formation of the gaseous chlorides as a function of temperature. The standard Gibbs energies of formation for the chromium chlorides, provided by Wagner and Stein [42], is more negative than the \( Ni \) halides although not quite as low as for the Al halides. Figure 21 shows that the partial pressures of Cr chlorides are higher than the partial pressures of \( Ni \) halides in a \( NaCl \) activated pack containing pure Cr or pure Ni respectively. Therefore it is expected that \( Ni \) will not participate to a great extent in a displacement reaction with \( CrCl_2 \).
Figure 20. Standard Gibbs energies of formation for gaseous Ni and Cr chlorides.
Figure 21. Log partial pressures of Cr and Ni chlorides as a function of temperature in NaCl-activated packs containing pure Ni or pure Cr.
Hoar and Croom point out that since displacement reactions are insignificant for Ni substrates, a $H_2$ atmosphere is essential for chromizing Ni. This is not necessarily true, since a disproportionation reaction of the type:

$$3CrCl_2 (v) = 2CrCl_3 (v) + Cr$$

(1.7)
could provide for Cr transport. Therefore, it should be possible to chromize Ni in an inert atmosphere.

Mazille [43] chromized pure Ni in an $NH_4Cl$-activated pack containing pure Cr. He correctly points out that displacement reactions of the type

$$CrCl_2 (v) + Ni (s) = NiCl_2 (v) + Cr$$

(1.8)
are not responsible for the coating process from free energy considerations. The most important coating reaction was attributed to

$$CrCl_2 (v) + H_2 (g) = Cr (s) + 2HCl (g)$$

(1.9)
Once again, the possibility of disproportionation of $CrCl_2$ was not considered.

Walsh [15] points out that the presence of $HCl$ in $NH_4Cl$ activated packs results in a side reaction

$$Al_2 O_3 (s) + 6HCl (g) = 2AlCl_3 (g) + 3H_2 O (v)$$

(1.10)
with the inert filler. The $H_2O (v)$ can undergo a further reaction

$$2CrCl_2 (s) + 3H_2O (g) = Cr_2O_3 (s) + 4HCl (g) + H_2(g)$$

(1.11)
with condensed \( \text{CrCl}_2 \). However, condensed \( \text{CrCl}_2 \) is unlikely to be present in cementation packs at coating temperatures of about 1000\(^\circ\) C (cf. Chap. IV). The possibility of \( \text{H}_2\text{O} \) oxidizing \( \text{Cr} \) to \( \text{Cr}_2\text{O}_3 \) also exists; the \( \text{Cr}_2\text{O}_3 \) formed by such reactions could coat the source alloy and impede further reactions.

Walsh proposes that if \( \text{H}_2 \) were eliminated by the use of \( \text{CrCl}_3 \) as an activator, then the \( \text{Cr}_2\text{O}_3 \) would be more likely to form on the \( \text{Al}_2\text{O}_3 \) (inert diluent) by

\[
2 \text{CrCl}_2 (\text{v}) + \text{Al}_2\text{O}_3 (\text{s}) = \text{Cr}_2\text{O}_3 (\text{s}) + 2 \text{AlCl}_2 (\text{v}) \quad (1.12)
\]

This would not interfere with the chromizing process according to Walsh [15]. However, the \( \text{AlCl}_2 (\text{v}) \) will aluminize the substrate and would therefore interfere with the chromizing process.

A controversy exists here with Walsh pointing out the deleterious effect of hydrogen and Hoar and Croom showing that it is the most significant species in chromizing \( \text{Ni} \). While Hoar and Croom did not consider the disproportionation of \( \text{CrCl}_2 \) as a possible chromizing reaction, Walsh did not consider using \( \text{CrCl}_2 \) as an activator. Therefore, if \( \text{CrCl}_2 \) is used as an activator in an inert atmosphere, it should be possible to chromize pure \( \text{Ni} \) via a disproportionation reaction.

1.2.3 Kinetics of Chromizing

Mazille [43] investigated the kinetics of chromizing pure \( \text{Ni} \) in an \( \text{NH}_4\text{Cl} \) activated pack containing pure \( \text{Cr} \) as the source. Figure 22a shows an external \( \alpha-\text{Cr} \) layer and Fig. 22b shows a coating on pure \( \text{Ni} \) after chromizing for 16 hours at 950\(^\circ\) C. The outer layer is an \( \alpha-\text{Cr} \) region with an inner single-phase, \( \text{Ni} \)-rich \( \gamma \) solid solution. Mazille estimated that
Figure 22. Microstructures of (a) the chromized Ni-surface showing $\alpha$-Cr particles (350 X) (b) cross-section of chromized Ni showing a 2-layer coating (350X).
the Cr content of the outer layer exceeded 90 w/o Cr (91 a/o Cr). From the activity-composition plot for Cr in a Ni−Cr alloy, shown in Fig. 23 [44], this composition is in the two-phase α+γ region and the activity of Cr is approximately 0.96.

From Fig. 24a, Mazille concluded that the chromizing of Ni is controlled by the slow solid state diffusion into austenitic Ni and not by transport in the gas or reactions at the substrate surface. The change of slope for the 950°C curve is attributed to the slower formation of the external α when compared to the 1000°C or 1050°C treatments. Once α forms, diffusion occurs more rapidly since it is a bcc structure.

Figure 24b shows the growth rate of γ. While a parabolic relation is observed at 1000 and 1050°C, the shape of the 950°C curve is different. This is attributed to the approximately equal diffusion rates through the γ-α and γ-pure Ni phase boundaries. This implies that the inner γ layer remains approximately of constant thickness once the slower growing outer α-layer forms.

1.3 ‘CHROM-ALUMINIZING’ AND SIMULTANEOUS CHROMIZING-ALUMINIZING

Research in the area of chromium-aluminum coatings has focussed on the two-step chromizing-aluminizing process. Godlewska and Godlewska [14] obtained chromium coatings initially in a pack containing pure chromium and subsequently the chromized coupons were aluminized in low or high Al-activity packs. Figure 25 shows the microstructures of aluminide and two-step chromaluminide coatings.
Figure 23. The activity of Cr in solid Ni-Cr alloys for various temperatures \([44]\).
Figure 24. Kinetic data for the chromizing of pure Ni (a) the specific weight gain as a function of time at different temperatures (b) variation of thickness of the inner layer with time at different temperatures [43].
Figure 25. Microstructures of (a) aluminide and (b) chromaluminide coatings on EI867 with Cr concentration profiles [14].
Galmiche [45, 46] was the first to propose a technique for simultaneous chromizing-aluminizing of Ni, Fe and Co-base alloys. The process, called chromaluminization, consists of heating the substrates in a pack containing

- Ultrafine chromium powder 40 w/o
- Very fine Al powder 10 w/o
- Fine calcined Al_2O_3 49.2 w/o
- NH_4Cl (or NH_4Br) 0.8 w/o

to a temperature in the range 750 - 1200° C. Although mention is made of "prealloyed" powders, clearly Galmiche has used mixtures of pure Cr and Al. The resulting coatings typically appear as in Fig. 26.

According to Galmiche, during the first 'phase' of the 'chromaluminizing' treatment, Cr is preferentially supplied and during the second 'phase' Al is preferentially supplied. This does not seem plausible because the partial pressures of the Al halides are significantly higher than that of the Cr halides and a pack containing a mixture of pure Cr and Al would therefore aluminize the substrate. Examination of Galmiche and Hivert's patent [46] indicates that pure Cr (40 w/o) and pure Al (10 w/o) were preheated in a pack containing alumina and NH_4Cl for 1 hour at 1000 - 1100° C. Under these conditions, aluminum chloride vapor pressures are much higher than chromium chloride vapor pressures and so Al is deposited on the Cr particles. Galmiche and Hivert also indicate that the addition of 0.5 - 1.0 w/o AlF_3 to the pack which already contains NH_4Cl would be advantageous. AlF_3 is a strong aluminizing agent [8]. Therefore, the following sequence of events is proposed by this author to account for Galmiche's results:
Figure 26. Chromaluminized coating on Inconel 713 (a) Microstructure of coating (×500) (b) Concentration profiles of Cr and Al in the chromaluminized regions of Inconel 713 [43]
1. During the pretreatment, Al is deposited on Cr particles via AlClₓ vapors (NH₄Cl-assisted) and AlFₓ vapors (AlF₃ assisted). The average Al content of the Cr-Al particles thus formed is likely to be quite low due to the very short duration of treatment, but the surfaces of the Cr particles should be quite rich in Al.

2. When the substrates are introduced into the pack and the coating operation begins, the remaining NH₄Cl generates volatile Al chlorides but negligible Cr chloride partial pressures over the Cr-Al particles. The partial pressures of the Al chlorides and fluorides due to the remaining pure Al would dominate and effect aluminizing. The Cr content of the substrate is conserved.

In conclusion, Galmiche's chromaluminization process is essentially an aluminizing treatment. The sharp increase in Cr concentration in the inner diffusion zone is attributed to outward Ni diffusion and consequent Ni depletion in this region.

Walsh [15] and Restall [9] have pointed out that it is impossible to codeposit Al and Cr in a one step process if pure Al and pure Cr are used. Figure 27 shows the partial pressures of gaseous halides in a NaCl-activated pack assumed to contain pure Al, pure Cr and pure Si as a function of temperature [47]. At 1273 K (1000°C), a typical coating temperature, the partial pressures of AlCl is 6-7 orders of magnitude higher than CrCl₂. Therefore, under these conditions, codeposition of Al and Cr would not be possible. Marjinissen [48] has shown experimentally that by choosing a special pack composition, simultaneous deposition of Cr and Al into a Ni-base alloy (IN 730) at 1100°C is possible. The chemical equilibrium in the pack used as the basis for codeposition of Cr and Al is
Figure 27. Log partial pressure of gaseous halides as a function of temperature in NaCl-activated packs containing pure Al, Si and Cr [47].
By reducing the $Al$ activity in the pack, $a_{Al}$, the partial pressure of volatile $Al$ halides can be moderated, leading to codeposition. However, the required composition of the source alloy and the effect of the activator on the coating process has not been treated.

Simultaneous chromizing-aluminizing is critically dependent on the choice of the masteralloy and the activator. For unit $Al$ activity, the partial pressure of the $Al$ halides are many orders of magnitude higher than those of the $Cr$ halides at unit $Cr$ activity. In order to achieve codeposition, the $Al$ activity has to be lowered by several orders of magnitude to generate comparable $Al$ and $Cr$ halide partial pressures.

Johnson, Komarek and Miller [49] have determined the activities of $Al$ and $Cr$ in binary $Al$-$Cr$ alloys at 1273 K (Fig. 28). The maximum solid solubility of $Al$ in $Cr$ is 43 a/o $Al$; for all $Al$ compositions lower than this, the activity of $Al$ is much lower than that of $Cr$ for $Cr$-rich, $Cr$-$Al$ alloy. The highly negative deviation from ideal solution behavior provides an $Al$ activity of 0.001 at 9 a/o $Al$. Therefore, the composition of a $Cr$-$Al$ masteralloy can be manipulated to adjust the activities of $Al$ and $Cr$ so that comparable partial pressures for the halides of $Cr$ and $Al$ are generated in a pack for codeposition of $Cr$ and $Al$. The specific activator also affects the magnitudes and ratios of the partial pressures.

In the next chapter, the basis for thermodynamic and kinetic evaluation of the simultaneous chromizing-aluminizing process is explained.
Al content of Al-Cr alloys at 1273 K [49].

Figure 28. Activities of Al and Cr as a function of the

[Graph showing the activities of Al and Cr as a function of Na\(_{11}\) (w%) with a peak at 1273 K.]
2.1 INTRODUCTION

The process of simultaneous chromizing-aluminizing is quite complicated and involves several reaction steps:

1. Reaction between the activator and masteralloy to produce volatile metallic halide vapor species.
2. Diffusion of vapor through the porous pack to the substrate surface.
3. Reaction at the substrate surface to deposit Al and Cr.
4. Subsequent diffusion of Al and Cr into the substrate.

Most previous workers have used unit activities for the coating components in their calculations. However, Walsh [15] and Nciri and Vandenbulcke [31] determined the partial pressures of vapor species for packs with reduced, but still high, Al activities. In the following, the calculation of equilibrium partial pressures of vapor species for low Al activity packs containing Cr-Al masteralloys and the activators NaCl, NH₄Cl, CrCl₂, NaF or AlF₃ using the computer program SOLGASMIX are described.
2.2 FEATURES OF THE SOLGASMIX PROGRAM

The evaluation of equilibrium compositions of complex gas-solid systems by hand calculations is tedious and prone to error. Several computer programs have been developed to calculate equilibrium compositions based on the following general constraints:

1. Conservation of each element involved.

2. Minimization of the Gibbs energy of the system.

White, Johnson and Dantzig [50] used the Gibbs energy minimization technique to determine equilibrium gas compositions in complex gas phases. Eriksson [51] extended this technique to include condensed phases of invariant stoichiometry with the SOLGAS program. Subsequently, Eriksson [52] developed the SOLGASMIX program to compute equilibrium compositions in complex systems containing non-ideal gases, liquids or gaseous mixtures by incorporating activity coefficients. Bessman [53] incorporated the features of calculating equilibrium compositions under a constraint of constant total volume and called it SOLGASMIX-PV which was later modified to run on the IBM personal computer by Lin [54].

Thermodynamic and Mathematical Basis for SOLGASMIX-PV

The total Gibbs energy of a system is expressed as

\[ G = \sum_i n_i g_i \] (2.1)
and

\[
\frac{G}{RT} = \sum_{i} n_i \left( \frac{g_i^0}{RT} \right)_i + \ln a_i
\]  

(2.2)

where \( n_i \) = number of modes of species \( i \).
\( R \) = gas constant
\( T \) = absolute temperature
\( g_i^0 \) = standard Gibbs energy of formation of species \( i \)
\( a_i \) = activity of species \( i \)

\( \frac{G}{RT} \) is minimized under the following constraints:

— \( n_i \) values corresponding to the equilibrium mixture must be non-negative.

— the mass balance is satisfied.

The mass balance relation is

\[
\sum_{p=1}^{q+s+1} \sum_{i=1}^{m_p} a_{pi} n_{pi} = b_j \quad (j = 1,2,\ldots)
\]  

(2.3)

where

\( a_{pi} \) is the number of atoms of the \( j \)th element in a molecule of the \( i \)th species in the \( p \)th phase.

\( p=1 \) represents the gaseous phase, \( p=2 \) to \( p=q+1 \) represents the solid and liquid mixtures, and \( p=q+2 \) to \( p=q+s+1 \) represents pure condensed phases.

\( m_p \) is the total number of substances in the \( p \)th phase.

Lagrange's method of undetermined multipliers is used to determine the constrained minimum. The equations thus obtained are logarithmic and are expanded in a Taylor series
about initially estimated $n_i$ values neglecting second and higher order derivatives. The linear equations thus obtained are solved using the Gaussian Elimination Method.

The SOLGASMIX-PV program consists of a data entry program called ENTRY and the SGMAIN program which calculates the equilibrium compositions of the various species. Data was also entered with the SENTRY program of the ITSOL package, developed by Flynn, Morris and Carter [55].

2.3 Input for the Entry Program

All calculations were performed at T=1273 K for a total pressure of 1 atmosphere. The input amounts for each element were fixed on the basis of 50 gm of pack containing 73% $\text{Al}_2\text{O}_3$, 25% Cr-Al masteralloy and 2% activator salt. The coating treatment calculation was performed for an Ar atmosphere. The input moles of Ar was calculated using the ideal gas law as $4 \times 10^{-4}$. The standard Gibbs energy values for most species were provided by Pankratz [56]. Thermodynamic data for the gaseous chromium chlorides were obtained from Wagner and Stein [57] and for gaseous chromium fluorides from Kent and Margrave [58] and Zmbov and Margrave [59]. The data were extracted in the manner described below.

2.3.1 Thermodynamic Data for Gaseous Chromium Chlorides

Standard Gibbs Energy of Formation for $\text{CrCl}_2 (v)$

The values of the equilibrium constant, ($K_p$) for the reaction

$$2 \text{HCl (g)} + \text{Cr (s)} = \text{H}_2 (g) + \text{CrCl}_2 (l)$$

is $\frac{1}{K_p^f}$ in the notation of Wagner and Stein [57] where

$$K_p^f = \left( \frac{p_{\text{HCl}}}{\sqrt[p]{p_{\text{H}_2}}} \right)^2,$$

and $p_{\text{HCl}}$ and $p_{\text{H}_2}$
are the partial pressures of $HCl$ (g) and $H_2$ (g). The values of $K_p^I$ and $\Delta G$ for this reaction calculated from Wagner and Stein's data for three different temperatures are summarized in Table 5. $\Delta G^0$ was obtained as a function of temperature by setting it equal to $a + \frac{b}{T} + cT$. The constants $a$, $b$ and $c$ were determined to be 21478.4, -3.4×10^7 and -4.24 respectively.

For the reaction

$$2 \text{HCl} \ (g) + \text{Cr} \ (s) = \text{H}_2 \ (g) + \text{CrCl}_2 \ (v) \quad (2.5)$$

the equilibrium constant is $K_p = p_{\text{CrCl}_2} \left[ \frac{\sqrt{p_{\text{H}_2}}}{p_{\text{HCl}}} \right]^2$. The partial pressure of $\text{CrCl}_2$, $p_{\text{CrCl}_2}$ is given by

$$p_{\text{CrCl}_2} = \frac{1}{K_p^{III}}$$

where $K_p^{III}$ has the same meaning as defined by Wagner and Stein [57]. Table 5 summarizes the data obtained for the reaction (2.5). The $p_{\text{CrCl}_2}$ values were obtained from Fig. 4 in Wagner and Stein. To obtain the standard Gibbs energy of formation of $\text{CrCl}_2$ from Eq (2.5), the following reaction

$$\text{H}_2 \ (g) + \text{Cl}_2 \ (g) = 2 \text{HCl} \ (g) \quad (2.6)$$

is added to reaction (2.5) to give

$$\text{Cr} \ (s) + \text{Cl}_2 \ (g) = \text{CrCl}_2 \ (v) \quad (2.7)$$

The Gibbs energy changes for the reaction (2.7) at different temperatures are summarized in Table 6.

**Standard Gibbs Energy of Formation for CrCl$_3$ (v)**

The Gibbs energy of formation data for CrCl$_3$ (v) is obtained from the following equations:
**TABLE 5.** Gibbs energy changes for the reactions (2.4) and (2.5)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta G^0$ [Eq. (2.4)] (cal)</th>
<th>$\ln \frac{1}{K^I_p}$</th>
<th>$\ln p_{\text{CrCl}_2}$</th>
<th>$\ln \frac{1}{K^II_p}$</th>
<th>$\Delta G^0_{II}$ [Eq. (2.5)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>-20115.4</td>
<td>11.25</td>
<td>-8.80</td>
<td>2.45</td>
<td>-4381.3</td>
</tr>
<tr>
<td>1000</td>
<td>-16761.6</td>
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<td>-7.37</td>
<td>1.07</td>
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</tr>
<tr>
<td>1100</td>
<td>-14094.7</td>
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<td>-6.19</td>
<td>0.26</td>
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</tr>
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<td>1200</td>
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<td>-5.01</td>
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</tr>
<tr>
<td>1400</td>
<td>-8743.3</td>
<td>3.14</td>
<td>-3.66</td>
<td>-0.52</td>
<td>1446.5</td>
</tr>
</tbody>
</table>

**TABLE 6.** $\Delta G^0_f$ for $\text{CrCl}_2$ (v) and $\text{CrCl}_3$ (v) in the temperature range 900-1400 K

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta G^0$ ($\text{CrCl}_2$ (v)) (cal/mole)</th>
<th>$\Delta G^0_{\text{CrCl}_3}$ (cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>-52251.3</td>
<td>-</td>
</tr>
<tr>
<td>1000</td>
<td>-50308.1</td>
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<tr>
<td>1100</td>
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<tr>
<td>1200</td>
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<td>1300</td>
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<td>-88996</td>
</tr>
<tr>
<td>1400</td>
<td>-47897.5</td>
<td>-</td>
</tr>
</tbody>
</table>
Adding Eq. (2.8) through (2.10), the following equilibrium reaction is obtained:

\[
Cr \ (s) + \frac{3}{2} \ HCl \ (g) = \frac{3}{2} \ H_2 \ (g) + CrCl_3 \ (s) \quad (2.8)
\]

\[
CrCl_3 \ (s) = CrCl_3 \ (v) \quad (2.9)
\]

\[
\frac{3}{2} \ H_2 \ (g) + \frac{3}{2} \ Cl_2 \ (g) = 3 \ HCl \ (g) \quad (2.10)
\]

The Gibbs energy of formation of \( CrCl_3 \ (v) \) for several temperatures is shown in Table 6.

**2.3.2 Thermodynamic Data for Gaseous Fluorides**

*Standard Gibbs Energy of Formation for \( CrF_3 \)*

Zmbov and Margrave [59] analyzed \( CrF_3 \) vapors over \( CrF_3 \) solid effusing from Knudsen cells using a mass spectrometer. For the equilibrium,

\[
CrF_3 \ (s) = CrF_3 \ (v) \quad (2.12)
\]

the partial pressure of \( CrF_3 \ (v) \) was obtained as

\[
\log p_{CrF_3} \ (atm) = \frac{(1.264 \pm 0.012) \times 10^4}{T} + 7.20 \pm 0.12 \quad (2.13)
\]

in the temperature range 906 - 1058 K. The Gibbs energy change associated with this reaction (\( \Delta G^0 \)) equals \(-RT \ \ln p_{CrF_3} \). The standard Gibbs energy of formation for solid \( CrF_3 \) associated with the reaction

\[
Cr \ (s) + \frac{3}{2} \ F_2 \ (g) = CrF_3 \ (s) \quad (2.14)
\]

as a function of temperature was provided by Pankratz [56]. The standard Gibbs energy of formation for \( CrF_3 \ (v) \),
Cr (s) + \frac{3}{2}F_2 (g) = CrF_3 (v) \tag{2.15}

is obtained by adding the energy changes associated with (2.12) and (2.14). Table 7 shows the Gibbs energies for reactions (2.12), (2.14) and (2.15) for temperatures in the range 900-1400 K.

**Standard Gibbs Energy of Formation of CrF_2**

Kent and Margrave [58] studied the sublimation and vaporization of CrF_2 from a Knudsen cell with a mass spectrometer. The partial pressure of CrF_2 for the equilibrium,

CrF_2 (s) = CrF_2 (v) \tag{2.16}

is expressed as

\[ \log p_{CrF_2}(\text{atm}) = -\frac{(1.822 \pm 0.030) \times 10^4}{T} + 9.14 \pm 0.18 \tag{2.17} \]

The partial pressure of CrF_2 (v) in equilibrium with liquid CrF_2 (melting point of CrF_2 is 1167 ± 6 K [56]) as shown in reaction (2.18)

CrF_2 (l) = CrF_2 (v) \tag{2.18}

is expressed as

\[ \log p_{CrF_2}(\text{atm}) = -\frac{(1.707 \pm 0.010) \times 10^4}{T} + 8.18 \pm 0.18 \tag{2.19} \]

The values of log \( p_{CrF_2} \) in the temperature range 900-1400 K are obtained from Eqs. (2.17) and (2.19). Table 8 shows the values of log \( p_{CrF_2} \) for different temperatures and the corresponding Gibbs energies. The Gibbs energy of formation of solid CrF_2 associated with the reaction

Cr (s) + F_2 (g) = CrF_2 (s) \tag{2.20}

was provided by Pankratz [56]. These values for different temperatures in the range
TABLE 7. Gibbs energy of formation for CrF\(_3\) (v)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>(\Delta G) [Eq. (2.12)] (cal)</th>
<th>(\Delta G^0) (CrF(_3) (s)) [Eq. (2.14)] (cal)</th>
<th>(\Delta G^0) (CrF(_3) (v)) [Eq. (2.15)] (cal)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-203320.5</td>
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</tr>
<tr>
<td>1400</td>
<td>-205610</td>
<td>11723.9</td>
<td>-193886.1</td>
</tr>
</tbody>
</table>

TABLE 8. Standard Gibbs energy of formation of CrF\(_2\) (v)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>(\log p_{\text{CrF}_2})</th>
<th>(\Delta G^0 = -RT \ln p_{\text{CrF}_2}) (cal)</th>
<th>(\Delta G^0) (CrF(_2) (s)) [Eq. (2.20)] (cal)</th>
<th>(\Delta G^0) (CrF(_2) (v)) [Eq. (2.21)] (cal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>-11.10</td>
<td>45714.8</td>
<td>-157086</td>
<td>-111371.2</td>
</tr>
<tr>
<td>1000</td>
<td>-9.08</td>
<td>41550.6</td>
<td>-154089</td>
<td>-112538.4</td>
</tr>
<tr>
<td>1100</td>
<td>-7.42</td>
<td>37349.8</td>
<td>-151119</td>
<td>-113769.2</td>
</tr>
<tr>
<td>1200</td>
<td>6.05</td>
<td>33194.7</td>
<td>-148181</td>
<td>-114986.3</td>
</tr>
<tr>
<td>1300</td>
<td>-4.95</td>
<td>29447.0</td>
<td>-145287</td>
<td>-115840.1</td>
</tr>
<tr>
<td>1400</td>
<td>-4.01</td>
<td>25690.0</td>
<td>-142404</td>
<td>-116714.0</td>
</tr>
</tbody>
</table>
The standard Gibbs energy of formation of CrF₂ associated with the reaction

\[ \text{Cr (s)} + \text{F}_2 \text{ (g)} = \text{CrF}_2 \text{ (v)} \]  \hspace{1cm} (2.21)

is obtained by adding reactions (2.16) and (2.20) in the temperature range 900-1100 K and (2.18) and (2.20) in the range 1200-1400 K (Table 8).

**Standard Gibbs Energy of Formation for CrF(v)**

The equilibrium constant for the reaction

\[ 2 \text{CrF } (v) = \text{Cr} (v) + \text{CrF}_2 \text{ (v)} \]  \hspace{1cm} (2.22)

is obtained from Kent and Margrave and the associated Gibbs energy values are shown in Table 9 for temperatures in the range 1269-1307 K. The variation of the Gibbs energy as a function of temperature for the reaction (2.22) was expressed as

\[ \Delta G^0 = a + \frac{b}{T} + cT \]  \hspace{1cm} (2.23)

where \( a = 1067712.9 \), \( b = -7.22 \times 10^8 \) and \( c = -401.45 \).

The standard Gibbs energy of formation of CrF (v) as expressed in the equation

\[ \text{Cr (s)} + \frac{1}{2} \text{F}_2 \text{ (g)} = \text{CrF} \text{ (v)} \]  \hspace{1cm} (2.24)

is obtained by adding Eqs. (2.21) and (2.22) and the Eq.

\[ \text{Cr (s)} = \text{Cr} \text{ (v)} \]  \hspace{1cm} (2.25)

Table 10 shows the Gibbs energies associated with reactions (2.21), (2.22), (2.24) and (2.25) in the temperature range 900-1300 K.
TABLE 9. Gibbs energies for reaction 2.22

<table>
<thead>
<tr>
<th>T (K)</th>
<th>log K</th>
<th>$\Delta G^0 = -RT \ln K$ (cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1269</td>
<td>1.839</td>
<td>-10679.1</td>
</tr>
<tr>
<td>1286</td>
<td>1.696</td>
<td>-9980.6</td>
</tr>
<tr>
<td>1290</td>
<td>1.668</td>
<td>-9846.4</td>
</tr>
<tr>
<td>1307</td>
<td>1.596</td>
<td>-9545.5</td>
</tr>
</tbody>
</table>

TABLE 10. Standard Gibbs energies of formation for $CrF_2$ (v), $Cr$ (v) and $CrF$ (v)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta G$ [Eq. (2.22)] (cal)</th>
<th>$-\Delta G^0 (CrF_2 \text{(v)})$ [Eq. (2.21)] (cal)</th>
<th>$-\Delta G^0 (Cr \text{(v)})$ [Eq. (2.25)] (cal)</th>
<th>$\Delta G^0 (CrF \text{(v)})$ [Eq. (2.24)] (cal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>-95814.3</td>
<td>111371.2</td>
<td>-63108</td>
<td>23775.6</td>
</tr>
<tr>
<td>1000</td>
<td>-55787.1</td>
<td>112538.4</td>
<td>-59688</td>
<td>1468.4</td>
</tr>
<tr>
<td>1100</td>
<td>-30245.7</td>
<td>113769.2</td>
<td>-56298</td>
<td>-13612.8</td>
</tr>
<tr>
<td>1200</td>
<td>-15693.8</td>
<td>114986.3</td>
<td>-52938</td>
<td>-23117.3</td>
</tr>
<tr>
<td>1300</td>
<td>-9556.7</td>
<td>115840.1</td>
<td>-49595</td>
<td>-28344.2</td>
</tr>
</tbody>
</table>
2.3.3 Thermodynamic Data for Complex Halide Species

In addition to simple molecules like $AlCl$, $AlCl_2$, $AlCl_3$, $CrCl_2$ and $CrCl_3$, complex molecules such as $CrAl_2Cl_8$, $NiAl_3Cl_{11}$ and $CrAl_3Cl_{12}$ have to be considered in the transport of $Cr$ and $Al$ to the substrate surface. Nciri and Vandenbulcke report thermodynamic data for the following complex species:

$$CrCl_2 (s) + AlCl_6 (v) = CrAl_2Cl_8 (v)$$  \hspace{1cm} (2.26)

$$NiCl_2 (s) + Al_2Cl_6 (v) = NiAl_2Cl_8 (v)$$  \hspace{1cm} (2.27)

$$2 CrCl_3 (s) + 3 Al_2Cl_6 (v) = 2CrAl_3Cl_{12}$$  \hspace{1cm} (2.28)

The standard Gibbs energies of formation of the complex halides were calculated with the following relations:

$$\Delta H^0 = \Delta H^0_{298} + \int_{298}^{T} \Delta c^0 P \, dT$$  \hspace{1cm} (2.29)

$$\Delta S^0 = \Delta S^0_{298} + \int_{298}^{T} \frac{\Delta c^0 P}{T} \, dT$$  \hspace{1cm} (2.30)

$$\Delta G^0_T = \Delta H^0_T - T \, \Delta S^0_T$$  \hspace{1cm} (2.31)

The value of the Gibbs energies as a function of temperature for Eqs. (2.26), (2.27) and (2.28) along with the standard enthalpy and entropy values at 298 K are shown in Table 11.

The standard Gibbs energy of formation for each species is worked out as the example for $CrAl_2Cl_8$ shown below:

$$CrCl_2 (s) + Al_2Cl_6 (v) = CrAl_2Cl_8 (v)$$  \hspace{1cm} (2.32)

$$2 Al (s) + 3 Cl_2 (g) = Al_2Cl_6 (v)$$  \hspace{1cm} (2.33)

$$Cr (s) + Cl_2 (g) = CrCl_2 (v)$$  \hspace{1cm} (2.34)

By adding the three equations shown above, Eq. (2.35) is obtained:
TABLE 11. Thermodynamic data for complex halides

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H_{298}^0$ (kcal/mole)</th>
<th>$\Delta S_{298}^0$ (cal/mole-K)</th>
<th>$\Delta C_P$ (cal/mole-K)</th>
<th>$\Delta G_f^0$ (cal/mole)</th>
<th>$\Delta G_{1273}^0$ (cal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CrAl_2Cl_8$</td>
<td>10</td>
<td>12</td>
<td>-1</td>
<td>10298-18.7T+T ln T</td>
<td>-296964</td>
</tr>
<tr>
<td>$NiAl_2Cl_8$</td>
<td>13</td>
<td>11</td>
<td>-1</td>
<td>13298-17.7T+T ln T</td>
<td>-261984</td>
</tr>
<tr>
<td>$CrAl_3Cl_{12}$</td>
<td>1</td>
<td>2.5</td>
<td>0</td>
<td>1000-2.5T</td>
<td>-419975</td>
</tr>
</tbody>
</table>
\[ \text{Cr} \, (s) + 2 \text{Al} \, (s) + 4 \text{Cl}_2 \, (g) = \text{CrAl}_2\text{Cl}_8 \, (v) \]  \hspace{1cm} (2.35)

Since the \( \Delta G^0 \) values for the \text{Al} and \text{Cr} halides are reported with respect to pure \text{Al} and pure \text{Cr} as standard states, the input for the ENTRY program had to be modified to incorporate activities of \text{Al} and \text{Cr} for binary \text{Al-Cr} masteralloys. This was achieved by modifying the \( \Delta G^0 \) values as shown below:

For a reaction such as

\[ \text{Al} \, (l) + \text{Cl}_2 \, (g) = \text{AlCl}_2 \, (v) \]  \hspace{1cm} (2.36)

the standard Gibbs energy, \( \Delta G^0 \) is -76009 cal/mole of \text{AlCl}_2 at 1300 K with pure liquid \text{Al} at 1300 K (activity of \text{Al} = 1) as the standard state.

For the reaction

\[ \text{Al} \, (l) = \text{Al}_{Cr} \]  \hspace{1cm} (2.37)

the Gibbs energy change \( \Delta G = RT \text{ln} \) (activity of \text{Al} in an \text{Al-Cr} alloy).

Subtraction of Eq. (2.37) from Eq. (2.36) yields

\[ \text{Al}_{Cr} + \text{Cl}_2 \, (g) = \text{AlCl}_2 \, (v) \]  \hspace{1cm} (2.38)

Tables 12 and 13 show the Gibbs energy values for the species input into chloride- and fluoride- activated packs for several compositions of the masteralloy. Table 14 shows the input moles of each element for packs utilizing different activators.

The outputs from the SGMAIN calculations will be presented and discussed in Chapter IV.
TABLE 12. Standard Gibbs energies of formation of the species used as input for the SOLGAS MIX program in chloride-activated packs at 1273 K for several masteralloy compositions

<table>
<thead>
<tr>
<th>Species</th>
<th>ΔG° kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>95Cr-5 w/o Al</td>
</tr>
<tr>
<td></td>
<td>a_{Al}=0.0013</td>
</tr>
<tr>
<td></td>
<td>a_{Cr}=0.889</td>
</tr>
<tr>
<td>Al</td>
<td>-16.809</td>
</tr>
<tr>
<td>Cr</td>
<td>-0.295</td>
</tr>
<tr>
<td>Cl (g)</td>
<td>11.761</td>
</tr>
<tr>
<td>Al (v)</td>
<td>56.446</td>
</tr>
<tr>
<td>AlCl2 (v)</td>
<td>-59.113</td>
</tr>
<tr>
<td>AlCl3 (v)</td>
<td>-106.516</td>
</tr>
<tr>
<td>Al2Cl6 (v)</td>
<td>-199.879</td>
</tr>
<tr>
<td>Cl2 (g)</td>
<td>0</td>
</tr>
<tr>
<td>NaCl (v)</td>
<td>-56.830</td>
</tr>
<tr>
<td>Na2Cl2 (v)</td>
<td>-126.466</td>
</tr>
<tr>
<td>Na2 (v)</td>
<td>5.546</td>
</tr>
<tr>
<td>Na (v)</td>
<td>0</td>
</tr>
<tr>
<td>CrCl2 (v)</td>
<td>-47.699</td>
</tr>
<tr>
<td>CrCl3 (v)</td>
<td>-88.262</td>
</tr>
<tr>
<td>CrCl4 (v)</td>
<td>-70.498</td>
</tr>
<tr>
<td>Cr (v)</td>
<td>50.768</td>
</tr>
<tr>
<td>CrCl2 (c)</td>
<td>-58.766</td>
</tr>
<tr>
<td>CrCl3 (c)</td>
<td>-65.532</td>
</tr>
<tr>
<td>CrAl₂Cl₅ (v)</td>
<td>-263.050</td>
</tr>
</tbody>
</table>
### TABLE 13. Standard Gibbs energies of formation of the species used as input for the SOLGASMIX program in fluoride-activated packs at 1273 K for several masteralloy compositions

<table>
<thead>
<tr>
<th>Species</th>
<th>( \Delta G^* ) (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>95 Cr-5 w/o Al ( a_{Al} = 0.0013 ) ( a_{Cr} = 0.889 )</td>
</tr>
<tr>
<td>Al</td>
<td>-16.809</td>
</tr>
<tr>
<td>Cr</td>
<td>-0.295</td>
</tr>
<tr>
<td>F (g)</td>
<td>0.410</td>
</tr>
<tr>
<td>( F_2 ) (g)</td>
<td>0</td>
</tr>
<tr>
<td>Al (v)</td>
<td>56.446</td>
</tr>
<tr>
<td>AlF (v)</td>
<td>-69.669</td>
</tr>
<tr>
<td>AlF_2 (v)</td>
<td>-156.237</td>
</tr>
<tr>
<td>AlF_3 (v)</td>
<td>-253.323</td>
</tr>
<tr>
<td>AlF_3F_6 (v)</td>
<td>-524.703</td>
</tr>
<tr>
<td>Cr (v)</td>
<td>50.768</td>
</tr>
<tr>
<td>CrF_3 (v)</td>
<td>-195.887</td>
</tr>
<tr>
<td>CrF_2 (v)</td>
<td>-115.313</td>
</tr>
<tr>
<td>CrF (v)</td>
<td>-27.024</td>
</tr>
<tr>
<td>AlF_3 (c)</td>
<td>-265.039</td>
</tr>
<tr>
<td>CrF_2 (c)</td>
<td>-145.775</td>
</tr>
<tr>
<td>CrF_3 (c)</td>
<td>-211.786</td>
</tr>
<tr>
<td>NaF (t)</td>
<td>-103.958</td>
</tr>
<tr>
<td>NaF (v)</td>
<td>-83.581</td>
</tr>
<tr>
<td>NaF_2F_2 (v)</td>
<td>-182.288</td>
</tr>
<tr>
<td>Na (v)</td>
<td>0</td>
</tr>
<tr>
<td>Na_2 (v)</td>
<td>5.546</td>
</tr>
</tbody>
</table>

### TABLE 14. Moles of elements of input into the SOLGASMIX program for different activators and a 95 Cr - 5 Al masteralloy (T = 1273 K, P = 1 atm)

<table>
<thead>
<tr>
<th>Activator</th>
<th>Number of moles input</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>Na</td>
</tr>
<tr>
<td>NaCl</td>
<td>4x10^{-4}</td>
</tr>
<tr>
<td>CrCl_2</td>
<td>4x10^{-4}</td>
</tr>
<tr>
<td>NH_4Cl</td>
<td>4x10^{-4}</td>
</tr>
<tr>
<td>NaF</td>
<td>4x10^{-4}</td>
</tr>
<tr>
<td>AlF_3</td>
<td>4x10^{-4}</td>
</tr>
</tbody>
</table>
2.4 KINETICS OF SIMULTANEOUS CHROMIZING-ALUMINIZING

The models proposed in literature have been restricted to aluminization using pure Al as the source. Since the activity of Al in the pure state is unity, the creation of a depletion zone follows as a consequence, as discussed in Chapter I. Seigle, Gupta, Shankar and Sarkhel [60] extended the Levine and Caves model to Ni-Al alloy packs. The Al transport rate was calculated by assuming that Ni-Al particles in the depletion zone have the same composition as the specimen surface, and that there is a sharp transition in Al composition from the pack to the depletion zone. Figure 29 shows a schematic concentration profile for such a Ni-Al pack. The Al depletion region is proposed to explain the difference in Al concentration in the bulk pack compared to the concentration at the specimen surface. The Al alone leaves the Ni-Al masteralloy particle to form volatile Al halides because the partial pressures of the Ni halides are insignificant. Although the activity of Al in the NiAl powder everywhere in the pack is lowered, the alloy powder close to the substrate is most likely to be coated by the Al halide vapors from the bulk pack. As the coating process proceeds, this situation is maintained because the bulk pack is essentially an infinite source of Al relative to the amount of Al actually incorporated into the substrate. Therefore, the model proposed in Fig. 29 is not tenable because a sharp or distinct depletion zone is unlikely to form for binary masteralloys.

If a Cr-rich Cr-Al masteralloy is used as the source, both Al and Cr form volatile halide species. If the activity of Al is significantly lowered in the masteralloy so that the partial pressures of Al and Cr halides are comparable, the sequence of events depicted in Fig. 30 is possible. At time $t=0$, the Cr-Al alloy particles are uniformly distributed throughout the pack. As the treatment proceeds, the Cr-Al particles everywhere in the pack...
Figure 29. Schematic concentration profiles in Ni-Al alloy packs. [60]
Figure 30. Proposed kinetic model for simultaneous chromizing-aluminizing of Ni; development of depletion zone at time $t$. 

Depletion zone

Undepleted pack

$P_{CrCl_2}$

$P_{AlCl_3}$

$P_{AlCl_2}$

Substrate
react with the activator to produce Al and Cr halide species. Since the partial pressures of the $AlCl$, $AlCl_2$ and $CrCl_2$ halides adjacent to the substrate drop due to incorporation of Al and Cr into the substrate, the Al and Cr masteralloy particles in this region are consumed at a faster rate than those in the bulk pack. Since the ratio of Cr to Al deposited in the substrate is on the order of 3 to 6, (for a 95 Cr-5 w/o Al masteralloy), the Al/Cr ratio in the masteralloy particle would drop as Al is consumed. Therefore, a driving force exists to deposit bulk Al from the pack into these Al-depleted particles. Thus, the masteralloy particles close to the substrate could maintain a nearly constant Al to Cr composition but be consumed at a rate proportional to the incorporation of Cr into the substrate. This is an approximation required for any analysis. The likely sources of error in this analysis are the loss of Al and Cr halide vapors out of the pack and the deposition of Cr and Al on the crucible wall. This would reduce the Cr/Al in the bulk pack but this reduction is assumed to be insignificant. Eventually, depending upon the coating time and temperature, the particles adjacent to the substrate will be consumed, creating a depletion zone. It should be possible to predict the number of moles of Cr and Al incorporated into the substrate if the width of the depletion zone is known. The depletion zone is calculated in the manner shown below:

For conservation of mass, the following equality holds:

$$\left\{ \text{Number of moles of Cr and Al lost from depletion zone of width } \delta \right\} = \left\{ \text{Number of moles of Cr and Al incorporated into substrate} \right\}$$

$$\left\{ \text{Number of moles of Cr and Al per unit volume of pack} \right\} \times \delta \times A_p = \left[ \int_0^\delta C_{Cr} \, dx + \int_0^\delta C_{Al} \, dx \right] A_s$$

(2.39)

(2.40)

where $C_{Cr}$ and $C_{Al}$ are the molar concentrations of Cr and Al in the substrate, $\delta$ is the width of the depletion zone, $A_s$ (area of substrate) = $A_p$ (area of pack adjacent to the substrate).
Since the volume of the pack is typically $49 \text{ cm}^3$, and the weight of the masteralloy contained in this volume is $12.5 \text{ gm}$, Eq. 2.39 can be expressed as:

$$\left( \frac{12.5 \text{ gm of M-A}}{49 \text{ cm}^3 \text{ of pack}} \right) \left( \frac{\text{w/o Cr in M-A}}{100 \times \text{A.W. Cr}} + \frac{\text{w/o Al in M-A}}{100 \times \text{A.W. Al}} \right) \delta =$$

$$\int_0^x \left( \frac{\text{w/o Cr}}{100 \times \text{A.W. Cr}} \right) \rho_{\text{alloy}} \, dx + \int_0^x \left( \frac{\text{w/o Al}}{100 \times \text{A.W. Al}} \right) \rho_{\text{alloy}} \, dx \quad (2.41)$$

where M-A represents the masteralloy, A.W.Cr and A.W.Al are the atomic weights of Cr and Al respectively, w/o Cr and w/o Al are the weight percent of Cr and Al and $\rho_{\text{alloy}}$ is the density of the alloy. The density of the alloy varies with distance and is expressed as

$$\rho_{\text{alloy}} = \frac{100}{\frac{\text{w/o Ni}}{\rho_{\text{Ni}}} + \frac{\text{w/o Cr}}{\rho_{\text{Cr}}} + \frac{\text{w/o Al}}{\rho_{\text{Al}}}} \quad (2.42)$$

where w/o Ni, w/o Cr and w/o Al are the weight percent of Ni, Cr of Al respectively, $\rho_{\text{Cr}}$, $\rho_{\text{Al}}$ and $\rho_{\text{Ni}}$ are the densities of pure Cr, Al and Ni respectively. The right-hand side of Eq. (2.41) is evaluated from experimental concentration profiles for Cr and Al to obtain the width of the depletion zone ($\delta$). As mentioned earlier, the number of moles of Cr and Al incorporated into the substrate can be predicted if the width of the depletion zone is known.

The experimentally determined diffusion profiles are compared to theoretically predicted profiles. The number of moles of Cr and Al incorporated into the substrate can be obtained from the theoretical profiles. In the following section, the procedure to obtain theoretical diffusion profiles is described.
2.5 PREDICTING DIFFUSION PROFILES IN TERNARY Ni-Cr-Al SYSTEMS

To predict diffusion profiles in ternary systems, it is necessary to solve Fick's second law of diffusion using appropriate boundary conditions.

Fick's second law of diffusion is expressed as:

$$\frac{\partial C}{\partial t} = \text{div}(D \text{ grad } C)$$  \hspace{1cm} (2.43)

where $C$ is the concentration, $t$ the time and $D$ the diffusion coefficient expressed in consistent units.

For a ternary Ni-Cr-Al system, Eq 2.43 can be written as:

$$\frac{\partial C_{Al}}{\partial t} = \frac{\partial D_{AlAl}^{Ni}}{\partial x} \frac{\partial C_{Al}}{\partial x} + D_{AlAl}^{Ni} \frac{\partial^2 C_{Al}}{\partial x^2} + \frac{\partial D_{AlCr}^{Ni}}{\partial x} \frac{\partial C_{Cr}}{\partial x} + \frac{\partial D_{AlAl}^{Ni}}{\partial x} \frac{\partial^2 C_{Cr}}{\partial x^2}$$  \hspace{1cm} (2.44)

$$\frac{\partial C_{Cr}}{\partial t} = \frac{\partial D_{CrCr}^{Ni}}{\partial x} \frac{\partial C_{Cr}}{\partial x} + D_{CrCr}^{Ni} \frac{\partial^2 C_{Cr}}{\partial x^2} + \frac{\partial D_{CrAl}^{Ni}}{\partial x} \frac{\partial C_{Al}}{\partial x} + \frac{\partial D_{CrAl}^{Ni}}{\partial x} \frac{\partial^2 C_{Al}}{\partial x^2}$$  \hspace{1cm} (2.45)

where $C$ is the concentration expressed in a/o, $D_{AlAl}^{Ni}$ and $D_{CrCr}^{Ni}$ are the main or diagonal interdiffusion coefficients and $D_{AlCr}^{Ni}$ and $D_{CrAl}^{Ni}$ are the cross-term or off-diagonal diffusion coefficients. $D_{AlCr}^{Ni}$ represents the effect of the concentration of Cr on the flux of Al while $D_{CrAl}^{Ni}$ represents the effect of the concentration of Al on the flux of Cr. Each of the four diffusion coefficients can be represented by

$$\frac{\partial D}{\partial x} = \frac{\partial D}{\partial C_{Al}} \frac{\partial C_{Al}}{\partial x} + \frac{\partial D}{\partial C_{Cr}} \frac{\partial C_{Cr}}{\partial x}$$  \hspace{1cm} (2.46)

A finite-element program was developed to predict the concentration profiles for Cr and Al given the surface concentration of these elements by solving Eqs. (2.44) and (2.45). The
logic of the program and the physical basis are explained below. Nesbitt and Heckel [5] have
determined diffusion coefficients for the Ni-rich Ni-Cr-Al system at 1100° C and 1200° C as a
function of the composition of Cr and Al. The Arrhenius equation

\[ D_{ij} = D_0 \exp \left( -\frac{Q}{RT} \right) \]  \hspace{1cm} (2.47)

was used to determine the diffusion coefficients as a function of the composition of Cr and Al
at 1000° C. These diffusion coefficients were used as input to the program.

Equations (2.44) and (2.45) are rewritten in the following manner to use the finite
element technique.

\[ (C_{i+1})_{Al} = (C_i)_{Al} + \frac{D_{AlAl}^i \Delta t}{(\Delta x)^2} \left[ (C_{i+1})_{Al} - 2 (C_i)_{Al} + (C_{i+1})_{Al} \right] + \]

\[ \frac{\Delta t}{(\Delta x)^2} \left[ (D_{Al-Al}^i)^{i+1} - (D_{Al-Al}^i)^i \right] \left[ (C_{Al})_{i+1} - (C_{Al})_i \right] + \]

\[ \frac{D_{AlCr}^i \Delta t}{(\Delta x)^2} \left[ (C_{i+1})_{Cr} - 2 (C_i)_{Cr} + (C_{i+1})_{Cr} \right] \]  \hspace{1cm} (2.48)

\[ (C_{i+1})_{Cr} = (C_i)_{Cr} + \frac{D_{CrCr}^i \Delta t}{(\Delta x)^2} \left[ (C_{i+1})_{Cr} - 2 (C_i)_{Cr} + (C_{i+1})_{Cr} \right] + \]

\[ \frac{\Delta t}{(\Delta x)^2} \left[ (D_{Al-Cr}^i)^{i+1} - (D_{Al-Cr}^i)^i \right] \left[ (C_{Cr})_{i+1} - (C_{Cr})_i \right] + \]

\[ \frac{D_{CrAl}^i \Delta t}{(\Delta x)^2} \left[ (C_{i+1})_{Al} - 2 (C_i)_{Al} + (C_{i+1})_{Al} \right] \]  \hspace{1cm} (2.49)

where \( C_i \) is the concentration of the species at the center of the ith element at the jth instant
of time.
The boundary conditions and the initial conditions for solving Eq.(2.43) assuming the substrate to be semi-infinite are $C_i = C_i^0$ at $x=0$ for all $t$ and $C_i = 0$ for $x>0$ at $t=0$. The time increment for each iteration was chosen such that

$$
\Delta t \leq 0.2 \frac{(\Delta x)^2}{\hat{D}_{ij}} \quad (2.50)
$$

This choice of time increment was found to eliminate numerical oscillations.

The results of the computation and the comparison between predicted and observed diffusion profiles are shown and discussed in Chapter IV.
CHAPTER III

EXPERIMENTAL METHODS AND MATERIALS

3.1 PACK PREPARATION

Alumina powder (100-200 µm) purchased from the Fisher Scientific Co. was used as the inert diluent in all the coating experiments. Cr-Al masteralloys (180-200 µm) of varying compositions (98 Cr-2 w/o Al, 95 Cr-5 w/o Al, 92 Cr-2 w/o Al, 90 Cr-10 w/o Al, 85 Cr-15 w/o Al) were obtained from Consolidated Astronautics. Reagent grade, anhydrous NaCl, AlCl₃, CrCl₂, NaF, AlF₃ and Na₃AlF₆, obtained from Fisher Scientific, were used as the activators.

The pack, consisting of 73 w/o of alumina filler, 25 w/o of the Cr-Al masteralloy and 2 w/o activator, was thoroughly mixed together.

Three types of substrates were used:

— Pure element (Ni)

— Binary alloy (Ni -20 w/o Cr)

— Ni-base superalloys (Rene 80 and IN 600)

The compositions and source for each substrate is shown in Table 15. The substrate material was cut in a low-speed diamond saw, abraded with metallographic paper down to 600 grit,
**TABLE 15.** Composition of substrates used in this study

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Composition (w/o)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>99.99</td>
<td>Materials Research Corp.</td>
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<tr>
<td>Ni-Cr</td>
<td>Ni-20Cr</td>
<td>Varian Specialty Metals</td>
</tr>
<tr>
<td>Rene 80</td>
<td>60Ni-14Cr-3Al-9.5Co-4Mo-5Ti-4W-balence C, B, Zr</td>
<td>General Electric Corp.</td>
</tr>
<tr>
<td>IN 600</td>
<td>Ni-15.8Cr-7.2Fe-0.2Si-0.2Mg-0.04C</td>
<td>Shell Development Co.</td>
</tr>
</tbody>
</table>
cleaned and degreased with acetone. The dimensions and weight of the substrate material were measured.

Alumina crucibles of two sizes 6.5 cm × 3.10 cm I.D. (49 cm³) and 9.4 cm long × 3.6 cm I.D. (96 cm³) - were obtained from L. H. Marshall Company. The pack was poured into the alumina crucible with the substrate buried in the pack. The crucible was then closed with an alumina lid and sealed with a porous ceramic cement (Ceramabond) (Fig. 31a).

3.2 PROCESS EQUIPMENT

The ceramic cement was allowed to dry at room temperature for 10 hours prior to inserting it into a horizontal alumina reaction tube passing through a horizontal tube furnace (Fig. 31b). The ends of the alumina reaction tube were sealed with a McDanel seal assembly. Cajon ultra-ton adaptors and flexible tubing were used to admit the thermocouple and gas flow tubes through the seal.

Prepurified Ar was admitted into the reaction tube after passing through a dehumidifier (Drierite) and Chemaloy R3-11 deoxidizer maintained at 180° C. A flow meter controlled the flow rate. Figure 32 is a flow chart of the coating process equipment.

Type K (chromel-alumel) thermocouples with Inconel sheaths obtained from L. H. Marshall were placed in contact with the ends of the alumina crucible and the temperatures were monitored using a Keithley digital voltmeter.

The furnace was heated to 120° C and maintained at that temperature for 2 hours to purge the system of air and water vapor. After the pre-heat period, the temperature of the furnace was raised to 1000° C (1½ hour heat-up time) and maintained at that temperature for
Figure 31. Experimental arrangement (a) pack constituents (b) furnace and gas train.
1. Ar cylinder  
2. Dri-rite (de-humidifier)  
3. R3-11 (deoxidizer)  
4. Thermocouple  
5. Vacuum seal  
6. Alumina reaction tube  
7. Furnace  
8. Alumina crucible containing pack

Figure 32. Process flow sheet.
the desired period. At the end of the coating period, the furnace was switched off and the pack was allowed to furnace cool with the Ar stream continuously flowing. The crucible was then removed from the reaction tube and lightly hammered to crack the ceramic cement and separate the lid. The samples were retrieved from the pack, cleaned with water and ultrasonically cleaned with acetone. The dimensions and the weight of the coated samples were measured.

3.3 CHARACTERIZATION OF COATED SAMPLES

The coated samples were cut in a direction perpendicular to the surface with a low speed Buehler diamond saw and mounted in bakelite. After grinding from 240 grit through 600 grit and polishing with 1 μm diamond, the samples were etched. The etchants used were:

1. 2 g CuCl₂ - 40 ml HCl - 80 ml ethanol

2. 10 ml HNO₃ - 15 ml HCl - 10 ml acetic acid - 5 ml glycerol.

The mounted specimens were examined in a JEOL-JXA-35 scanning electron microscope. Energy dispersive analysis was performed on the coating with an EDAX-SW-9100 system. The operating voltage in the microscope was 25 kV for all analyses. Once the secondary electron image of the specimen was obtained, the X and Y specimen translation knobs were coupled to the motors which were controlled by an electronic control box with a digital read-out. The X and Y movements of the specimen were adjusted so that they were mutually perpendicular. The edge of the sample was made parallel to one of the directions and the sample was moved in the perpendicular direction. The counting time was 200
seconds for each position. The coating on Ni and Ni-20Cr was analyzed at 5 μm intervals up to 40 μm from the edge of the specimen and then at 15 and 20 μm intervals. Analysis was stopped when the Al and Cr signals could not be detected.

The chemical composition was determined at each point by comparing with pure elemental standards acquired under the same conditions. Concentration in w/o and a/o were obtained with the SW9100 system in the QUAN mode by applying the FRAM analysis [61]. Compositions at surface were determined by extrapolating from the internal concentration profiles because of uncertainties in the surface concentrations due to pack entrapment. X-ray dot maps of the coated superalloys were taken to reveal Cr-, Al- and Ni- rich regions. Each dot map was taken for 20,000 counts.

3.4 HOT CORROSION TESTS

The performance of the coating under type II hot corrosion conditions was evaluated. Test coupons 2cm×1cm×0.1cm in dimensions with a 1.5mm hole drilled in them were coated with appropriate pack composition. The coated samples were cleaned and pre-heated to 200°C before spraying them with a saturated solution of sodium sulfate. The samples were reweighed and resprayed until a salt layer of 3 mg/cm² was obtained.

The samples were then suspended in an alumina crucible with an alumina rod (Fig. 33). The alumina crucible was inserted into a vertical tube furnace which was then sealed with a McDanel sealing assembly. A 1% SO₂/O₂ mixture was passed through the furnace which was then heated to 730°C. At the end of 16 hours, the furnace was switched off, the samples were allowed to furnace cool and then removed. Some of the samples were retained
Figure 33. Schematic of the hot corrosion test apparatus.
for examination while the remaining samples were resprayed with salt to obtain 3 \( \text{mg/cm}^2 \) salt coating. The salt sprayed samples were introduced into the furnace and kept at temperature 730°C in the \( SO_2/O_2 \) atmosphere for 56 hours. (total exposure time = 72 hours). Each run contained an uncoated sample as reference. In addition, the tests with Rene 80 also contained General Electric’s "Codep" coated samples for comparison.

All the coupons from the hot corrosion tests had to be metallographically prepared under alcohol since the corrosion products are water soluble.
CHAPTER IV

RESULTS AND DISCUSSION

4.1 THERMODYNAMIC ANALYSIS

Tables 16-21 show the equilibrium partial pressures of gaseous species and the number of moles of solid species in cementation packs containing 95 Cr-5 w/o Al as the masteralloy activated by NaCl, CrCl₂, AlCl₃, NH₄Cl, NaF and AlF₃. The chlorine activity for the NaCl and CrCl₂ packs are necessarily high and the partial pressures of AlCl₃ and CrCl₃ are correspondingly high. However, these species are not expected to deposit Al or Cr, since they could only function to return the halogen from the substrate to the pack. However, the dominant deposition species AlCl, AlCl₂ and CrCl₂ have considerably high magnitudes for partial pressures in the pack, with the CrCl₂ partial pressures 10-100 times higher than the AlCl and AlCl₂ partial pressures. From Tables 16 to 19, it is seen that stable activators such as NaCl generate lower partial pressures of AlCl, AlCl₂ and CrCl₂ than the relatively unstable activators such as CrCl₂, AlCl₃ and NH₄Cl. Tables 20 and 21 indicate that the partial pressures of the AlFₓ species are higher than the CrFₓ partial pressures in both NaF- and AlF₃- activated packs even if the activity of Al in the masteralloy is very low. No change occurs in the number of moles of alumina at equilibrium, which confirms its role as an inert filler. Therefore, the oxidation of Cr to Cr₂O₃ by the following reaction as suggested by Walsh [15]
TABLE 16

Output From SOLGASMIX Calculation For A NaCl-Activated Pack (95Cr-5 w/o Al Masteralloy) Showing Initial And Final Amounts Of Gaseous And Condensed Species. (Temperature, Pressure And Moles Of Each Species Input Into The Program As Indicated.

Chromaluminization of Ni with a 95 Cr-5 Al(w/o)/NaCl

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\[ T = 1273.00 \text{ K} \]

\[ P = 1.000E+00 \text{ ATM} \]

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**EQUILIBRIUM COMPOSITIONS:**

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<th>ACTIVITY</th>
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**PHASE Alloy**

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**INVARIANT CONDENSED PHASES**

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</thead>
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<td>CrCl3</td>
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Output From SOLGASMIX Calculation For A CrCl$_2$-Activated Pack (95Cr-5 w/o Al Masteralloy) Showing Initial And Final Amounts Of Gaseous and Condensed Species. (Temperature, Pressure And Moles Of Each Species Input Into The Program As Indicated.

**Chromalumination of Ni with a 95 Cr-5 Al(w/o)/CrCl2**

**STEP NO: 1**

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**EQUILIBRIUM COMPOSITIONS:**

**PHASE Gas**

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**INVARIANT CONDENSED PHASES**

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TABLE 18

Output From SOLGASMIX Calculation For An AlCl₃-Activated Pack (95Cr-5 w/o Al Masteralloy) Showing Initial And Final Amounts Of Gaseous And Condensed Species. (Temperature, Pressure And Moles Of Each Species Input Into The Program As Indicated.

Chromaluminization of Ni with a 95 Cr-5 Al(w/o)/AlCl₃

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EQUILIBRIUM COMPOSITIONS:

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<td>CrAl₃Cl₁₁</td>
<td>0.0000E+00</td>
<td>1.2709E-10</td>
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<td>1.6832E-08</td>
</tr>
<tr>
<td>Cr</td>
<td>0.0000E+00</td>
<td>1.1936E-10</td>
<td>1.5093E-08</td>
<td>1.5093E-08</td>
</tr>
<tr>
<td>Cl₂</td>
<td>0.0000E+00</td>
<td>5.9394E-12</td>
<td>7.8667E-10</td>
<td>7.8667E-10</td>
</tr>
<tr>
<td>Al</td>
<td>0.0000E+00</td>
<td>2.3527E-15</td>
<td>3.1161E-13</td>
<td>3.1161E-13</td>
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PHASE Alloy

<table>
<thead>
<tr>
<th>SPECIE</th>
<th>INIT. EST.</th>
<th>EQ. MOLES</th>
<th>MOL FRAC</th>
<th>ACTIVITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.2100E+00</td>
<td>2.0400E+00</td>
<td>0.8226E+00</td>
<td>0.8226E+00</td>
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<tr>
<td>Al</td>
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INVARIANT CONDENSED PHASES

<table>
<thead>
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<th>EQ. MOLES</th>
</tr>
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<tr>
<td>CrCl₂</td>
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<td>0.0000E+00</td>
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<tr>
<td>CrCl₃</td>
<td>0.0000E+00</td>
<td>0.0000E+00</td>
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</table>
TABLE 19

Output From SOLGASMIX Calculation For An NH\textsubscript{4}Cl-Activated Pack (95Cr-5 w/o Al Masteralloy) Showing Initial And Final Amounts Of Gaseous And Condensed Species. (Temperature, Pressure And Moles Of Each Species Input Into The Program As Indicated.)

Chromaluminization of Ni/95Cr-5Al/NH\textsubscript{4}Cl

NO. OF ELEMENTS = 7
NO. OF MIXTURES = 2
NO. OF INVARIANT SOLIDS = 4
NO. OF SPECIES PER MIXTURE = 26, 3,
T = 1273.00 K
P = 1.000E+00 ATM

Input Amount

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<thead>
<tr>
<th>N</th>
<th>Cl</th>
<th>H</th>
<th>Ar</th>
<th>Cr</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.187E-01</td>
<td>9.187E-01</td>
<td>7.46E-01</td>
<td>4.00E-03</td>
<td>2.28E+00</td>
<td>2.31E-01</td>
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</table>

Equilibrium compositions :

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<tr>
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<th>X/MOLE</th>
<th>Y/MOLE</th>
<th>P/ATM</th>
<th>ACTIVITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>7.4800E-01</td>
<td>1.1242E-10</td>
<td>2.7376E-09</td>
<td>2.7376E-09</td>
</tr>
<tr>
<td>Ar</td>
<td>4.0000E-03</td>
<td>4.0000E-03</td>
<td>9.0189E-02</td>
<td>9.0189E-02</td>
</tr>
<tr>
<td>Al</td>
<td>0.0000E+00</td>
<td>4.8183E-15</td>
<td>1.0864E-13</td>
<td>1.0864E-13</td>
</tr>
<tr>
<td>C12</td>
<td>0.0000E+00</td>
<td>1.0114E-11</td>
<td>2.2805E-10</td>
<td>2.2805E-10</td>
</tr>
<tr>
<td>AICl</td>
<td>0.0000E+00</td>
<td>2.4084E-07</td>
<td>5.4304E-06</td>
<td>5.4304E-06</td>
</tr>
<tr>
<td>AlCl2</td>
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<td>1.6376E-04</td>
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<tr>
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<td>1.0558E-01</td>
</tr>
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<td>6.1836E-06</td>
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<td>Cr</td>
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<td>1.6760E-08</td>
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<td>1.2800E+00</td>
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<td>5.4880E-09</td>
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<td>8.2400E-06</td>
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<td>H2</td>
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<td>8.4326E+00</td>
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<td>N2</td>
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<td>4.6077E-07</td>
</tr>
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<td>AlH</td>
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<td>1.1667E-11</td>
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<td>2.6307E-10</td>
</tr>
<tr>
<td>H2N</td>
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<td>5.2478E-11</td>
</tr>
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<td>2.8397E-15</td>
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<tr>
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<td>6.5175E-06</td>
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<td>N</td>
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MOLE FRACTION

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<thead>
<tr>
<th>Species</th>
<th>X/MOLE</th>
<th>Y/MOLE</th>
<th>P/ATM</th>
<th>ACTIVITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>2.2310E-01</td>
<td>8.8583E-02</td>
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<td>0.0000E+00</td>
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<tr>
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<td>0.0000E+00</td>
<td>0.0000E+00</td>
<td>0.0000E+00</td>
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</tbody>
</table>
Output From SOLGASMIX Calculation For A NaF-Activated Pack (95Cr-5 w/o Al Masteralloy) Showing Initial And Final Amounts Of Gaseous And Condensed Species. (Temperature, Pressure And Moles Of Each Species Input Into The Program As Indicated.

Chromiumization of Ni/1273K/NaF/95-5Al

NO. OF ELEMENTS = 5
NO. OF MIXTURES = 2
NO. OF INVARIANT SOLIDS = 4
NO. OF SPECIES PER MIXTURE = 16, 2

TEMP = 1273.00 K
P = 1.0000E+00 ATM

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>MOLES</th>
</tr>
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<tbody>
<tr>
<td>Ar</td>
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</tr>
<tr>
<td>Al</td>
<td>0.0213</td>
</tr>
<tr>
<td>Cr</td>
<td>0.21</td>
</tr>
<tr>
<td>F</td>
<td>0.0238</td>
</tr>
<tr>
<td>Na</td>
<td>0.0238</td>
</tr>
</tbody>
</table>

EQUILIBRIUM COMPOSITIONS:

PHASE Gas

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>INIT. EST.</th>
<th>EQ.MOLES</th>
<th>P/ATM</th>
<th>ACTIVITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0.40000E-04</td>
<td>0.40000E-04</td>
<td>0.99907E+00</td>
<td>0.99907E+00</td>
</tr>
<tr>
<td>Na</td>
<td>0.00000E+00</td>
<td>0.17791E-07</td>
<td>0.44436E-03</td>
<td>0.44436E-03</td>
</tr>
<tr>
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<td>0.31210E-03</td>
<td>0.31210E-03</td>
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<td>0.00000E+00</td>
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<tr>
<td>Al</td>
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<td>0.27098E-14</td>
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<tr>
<td>F2</td>
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<td>0.39583E-33</td>
<td>0.98865E-29</td>
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</tr>
</tbody>
</table>

PHASE Alloy

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>INIT. EST.</th>
<th>EQ.MOLES</th>
<th>MOL FRACTION</th>
<th>ACTIVITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
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<td>0.21000E+00</td>
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<td>0.50791E+00</td>
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INvariant Condensed Phases

<table>
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<th>INIT. EST.</th>
<th>EQ.MOLES</th>
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</tr>
<tr>
<td>CrF3</td>
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<td>0.00000E+00</td>
</tr>
<tr>
<td>AlF3</td>
<td>0.00000E+00</td>
<td>0.00000E+00</td>
</tr>
</tbody>
</table>
Output From SOLGAS MIX Calculation For An AlF$_3$-Activated Pack (95Cr-5 w/o Al Masteralloy) Showing Initial And Final Amounts Of Gaseous And Condensed Species. (Temperature, Pressure And Moles Of Each Species Input Into The Program As Indicated.

<table>
<thead>
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</tr>
</thead>
<tbody>
<tr>
<td>NO. OF ELEMENTS = 4</td>
</tr>
<tr>
<td>NO. OF MIXTURES = 2</td>
</tr>
<tr>
<td>NO. OF INVARIANT SOLIDS = 3</td>
</tr>
<tr>
<td>NO. OF SPECIES PER MIXTURE = 12, 2,</td>
</tr>
<tr>
<td>TEMP = 1273.00 K</td>
</tr>
<tr>
<td>P = 1.000E+00 ATM</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>MOLES</th>
</tr>
</thead>
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<tr>
<td>Cr</td>
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</tr>
<tr>
<td>F</td>
<td>0.0357</td>
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</table>

**EQUILIBRIUM COMPOSITIONS:**

**PHASE Gas**

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>INIT. EST.</th>
<th>EQ. MOLES</th>
<th>P/ATM</th>
<th>ACTIVITY</th>
</tr>
</thead>
<tbody>
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<td>.40000E-04</td>
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<td>.86713E+00</td>
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<td>.12305E+00</td>
<td>.12305E+00</td>
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**PHASE Alloy**

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>INIT. EST.</th>
<th>EQ. MOLES</th>
<th>MOL FRAC</th>
<th>ACTIVITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
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<td>.21000E+00</td>
<td>.90791E+00</td>
<td>.90791E+00</td>
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<td>.92086E-01</td>
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</table>

**INVARIANT CONDENSED PHASES**

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>INIT. EST.</th>
<th>EQ. MOLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlF3</td>
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<td>.11800E-01</td>
</tr>
<tr>
<td>CrF2</td>
<td>.00000E+00</td>
<td>.00000E+00</td>
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<tr>
<td>CrF3</td>
<td>.00000E+00</td>
<td>.00000E+00</td>
</tr>
</tbody>
</table>
2 \text{CrCl}_2 (v) + \text{Al}_2\text{O}_3(s) = \text{AlCl}_2 (v) + \text{Cr}_2\text{O}_3 (s) \tag{4.1}

does not seem possible.

The vapor pressures of \text{Al} and \text{Cr} are significantly less than the partial pressures of \text{CrCl}_x and \text{AlCl}_x vapors. The low \(p_{\text{Al}}\) and \(p_{\text{Cr}}\) implies that deposition of \text{Al} and \text{Cr} by direct transport is not significant compared to the transport by the halide vapors.

Figures 34 to 44 present the partial pressures of the gaseous species as a function of the activity of \text{Al} in \text{NaCl-}, \text{NH}_4\text{Cl-}, \text{CrCl}_2-, \text{NaF-} and \text{AlF}_3-activated packs on \text{Ni} substrates for \text{Ar} and \text{H}_2 atmospheres. Since the partial pressures of the gaseous halides of \text{Ni} are insignificant (cf. Fig. 10), Figs. 34 to 44 also represent the partial pressures of gases within the pack far from any substrate.

Figure 34 shows that the partial pressure of chromium dichloride is greater than that for aluminum monochloride in a \text{NaCl}-activated pack only at low \text{Al} activities; a crossover occurs at an \text{Al} activity corresponding to a masteralloy of approximately 10 w/o \text{Al}. This crossover composition depends upon the choice of the activator which decides the chlorine activity for a given pack. For a given masteralloy, a less stable halide activator salt produces a higher halogen activity and raises the ratio of partial pressures for the chromium species relative to the aluminum species. These computations suggest the potential of the pack to aluminize or chromize as indicated by the absolute and relative magnitudes of the partial pressures of the \text{Al} and \text{Cr} halides. According to Fig. 34, if \text{NaCl} were used as the activator, the codeposition of \text{Al} and \text{Cr} should be possible if the \text{Cr-Al} masteralloy contained between 10 and 13 w/o \text{Al}. 
Figure 34. Equilibrium partial pressures of gaseous species in a NaCl-activated pack as a function of Al activity in the masteralloy (Ar, 1273 K).
Figure 35 shows the partial pressures of gaseous species for NaCl-activated packs in a $H_2$ atmosphere. The partial pressure of $CrCl_2$ is lowered by three orders of magnitude and $PAICl$ and $PAICII$ are reduced by two orders and one order of magnitudes respectively for a 95 Cr - 5 Al masteralloy. This decrease in partial pressures of the Cr and Al halides is due to reduced $Cl_2$ activity resulting from the formation of $HCl$. Since the partial pressures of $HCl$ and $H_2$ are significantly higher than $CrCl_2$, $AlCl$ and $AlCl_2$, the reduced kinetics of chlorine removal reactions such as

$$2AlCl + H_2 (g) = 2HCl + 2Al$$
$$AlCl_2 + H_2 (g) = 2HCl + Al$$
$$CrCl_2 + H_2 = 2HCl + Cr$$

at the substrate surface should decrease the kinetics of Al and Cr transport. This observation agrees with those of Kung and Rapp [47] for packs activated with pure Cr and Si. These workers found that in NaCl-activated packs containing pure Cr and pure Si, the partial pressures of the Cr and Si halides decreased by two orders of magnitude relative to packs in an Ar-atmosphere. In packs containing pure Al, they found no change in the partial pressure of the AlCl$_x$ vapors between Ar and $H_2$ atmospheres. This is to be expected because the high stability of the AlCl$_x$ species results in higher AlCl and AlCl$_2$ partial pressures than HCl even in an $H_2$ atmosphere. However, in the present case, the significant lowering of the Al activity relative to Cr in the masteralloy results in lowered $AlCl_x$ partial pressures even in Ar atmospheres. The high $HCl$ partial pressures in $H_2$ atmospheres and consequent lowering of chlorine activity results in a lowering of the partial pressures of $AlCl_x$ vapors.
Figure 35. Equilibrium partial pressures of gaseous species in a NaCl-activated pack as a function of Al activity in the masteralloy (H₂, 1273 K).
Therefore, the presence of $H_2$ in NaCl-activated packs shifts the equilibrium conditions and decreases the overall coating kinetics.

Figure 36 shows the equilibrium partial pressures of the metallic halides in a CrCl$_2$-activated pack (Ar atmosphere). Once again, at low Al activities, the CrCl$_x$ partial pressures are higher than those of AlCl$_x$. Comparing Figs. 34 and 36, the partial pressures of the CrCl$_x$ and AlCl$_x$ species in the CrCl$_2$-activated pack are higher than those in the NaCl-activated pack. This results from the lower thermodynamic stability of condensed CrCl$_2$ compared to NaCl. The less stable CrCl$_2$-activator stabilizes a higher p$_{Cl_2}$ which favors CrCl$_x$ formation in preference to AlCl$_x$. Not only are the magnitudes of the partial pressures of both the Cr and Al halides in the CrCl$_2$ pack higher than in the NaCl-activated pack, but the crossover occurs at higher activities of Al. Therefore codeposition should be possible for higher aluminum activities in the CrCl$_2$ pack than for the NaCl pack. The partial pressures of the ternary species CrAl$_2$Cl$_8$ is significant and could permit simultaneous Cr and Al transport. The 2 w/o of CrCl$_2$ activator also provides a minor increase in the Cr content within the pack:

$$\text{CrCl}_2 \ (l) = \text{CrCl}_2 \ (v) \quad (4.5)$$

The NaCl-activated pack has no analogous contribution.

Figure 37 shows the equilibrium partial pressures of gaseous species in CrCl$_2$-activated packs when $H_2$ is introduced into the system. The partial pressures of the Al and Cr chlorides are only slightly affected. The high partial pressures of CrCl$_2$ and CrCl$_3$ compared to HCl and $H_2$ is a consequence of the relatively unstable CrCl$_2$ activator. No change in overall coating kinetics is expected.
Figure 36. Equilibrium partial pressures of gaseous species in a $\text{CrCl}_2$-activated pack as a function of Al activity in the masteralloy (Ar, 1273 K).
Figure 37. Equilibrium partial pressures of gaseous species in a CrCl₂-activated pack as a function of Al activity in the masteralloy (H₂, 1273 K).
Figure 38 shows the results of calculations for a NH$_4$Cl- activated pack. The CrCl$_x$ pressures are higher than in the NaCl- pack but lower than for the CrCl$_2$ packs and the crossover points occur at even higher Al activities. The significant pressure of the ternary compound CrAl$_2$Cl$_8$ in Fig. 38 is to be noted. The ammonium chloride pack has the following additional reactions which may affect coating reactions:

\[
\begin{align*}
\text{NH}_4\text{Cl} (s) &= \text{NH}_3 (g) + \text{HCl} (g) \\
2 \text{Al} (s) + 2 \text{HCl} (g) &= 2 \text{AlCl} (v) + \text{H}_2 (g) \\
2 \text{NH}_3 (g) &= \text{N}_2 (g) + 3 \text{H}_2 (g)
\end{align*}
\]

Although AlN is a marginally stable phase, its formation kinetics are trivial.

The decomposition of NH$_4$Cl into NH$_3$ and HCl (Eq. (4.6)) at relatively low temperatures (612 K) and the dissociation of NH$_3$ into N$_2$ and H$_2$ (Eq. (4.8)) imply that the calculated partial pressures for the gaseous species depends greatly upon the amount of activator and the venting pressure for the system. Significant loss of activator from the pack would result in the calculated gas compositions varying as a function of time. Therefore, the calculation for the NH$_4$Cl-activated pack represent only the equilibrium condition for a pack vented to 1 atmosphere. The unstable NH$_4$Cl-activator generates a higher p$_{\text{Cl}_2}$ than in the stable NaCl-activated packs. However, the p$_{\text{Cl}_2}$ is lower than in CrCl$_2$-activated packs because some of the chlorine gas is consumed to form HCl (g). The high H$_2$ and HCl partial pressures therefore reduce the partial pressures of the CrCl$_x$ species.

Figure 39 presents the partial pressures of Cr and Al chlorides in AlCl$_3$-activated packs. AlCl$_3$ melts at 466 K and has a triple point at 467 K with a vapor pressure of 2.3 atm. Therefore, the partial pressures of the gaseous species would depend on the amount of
Figure 38. Equilibrium partial pressures of gaseous species in an NH₄Cl-activated pack as a function of Al activity in the masteralloy (Ar, 1273 K).
Figure 39. Equilibrium partial pressures of gaseous species in an AlCl₃-activated pack as a function of Al activity in the masteralloy (Ar, 1273 K).
activator and the venting pressure for the system. The loss of AlCl$_3$ from the pack results in the variation of the gas phase composition as a function of time. Thus, Fig. 39 represents the results of calculations for AlCl$_3$-activated packs vented to 1 atmosphere. The partial pressures of the CrCl$_2$ and AlCl$_2$ are higher than those for the NH$_4$Cl and NaCl activated packs and comparable to the CrCl$_2$-activated packs. This is again a consequence of higher $p_{Cl_2}$ in AlCl$_3$-activated packs relative to NH$_4$Cl- and NaCl-activated packs. The partial pressure formation of the CrAl$_2$Cl$_8$ is significant in this pack.

Figure 40 shows the partial pressures of AlCl$_3$-activated packs in the presence of H$_2$. As in the case of CrCl$_2$-activated packs, very minor changes in the partial pressures of the gaseous species are observed. The highly unstable AlCl$_3$ maintains high AlCl$_3$, CrCl$_2$ and CrCl$_3$ partial pressures relative to H$_2$ and HCl.

Figures 41 to 44 indicate partial pressures in NaF- and AlF$_3$-activated packs. In both packs, the AlF$_x$ partial pressures are higher than those for CrF$_x$ and no crossover occurs. Therefore the use of fluoride-activated pack is unlikely to result in codeposition of Al and Cr. The fluoride packs tend to be strongly aluminizing even at low aluminum activities in the masteralloy.

Figures 42 and 44 represent the partial pressures of gaseous species in NaF- and AlF$_3$-activated packs in the presence of hydrogen. No significant difference in equilibrium conditions is observed. This is explained by the extremely low partial pressure of F$_2$ in Ar and H$_2$ atmospheres. The presence of H$_2$ and the consequent formation of HF ($p_{HF}=10^{-3}$ atm) causes only a minor change in the already low AlF and CrF partial pressures.
Figure 40. Equilibrium partial pressures of gaseous species in an AlCl₃-activated pack as a function of Al activity in the masteralloy (H₂, 1273 K).
Figure 41. Equilibrium partial pressures of gaseous species in a NaF-activated pack as a function of Al activity in the masteralloy (Ar, 1273 K).
Figure 42. Equilibrium partial pressures of gaseous species in an NaF-activated pack as a function of Al activity in the masteralloy ($H_2$, 1273 K).
Figure 43. Equilibrium partial pressures of gaseous species in an AlF₃-activated pack as a function of Al activity in the masteralloy (Ar, 1273 K).
Figure 44. Equilibrium partial pressures of gaseous species in an AlF3-activated pack as a function of Al activity in the masteralloy (H₂, 1273 K).
Based on the results of the thermodynamic analyses, appropriate pack compositions can be predicted with chloride activators to achieve codeposition of Cr and Al. The activity of Al has to be very low ($\approx 10^{-3}$) relative to nearly unit activity of Cr to achieve comparable partial pressures of the halides. This Al activity corresponds to a quite Cr-rich binary Cr-Al alloy.

Figure 45 shows the partial pressures of Al and Cr chlorides in packs containing Al-Cr masteralloys and activated by $NH_4Cl$ compiled by Nciri and Vandenbulcke (N-V)[31]. There is no crossover of $CrCl_2$ and $AlCl$ or $AlCl_2$ even at very low Al activities. A probable reason is that N-V used extrapolated data for solid $CrCl_2$ and $CrCl_3$ from Kubaschewski [62] which is inappropriate. Even at Al activities as low as $10^{-3}$ the $AlCl$ partial pressure is as high as 0.2 torr and $AlCl_2$ is as high as 100 torr.

Figures 46 and 47 are Kellogg plots of Cr and Al halides as a function of the chlorine and fluorine activity in the pack. The range of $p_{Cl_2}$ and $p_{F_2}$ for which the calculations are performed are typical of chloride and fluoride activated packs. The Al chloride and fluoride partial pressures are those in equilibrium with an activity of Al, $a_{Al}$, equal to $10^{-3}$ while the chromium chloride and fluoride partial pressures are those in equilibrium with pure chromium ($a_{Cr} = 1$). These Kellogg plots are useful in chemical vapor deposition rather than in pack cementation because in the latter the pack activator has to be considered in the equilibrium calculations. Nevertheless, approximate partial pressures of the metallic halide species can be obtained for various chlorine partial pressures.

For a partial pressure of chlorine equal to $10^{-10}$ atm, the partial pressures of the $AlCl$, $AlCl_2$ and $AlCl_3$ are $1.6\times10^{-2}$, 1 and $10^3$ atm respectively. The partial pressures of $CrCl_2$ and $CrCl_3$ corresponding to unit activity of Cr and for a partial pressure of chlorine equal to
Figure 45. Equilibrium partial pressures of gaseous species in a NH$_4$Cl-activated pack as a function of Al activity in the masteralloy (Ar, 1200°K)[31]
Figure 46. Partial pressures of Al and Cr chlorides as a function of the partial pressure of Cl₂ at 1273 K in equilibrium with Al at an activity, $a_{Al} = 10^{-3}$ and Cr at an activity, $a_{Cr} = 1$. 
Figure 47. Partial pressures of Al and Cr fluorides as a function of the partial pressure of F$_2$ at 1273°K in equilibrium with Al at an activity, $a_{\text{Al}} = 10^{-3}$ and Cr at an activity, $a_{\text{Cr}} = 1$. 
10^{-10} \text{ atm}, are 1.58 \times 10^{-2} and 1.6 \text{ atm}, respectively. Since the \text{CrCl}_2 and partial pressure is comparable to the \text{AlCl}_x vapor pressures, codeposition of \text{Cr} and \text{Al} should be possible at chlorine partial pressures where Nciri and Vandenbulcke predict only aluminization. Corresponding to a partial pressure of \text{F}_2 \text{ of } 10^{-25} \text{ atm. the partial pressures of } \text{AlF}, \text{AlF}_2 \text{ and } \text{AlF}_3 \text{ are } 3.7 \times 10^{-4}, 8.5 \times 10^{-2} \text{ and } 7.9 \times 10^{-4} \text{ and that of } \text{CrF}, \text{CrF}_2 \text{ and } \text{CrF}_3 \text{ are } 1.2 \times 10^{-8}, 5.6 \times 10^{-6} \text{ and } 1.2 \times 10^{-4} \text{ respectively. To achieve codeposition of } \text{Cr} \text{ and } \text{Al} \text{ in halide-activated cementation packs where the partial pressure of } \text{F}_2 \text{ is even lower than } 10^{-25} \text{ is virtually impossible since the } \text{AlF}_x \text{ partial pressures dominate the } \text{CrF}_x \text{ partial pressures.}

4.1.1 Complex and compound activators

Rapp, Wang and Weisert [16] investigated the effect of \text{AlCl}_3/\text{NaCl} salt mixtures on the simultaneous chromizing-aluminizing of \text{Fe} \text{ and } \text{Fe}-\text{base alloys. The optimum substrate surface concentration of } 20 \text{ w/o } \text{Cr} \text{ and } 4 \text{ w/o } \text{Al} \text{ was obtained for a pack activated with a } 2:1 \text{ ratio of } \text{AlCl}_3 \text{ to } \text{NaCl} \text{ and containing a 95 } \text{Cr}-5 \text{ w/o } \text{Al} \text{ masteralloy. However, the thermodynamics of the process for this activator have not been explained. The sublimation temperature of } \text{AlCl}_3 \text{ at } 178^\circ \text{C and the melting point of } \text{NaCl} \text{ at } 801^\circ \text{C differ widely, making it difficult to quantify the thermodynamics of the coating process. It is proposed that the unstable } \text{AlCl}_3 \text{ generates volatile metallic halide species upon heating during the initial stages of the process. The very high } p_{\text{Cl}_2} \text{ corresponding to } 1 \text{ atm of } \text{AlCl}_3 \text{ (v) would favor } \text{Cr} \text{ transfer at short times and low temperatures. The substrate is likely to be enriched in } \text{Cr} \text{ but not to any significant depth at low temperatures and short times. At longer times and higher temperatures, there is a significant loss of } \text{AlCl}_3 \text{ from the pack through the porous cement and liquid } \text{NaCl} \text{ regulates the formation of volatile metallic halide species. The lower}
associated with NaCl-activated packs generate much lower CrCl₅ and higher AlClₓ partial pressures than packs activated by AlCl₃. Therefore, over longer times and higher temperatures, AlCl₃/NaCl-activated packs favor simultaneous chromizing (with both AlCl₃ and NaCl contributing) and aluminizing (with only NaCl contributing). Since there is a significant loss of AlCl₃ from the pack through the porous cement, the liquid NaCl controls the formation of volatile halide species in the latter stage of the process.

Dewing [63] measured the activities of NaCl and AlCl₃ and analyzed the NaCl-AlCl₃ phase diagram. The standard enthalpy of NaAlCl₄ (s) was measured. Partial molar Gibbs energies in the NaCl-AlCl₃ system have been reported as a function of the mole fraction of AlCl₃ at a temperature of 473 K. Extrapolation of this data to 1273 K is not possible due to the significant volatilization of NaAlCl₄ and AlCl₃.

Compound activators such as cryolite, Na₃AlF₆, are expected to produce results significantly different from complex activators because of the reduced activities of the constituent species (NaF and AlF₃) in the compound. SOLGASMIX calculations for Na₃AlF₆-activated packs indicate that the partial pressures of the Al fluorides are higher than the Cr fluorides even at low Al activities as in the case of NaF and AlF₃-activated packs. However, the results of this analysis are expected to be affected by the following factors:

- Cryolite dissolving up to 15 mole per cent of the alumina in the pack,
- possible formation of complex Cr and Al fluorides
- reduced activities of NaF and AlF₃ which affect the fluoride partial pressures.
In summary, thermodynamic evaluation of the pack cementation process reveals that:

— Comparable partial pressures of Cr and Al chlorides can be achieved in chloride-activated packs and not in fluoride activated packs.

— Comparable Cr and Al halide partial pressures are also expected to be obtained in packs containing a mixture of salts or a salt solution.

4.1.2 Error Analysis

Table 22 shows the physical properties of the activators used in this study. At 1000°C, NaCl, NaF and CrCl₂ are liquid, AlF₃ is solid and AlCl₃ and NH₄Cl are gases. Moreover, NH₄Cl decomposes into NH₃ and HCl at 612 K [64]. AlCl₃ sublimates at the relatively low temperature of 177.8 K. The activators in condensed form serve to regulate the partial pressures of the gaseous metallic halide species by providing a source of halide molecules. Activators such as NH₄Cl and AlCl₃ sublime even before the coating temperature is attained and a significant amount is lost through the porous cement. The SOLGASMIX computations therefore are more representative of the conditions prevailing in non-volatile activator packs since the loss of activator is insignificant. The results of computations for the volatile activators only approximate actual coating conditions since the loss of activator may be significant. However, the activator and masteralloy are assumed to be present in sufficient quantities to validate the SOLGASMIX results.

The results of all the computations are dependent upon the accuracy of the thermodynamic data sources used.
TABLE 22. Physical properties of the halide salt activators used in this study (source: CRC handbook of Physics and Chemistry [64] and Pankratz [26])

<table>
<thead>
<tr>
<th>Salt</th>
<th>Melting point (°C)</th>
<th>Sublimation point (°C)</th>
<th>Boiling point (°C)</th>
<th>Molecular weight</th>
<th>Relative density</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>801</td>
<td></td>
<td>1413</td>
<td>58.44</td>
<td>2.17</td>
</tr>
<tr>
<td>AlCl₃</td>
<td></td>
<td>177.8</td>
<td></td>
<td>133.4</td>
<td>1.31</td>
</tr>
<tr>
<td>CrCl₂</td>
<td>824</td>
<td></td>
<td></td>
<td>-2.44</td>
<td></td>
</tr>
<tr>
<td>NH₄Cl</td>
<td></td>
<td>340 *</td>
<td></td>
<td>520</td>
<td>2.88</td>
</tr>
<tr>
<td>NaF</td>
<td>993</td>
<td></td>
<td>1695</td>
<td>41.99</td>
<td>2.56</td>
</tr>
<tr>
<td>AlF₃</td>
<td></td>
<td>1291</td>
<td></td>
<td>83.98</td>
<td>2.88</td>
</tr>
<tr>
<td>Na₃AlF₆</td>
<td>1010</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*decomposes into NH₃ and HCl
4.2 MICROSTRUCTURAL AND CHEMICAL ANALYSIS OF PURE Ni COATED UNDER DIFFERENT CONDITIONS

The discussion in section 4.1 reveals that on a thermodynamic basis, chloride activators are likely to simultaneously chromize-aluminize Ni substrates while fluoride activators will not. Moreover, the masteralloy has to be substantially rich in chromium to achieve codeposition of Al and Cr. To verify these predictions, a series of coating experiments was performed with chloride and fluoride activators and a 95 Cr-5 w/o Al masteralloy. All of the coatings were applied at 1000° C in an Ar atmosphere.

Representative microstructures for pure Ni coated in chloride-activated packs containing condensed activators (CrCl$_2$), gaseous activators (NH$_4$Cl, AlCl$_3$), mixed activators (NaCl/AlCl$_3$) and compound activators (Na$_3$AlF$_6$) will be discussed in the following.

4.2.1 Simple Activators

Figure 48a is an optical micrograph of the cross-section of a pure Ni sample coated in a CrCl$_2$-activated pack at 1000° C in an Ar atmosphere for 25 hours. There is little or no evidence of porosity indicating that the coating grew by the inward diffusion of Cr. There is very little pack entrapment which also indicates inward growth.

Figure 48b shows the atom percent of Al and Cr as a function of distance into the substrate. The concentration of Cr and Al at the surface are 40 a/o and 5 a/o respectively. This concentration of Cr is fairly constant up to 10 μm below the surface. The penetration depth of Cr and Al into the substrate is approximately 70 μm. An isothermal section of the Ni-Cr-Al ternary equilibrium diagram at 1273 K [65] is shown in Fig. 49 along with the
(a) Optical micrograph of cross section of coated sample.

(b) Concentration (a/o) of Cr and Al as a function of distance into sample.

Figure 48. Pure Ni coated in a CrCl$_2$-activated pack containing a 95Cr-5 w/o Al masteralloy at 1273°C in an Ar atmosphere for 25 hours.
Figure 49. 1273°C isothermal section of the Ni-Cr-Al equilibrium diagram [65] showing the diffusion path from the outer surface of the coating into the substrate (cf. Figure 48 (b)).
diffusion path from the surface into the substrate. The surface composition lies on the boundary between the α+γ and γ phase fields where α is the Cr-rich bcc solid solution and γ is the Ni-rich fcc solid solution. The lever rule predicts that the fraction of α in an alloy of this composition is almost zero. Therefore, the α phase is not observed in the outer layer.

Figure 50a shows an optical micrograph of the cross-section of a pure Ni sample coated in an AlCl₃ activated pack containing a 95 Cr-5 w/o Al masteralloy at 1273 K in an Ar atmosphere. The coating consists of an outer Cr-rich layer containing 22 a/o Cr and very little Al. The diffusion path corresponding to Fig. 50b is shown in the 1273 K isothermal section of the ternary Ni-Cr-Al equilibrium diagram (Fig. 51). AlCl₃ is an unstable activator and generates very high partial pressures of CrCl₂ for a 95 Cr-5 w/o Al masteralloy composition. So a Cr-rich coating forms with almost no Al incorporation.

Figure 52a shows an optical micrograph of the cross-section of a pure Ni sample coated for 25 hours at 1273 K in a NH₄Cl-activated pack containing a 95 Cr-5 w/o Al masteralloy. Figure 52b shows the atom percent of Cr and Al into the substrate for the coating in Fig. 52a. An outer Cr-rich layer whose composition is in the α field (approximately 40 μm thick) forms along with an inner diffusion zone approximately 60 μm thick. The diffusion path of the coating elements into the substrate is indicated in the 1273 K isotherm of the Ni-Cr-Al phase diagram [65] in Fig. 53. The coating composition for the outer layer lies outside the composition limits of the phase diagram.

The unstable NH₄Cl activator generates higher chromium chloride partial pressures than the relatively stable CrCl₂ activator for the same masteralloy composition (95 Cr-5 Al).
(a) Optical micrograph of cross section of coated sample.

(b) Concentration (a/o) of Cr and Al as a function of distance into sample.

Figure 50. Pure Ni coated in an AlCl$_3$-activated pack containing a 95Cr-5 w/o Al masteralloy at 1273°K in an Ar atmosphere for 25 hours.
Figure 51. 1273°K isothermal section of the Ni–Cr–Al equilibrium diagram [65] showing the diffusion path from the outer surface of the coating into the substrate (cf. Figure 50 (b)).
(a) Optical micrograph of cross section of coated sample.

(b) Concentration (a/o) of Cr and Al as a function of distance into sample.

Figure 52. Pure Ni coated in a NH₄Cl-activated pack containing a 95Cr-5 w/o Al masteralloy at 1273°C in an Ar atmosphere for 25 hours.
Figure 53. 1273°K isothermal section of the Ni-Cr-Al equilibrium diagram [65] showing the diffusion path from the outer surface of the coating into the substrate (cf. Figure 52 (b)).
Figure 54a is the optical micrograph of the cross-section of a pure Ni sample coated in an AlF$_3$ activated pack containing a 95 Cr-5 w/o Al masteralloy at 1273 K for 25 hours in an Ar atmosphere. Significant porosity is observed near the coating substrate interface indicating outward growth of the coating due to preferential outward Ni diffusion. The atom percent of Al and Cr as a function of distance into the substrate is shown in Fig. 54b. The outer surface of the coating contains about 65 a/o Al and very little Cr (approximately 1 a/o). At 90 μm within the coating, the Al composition drops sharply to approximately 15 a/o. From the 1273 K isothermal section of the Ni-Cr-Al phase diagrams, the outer layer of the coating is β-NiAl and the inner layer is γ-Ni solid solution.

Figures 55 and 56 are the concentration profiles (a/o) of the Al and Cr into Ni substrates coated in NaF-activated packs containing 95 Cr - 5 w/o Al for 25 hours at 1273 K in an Ar atmosphere. As expected, the pack is aluminizing and has a surface concentration of 22 Al - 4 a/o Cr. The partial pressure of fluorine in AlF$_3$ packs containing 95 Cr - 5 w/o Al is one order of magnitude higher than the $p_{F_2}$ in NaF-packs and a higher surface concentration of Al is expected for AlF$_3$-activated packs. Likewise, the NaF-pack introduced more Cr in the substrate than the AlF$_3$ pack.

From the microstructural and chemical analysis of the coated Ni samples it is seen that

— Chloride activators are strongly chromizing in packs containing a 95 Cr-5 w/o Al masteralloy, and

— Fluoride activators are strongly aluminizing even in packs containing Cr-rich masteralloy.
(a) Optical micrograph of cross section of coated sample.

(b) Concentration (a/o) of Cr and Al as a function of distance into sample.

Figure 54. Pure Ni coated in an AlF₃-activated pack containing a 95Cr-5 w/o Al masteralloy at 1273°K in an Ar atmosphere for 25 hours.
Figure 55. Concentration (a/o) of Cr and Al as a function of distance into a sample of pure Ni coated in a NaF-activated pack containing a 95Cr-5 w/o Al master-alloy at 1273°K in an Ar atmosphere for 25 hours.
Figure 56. 1273°C isothermal section of the Ni-Cr-Al equilibrium diagram [65] showing the diffusion path from the outer surface of the coating into the substrate (cf. Figure 55.)
Moreover, unstable activators such as \( NH_4Cl \) and \( AlCl_3 \) tend to form a Cr-rich \( \alpha \) outer layer while relatively stable activators such as \( CrCl_2 \) do not form an \( \alpha-Cr \) outer layer.

The surface composition of 40 a/o Cr-5 a/o Al specimens coated in \( CrCl_2 \)-activated packs is higher in \( Cr \) content relative to the desired surface composition of 18-25 a/o Cr and 5-10 a/o Al. However, Luthra and Wood [67] observed that \( Cr \) composition greater than 39 a/o in Ni-Cr alloys were the most effective against hot corrosion attack. Therefore, the surface compositions obtained for \( CrCl_2 \)-activated packs were close to the desired composition.

4.2.2 Complex Activators

A surface composition of Fe-18 Cr-5 Al on pure Fe and Fe-base alloys was achieved by Wang [68] using pack activated by 2:1 \( AlCl_3 \) to \( NaCl \) salt mixture containing a 95 Cr-5 w/o Al masteralloy. Moreover, the thermodynamic analysis of complex activator packs in Section 4.1.2 indicates that simultaneous chromizing-aluminizing of \( Ni \) in packs activated by \( AlCl_3/NaCl \) should be feasible on a thermodynamic basis.

Two types of complex activators - \( AlCl_3/NaCl \) and \( AlCl_3/AlF_3 \) were chosen based on the thermodynamic evaluation of the individual activators. The choice of the \( AlCl_3/NaCl \) activator has been explained above. \( AlF_3 \) was predicted to be a strong aluminizing activator and this was confirmed by the microstructural examination of pure \( Ni \) coated in a pack containing a 95 Cr-5 w/o Al masteralloy. It was expected that \( AlCl_3 \) would function as a strong chromizing agent in the early stages of the coating process as in the case of the \( AlCl_3/NaCl \) activated pack and the stable strongly aluminizing \( AlF_3 \) would regulate the coating kinetics in the later part of the coating process.
The results of the coating treatments using these two sets of complex activators are discussed below.

Figure 57a is an optical micrograph of the cross-section of a pure Ni sample coated at 1273 K for 25 hours in an AlCl₃/NaCl (2/1)-activated pack containing a 95 Cr-5 w/o Al masteralloy. A 10 µm thick outer Cr-rich α layer containing 70 a/o Cr and 12 a/o Al is observed. The coating thickness is 50 µm. As discussed earlier, it is expected that the AlCl₃- is strongly chromizing during the early part of the coating process and thereafter, the coating thermodynamics and kinetics is regulated by the NaCl (l). Since NaCl (l) is more aluminizing than AlCl₃, the Al concentration attained in AlCl₃/NaCl activated packs is higher than in AlCl₃-activated packs. The surface concentration of Al is close to the desired composition of 10 a/o and Cr is higher than the desired composition range of 18-25 a/o (Fig. 57b); but the composition at the α-Cr/γ interface (Fig. 58), is close to the desired composition.

Figure 59a is an optical micrograph of the cross-section of a pure Ni sample coated at 1273 K for 25 hours in an AlCl₃/AlF₃-activated pack containing a 95 Cr-5 w/o Al masteralloy. A 5 µm thick Cr-rich outer layer containing 38 a/o Cr and 6 a/o Al is observed (Fig. 59b). The coating thickness (outer layer+inner diffusion zone) is 90 µm. Figure 60 shows the diffusion path corresponding to Fig. 59b. The AlF₃ did not aluminize the Ni substrate as strongly as was expected probably because the AlCl₃ did not completely escape from the pack and generated sufficient chlorine partial pressures throughout the process to chromize the substrate. A possible method to increase the aluminum content of the substrate is to increase the AlF₃/AlCl₃ ratio or use an unstable fluoride activator such as NH₄F in
(a) Optical micrograph of cross section of coated sample.

(b) Concentration (a/o) of Cr and Al as a function of distance into sample.

Figure 57. Pure Ni coated in an AlCl₃/NaCl-activated pack containing a 95Cr-5 w/o Al masteralloy at 1273°K in an Ar atmosphere for 25 hours.
Figure 58. 1273°K isothermal section of the Ni-Cr-Al equilibrium diagram [65] showing the diffusion path from the outer surface of the coating into the substrate (cf. Figure 57 (b)).
(a) Optical micrograph of cross section of coated sample.

(b) Concentration (a/o) of Cr and Al as a function of distance into sample.

Figure 59. Pure Ni coated in an AlCl₃/AlF₃-activated pack containing a 95Cr-5 w/o Al masteralloy at 1273°K in an Ar atmosphere for 25 hours.
Figure 60. 1273°K isothermal section of the Ni-Cr-Al equilibrium diagram [65] showing the diffusion path from the outer surface of the coating into the substrate (cf. Figure 59 (b)).
conjunction with $AlCl_3$.

### 4.2.3 Compound Activators

The salt mixtures used in the complex activator packs described in Section 4.2.2 were mechanically mixed. A premixed salt solution or a compound would have reduced salt activities. The reduced salt activities affect the equilibrium partial pressures of the gaseous species in the pack and consequently the coating compositions.

Cryolite ($Na_3AlF_6$) has been reported in patent literature [63] as an activator for chromizing and aluminizing processes. Therefore, $Na_3AlF_6$ was chosen as a possible activator for simultaneous chromizing-aluminizing although $NaF$ and $AlF_3$ are individually strong aluminizing agents even when high chromium activity masteralloys are used. As explained in Section 4.1.3, complex gaseous species are expected to be present in packs activated by compound activators and these would contribute to the chromizing-aluminizing process.

Figure 61a shows the optical micrograph of a pure Ni substrate coated at 1273 K for 25 hours in a $Na_3AlF_6$-activated pack containing a 95 Cr-5 w/o Al masteralloy. No porosity is observed and the coating appears to be homogeneous. Figure 61b shows the concentration (a/o) of Cr and Al as a function of distance into the substrate. The surface concentration of Cr and Al are 45 a/o and 5 a/o respectively. The coating thickness is 70 μm.

Figure 62 shows the 1273 K isothermal section of the Ni-Cr-Al phase diagram along with a portion of the diffusion path corresponding to Fig. 59b.
Figure 6.1. Pure Ni coated in a NaF-activated pack containing a 95Cr-5Al master alloy at 1273 K in an Ar atmosphere for 25 hours.

(b) Concentration (at%) of Cr and Al as a function of distance into sample.

Distance in substrate (in μm)

Atom percent

(a) Optical micrograph of cross section of coated sample.
4.2.4 Effect of masteralloy composition on coating composition

For a given activator, as the concentration of Al in the masteralloy increases, an increase in the surface concentration of Al is expected.

When the masteralloy composition was 90 Cr-10 w/o Al, the surface Cr concentration on the Ni substrates was significantly reduced (< 10 a/o Cr) for chloride activated packs. Therefore, a masteralloy composition of 92½ Cr-7½ w/o Al was used to reduce surface Cr concentration and increase surface Al concentration. Figure 63 shows the concentration (a/o) of Al and Cr as a function of distance in to a pure Ni substrate coated at 1273 K in a CrCl$_2$-activated pack containing a 92½ Cr-7½ w/o Al masteralloy. The surface composition is 58 a/o Al and 3 a/o Cr. The outer layer is the Al-rich β phase [65] and the inner layer is the fcc γ-Ni solid solution. The outer layer is approximately 70 μm thick and the inner diffusion zone is 60 μm thick.

Clearly, even a small change in the concentration of the masteralloy causes a significant change in the coating composition.

4.3 ANALYSIS OF THE KINETICS OF SIMULTANEOUS CHROMIZING-ALUMINIZING

The study of the kinetics of the coating process is divided into two categories - weight-gain measurements and concentration profile measurements.

Pure Ni samples were coated at 1273 K in CrCl$_2$-activated packs containing a 95 Cr-5
Figure 62. 1273°K isothermal section of the Ni-Cr-Al equilibrium diagram [65] showing the diffusion path from the outer surface of the coating into the substrate (cf. Figure 61 (b)).
Substrate is Ni
Activator is CrCl$_2$
Masteralloy is 92$\frac{1}{2}$ Cr 7$\frac{1}{2}$ w/o Al

Figure 63. Concentration (a/o) of Cr and Al into pure Ni coated in a CrCl$_2$-activated pack containing a 92$\frac{1}{2}$Cr-7$\frac{1}{2}$ w/o Al masteralloy (1273°K, 25 hours, Ar atmosphere).
w/o Al masteralloy for different times. The CrCl$_2$ activator and the 95 Cr-5 w/o Al masteralloy were chosen because this combination achieved the desired surface composition of Cr and Al.

Dimensional and weight-gain changes were recorded. Figure 64 shows the weight-gain per unit area as a function of time for pure Ni substrates coated in packs activated by CrCl$_2$ and containing a 95 Cr-5 w/o Al masteralloy.

The linear behavior suggests that the kinetics of the coating process is controlled by diffusion of the halide vapor in the pack and solid state diffusion of Al and Cr into the substrate. Since the weight-gain per unit area follows a relation of the type:

$$\frac{\Delta m}{A} = \left(\frac{\Delta m_0}{A}\right) + \sqrt{k_p t}$$

(4.10)

where \(\frac{\Delta m_0}{A}\) is almost zero, and \(k_p\), the rate constant, can be determined from the slope of the line. The value of \(k_p\) thus obtained is $1.3 \times 10^{-6}$ \(gm^2 cm^{-4} hr^{-1}\). This compares with the value of \(k_{solid}\) of $2.5 \times 10^{-6}$ \(gm^2 cm^{-4} hr^{-1}\) obtained by Seigle, Gupta, Shankar and Sarkhel [60] for the aluminization of pure Ni. The lower value of \(k_p\) is probably due to the slower diffusion of Cr in Ni.

Figure 65 is a plot of atom percent of Cr and Al as a function of distance into Ni substrates coated in CrCl$_2$- activated packs containing a 95 Cr-5 w/o Al masteralloy for different times. The surface composition of Al attains an almost constant value of 4-5 a/o while the Cr concentration is also fairly constant, remaining at 40 a/o for all times after 4 hours. The coating thickness also progressively increases with coating time as expected.
Figure 64. Weight gain per unit area (m/A) as a function of time (t) for pure Ni samples coated in CrCl$_2$-activated packs containing a 95Cr-5 w/o Al masteralloy (1273 K, Ar atmosphere).
Figure 65. Concentration (a/o) of Cr and Al as a function of distance into Ni-substrates coated in CrCl$_2$-activated packs containing a 95Cr-5 w/o Al masteralloy (1273 K, Ar atmosphere) for several coating times.
The atom percent versus distance plots are converted to w/o versus distance plots to calculate the weight-gain in the coated substrates. Figure 66 represents the weight percent of Cr and Al as a function of distance into the substrate for different coating times. The weight-gain per unit area is expressed as:

\[
\frac{\Delta m}{A} = \frac{1}{100} \left[ \int_0^x w/o \, Cr \, \rho_{alloy} \, dx + \int_0^x w/o \, Al \, \rho_{alloy} \, dx \right]
\]  

(4.11)

where \( w/o \, Cr \) and \( w/o \, Al \) are the weight percents of Cr and Al, \( \rho_{alloy} \) is the density of the Ni-Cr-Al alloy expressed as

\[
\rho_{alloy} = \frac{w/o \, Ni}{\rho_{Ni}} + \frac{w/o \, Cr}{\rho_{Cr}} + \frac{w/o \, Al}{\rho_{Al}}
\]  

(4.12)

and \( x \) the penetration depth into the substrate. Equation (4.12) was numerically evaluated to obtain the weight-gain per unit area. Table 23 compares the measured weight-gain to the calculated weight-gain. The measured values are slightly different from the calculated values. This discrepancy could arise due to several factors uncertainty in the determination of the concentration values close to the surface of the sample and uncertainty in measured weight-gain due to pack entrapment.

Table 24 shows the measured weight-gain per unit area for pure Ni substrates coated for 20-25 hours in packs containing a 95 Cr-5 w/o Al masteralloy and for different activators along with the surface compositions of the coated samples. The use of unstable activators such as \( NH_4Cl \) and \( AlCl_3 \) results in the maximum weight gain per unit area. Stable activators, especially liquids, at the coating temperatures such as \( NaCl \) and \( NaF \), condense on the substrate and coat it. The gaseous metallic halide species from the pack have to diffuse
CONCENTRATION PROFILES FOR CHROMIUM AND ALUMINUM

Figure 66. Concentration (w/o) of Cr and Al as a function of distance into Ni-substrates coated in CrCl$_2$-activated packs containing a 95Cr-5 w/o Al masteralloy (1273 K, Ar atmosphere) for several coating times.
TABLE 23. Comparison of theoretical and experimental weight change per unit area

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>( \Delta m/A ) (mg/cm(^2))</th>
<th>Measured</th>
<th>Calculated from diffusion profile</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.28</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.77</td>
<td>2.76</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>3.46</td>
<td>3.45</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>4.43</td>
<td>4.43</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>6.37</td>
<td>6.39</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 24. Weight gain per unit area for a pure Ni substrate coated in a pack containing a 95 Cr - 5 Al masteralloy

<table>
<thead>
<tr>
<th>Activator</th>
<th>Coating time (hours)</th>
<th>( \Delta M/A ) (mg/cm(^2))</th>
<th>Coating surface composition (a/o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl (l)</td>
<td>25</td>
<td>2.83</td>
<td>90 Cr - 8 Al</td>
</tr>
<tr>
<td>AlCl(_3) (v)</td>
<td>25</td>
<td>14.8</td>
<td>22 Cr - 0.2 Al</td>
</tr>
<tr>
<td>CrCl(_2) (v)</td>
<td>25</td>
<td>6.2</td>
<td>40 Cr - 5 Al</td>
</tr>
<tr>
<td>NH(_4)Cl (v)</td>
<td>25</td>
<td>22.2</td>
<td>94 Cr - 6 Al</td>
</tr>
<tr>
<td>AlCl(_3)/NaCl</td>
<td>20</td>
<td>2.4</td>
<td>72 Cr - 12 Al</td>
</tr>
<tr>
<td>AlCl(_3)/AlF(_3)</td>
<td>25</td>
<td>5.06</td>
<td>36 Cr - 5 Al</td>
</tr>
<tr>
<td>NaF</td>
<td>25</td>
<td>2.38</td>
<td>22 Al - 6 Cr</td>
</tr>
<tr>
<td>AlF(_3)</td>
<td>25</td>
<td>3.91</td>
<td>65 Cr - 1 Al</td>
</tr>
<tr>
<td>Na(_3)AlF(_6) (l)</td>
<td>25</td>
<td>3.8</td>
<td>42 Cr - 5 Al</td>
</tr>
</tbody>
</table>
through this liquid film to reach the substrate. The coating kinetics may therefore be slowed to result in a reduced weight-gain. Substrates coated in packs activated by solid activators such as AlF$_3$ indicate a slightly higher weight-gain since they may not completely cover the substrate. The halide vapors can therefore arrive at the substrate surface without necessarily diffusing through the condensed activator.

The complex activators, AlCl$_3$/NaCl and AlCl$_3$/AlF$_3$, result in weight-gains of the substrate which lie between those of the individual constituents. As explained earlier in section 4.2.2 the initial large weight-gain is due to the unstable AlCl$_3$ and the latter slower weight-gain is due to the stable, liquid NaCl. Similarly in AlCl$_3$/AlF$_3$-activator packs, the initial, high transport rates are provided by AlCl$_3$ and thereafter, AlF$_3$ controls the metal transfer from the pack to the substrate. The compound activator cryolite results in a weight-gain between that of NaF and AlF$_3$.

**Determining the width of the depletion zone**

The data in Tables 23 and 24 are used to determine the width of the depletion zone ($\delta$) with Eq. (2.41). Table 25 shows the values of $\delta$ thus obtained. The magnitude of $\delta$ for different activators is in the range 0.1 to 0.8 mm. Therefore, the masteralloy was in great excess and no global depletion occurred.
TABLE 25. Thickness of depletion zone in packs containing different activators

<table>
<thead>
<tr>
<th>Activator</th>
<th>Coating time (hours)</th>
<th>ΔM/A (mg/cm²)</th>
<th>Depletion zone width (δ) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrCl₂ (v)</td>
<td>1</td>
<td>1.28</td>
<td>50</td>
</tr>
<tr>
<td>CrCl₂ (v)</td>
<td>4</td>
<td>2.77</td>
<td>109</td>
</tr>
<tr>
<td>CrCl₂ (v)</td>
<td>9</td>
<td>3.46</td>
<td>136</td>
</tr>
<tr>
<td>CrCl₂ (v)</td>
<td>25</td>
<td>4.97</td>
<td>255</td>
</tr>
<tr>
<td>NaCl (l)</td>
<td>25</td>
<td>2.83</td>
<td>111</td>
</tr>
<tr>
<td>AlCl₃ (v)</td>
<td>25</td>
<td>14.8</td>
<td>580</td>
</tr>
<tr>
<td>NH₄Cl (v)</td>
<td>25</td>
<td>22.2</td>
<td>870</td>
</tr>
<tr>
<td>AlCl₃/NaCl</td>
<td>20</td>
<td>2.4</td>
<td>94</td>
</tr>
<tr>
<td>AlCl₃/AlF₃</td>
<td>25</td>
<td>5.06</td>
<td>198</td>
</tr>
<tr>
<td>NaF</td>
<td>25</td>
<td>2.38</td>
<td>93</td>
</tr>
<tr>
<td>AlF₃</td>
<td>25</td>
<td>3.91</td>
<td>153</td>
</tr>
<tr>
<td>Na₃AlF₆ (l)</td>
<td>25</td>
<td>3.8</td>
<td>149</td>
</tr>
</tbody>
</table>
4.4 ANALYSIS OF DIFFUSION IN THE Ni-Cr-Al SYSTEM

A study of the solid-state diffusion of the coating elements Cr and Al into Ni is important because the diffusion depth (coating thickness) can be predicted if surface concentrations are known and the total weight-gain can be predicted given the coating time and surface concentration.

A finite element program was developed to predict the diffusion profiles of Cr and Al into Ni for a given surface concentration. A description of the algorithm for the program is given in Section 2.3.

Figures 67 to 70 show the concentration profiles of Cr and Al into Ni substrates coated in CrCl₂-activated packs containing 95 Cr - 5 w/o Al masteralloy at 1273 K for four different coating times. If the measured surface concentration is input to the program, significant disagreement between measured and predicted concentration values is noticed. However, if the concentration of Cr and Al at 10 μm into the substrate is used as input to the program, excellent agreement between measured and predicted profiles is obtained. The discrepancy in the former case is attributed to the inaccuracy of Nesbitt and Heckel’s [5] diffusion data in the high Cr (α + β) regime.
Figure 67. Concentration (a/o) of Cr and Al as a function of distance into Ni substrates coated in CrCl$_2$-activated packs containing a 95 Cr-5 w/o Al masteralloy (1273 K, Ar atmosphere) for 1 hour.
Figure 68. Concentration (a/o) of Cr and Al as a function of distance into Ni substrates coated in CrCl$_2$-activated packs containing a 95 Cr-5 w/o Al masteralloy (1273 K, Ar atmosphere) for 4 hours.
Figure 69. Concentration (a/o) of Cr and Al as a function of distance into Ni substrates coated in CrCl₂-activated packs containing a 95 Cr-5 w/o Al masteralloy (1273 K, Ar atmosphere) for 9 hours.
Figure 70. Concentration (a/o) of Cr and Al as a function of distance into Ni substrates coated in CrCl$_2$-activated packs containing a 95 Cr-5 w/o Al masteralloy (1273 K, Ar atmosphere) for 25 hours.
The coating thickness measured from the experimental profiles and predicted by theoretical curves are compared in Table 26. There is very good agreement between the two values indicating that the program can be used with confidence to predict weight-gains. The predicted values would be more accurate if the coating composition was in the $\gamma$ phase field of the Ni-Cr-Al ternary system.

4.5 APPLICATION OF THE SIMULTANEOUS CHROMIZING-ALUMINIZING PROCESS TO ENGINEERING ALLOYS

The thermodynamics, microstructures and kinetics of the simultaneous chromizing-aluminizing process for pure Ni have been analyzed. Since the partial pressures of the Ni halides are insignificant, substrate effects on the thermodynamics of the coating process were neglected. If Ni-base alloys are to be coated, however, the alloying elements in the substrate could have a significant effect on the equilibrium partial pressures of the gaseous species and on the kinetics of the coating process.

For example, if a Ni-20 w/o Cr alloy is aluminized in a pack containing pure Al or a Ni-Al source alloy, it is conceivable that the Cr in the substrate could form volatile chromium chlorides especially if an unstable activator such as $\text{NH}_4\text{Cl}$ is used. Multicomponent Ni-base superalloys which contain Fe, such as Inconel 600, may undergo substrate-environment reactions of the type:

$$\text{CrCl}_2 (v) + \text{Fe} (s) = \text{Cr} + \text{FeCl}_2 (v)$$

(4.13)
TABLE 26. Comparison of coating thickness - theoretical and experimental

<table>
<thead>
<tr>
<th>Coating duration (hours)</th>
<th>Depth of coating (μm)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
<td>Experimental</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>35</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>50</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>60</td>
<td>70</td>
<td></td>
</tr>
</tbody>
</table>
in chromizing packs. Although the above reaction aids the coating process by incorporating Cr into the substrate, significant losses of alloying elements may affect the properties of the substrate.

Although the details of the coating process may be more complicated for the Ni-base alloys than for pure Ni substrates, the general principles discussed in Section 4.1 through 4.4 are still valid.

In the following, the microstructures and chemical compositions of Ni-20 w/o Cr and Ni-base superalloys are discussed.

4.5.1 Ni-20 w/o Cr

On a thermodynamic basis, the chloride activators are expected to chromize and the fluoride activators are expected to aluminize the Ni-20 w/o Cr substrates. Representative microstructures of Ni-20 w/o Cr coated in CrCl₂-activated packs (predominantly chromizing) and in AlF₃-activated packs (predominantly aluminizing) are presented.

Figure 71 shows a secondary electron image of the cross-section of a Ni-20 w/o Cr alloy coated at 1273 K for 9 hours in a CrCl₂-activated pack containing a 95 Cr-5 w/o Al masteralloy. The outer layer of the coating (10 μm thick) contains 98 a/o Cr and less than 2 a/o Al (Fig. 71b). There is a sharp drop in the Cr concentration at the α/γ interface and the Cr concentration falls off to 20 w/o at approximately 25 μm from the α/γ interface.

Nesbitt and Heckel [5] report that the interdiffusion coefficient \( \tilde{D}_{CrCr}^{Ni} \) in ternary Ni-Cr-Al alloys in the single phase γ region shows only a weak dependence on the Cr concentration, but increases with increases in Al concentration. The cross-term interdiffusion coefficient
(a) Secondary electron image of the coated cross section of the substrate.

(b) Concentration (a/o) of Cr and Al as a function of distance (μm) into the substrate.

Figure 71. Ni-20 w/o Cr substrate coated in a CrCl7-activated pack containing a 95Cr-5 w/o Al masteralloy (1273°K, 9 hours, Ar atmosphere).
$\bar{D}_{CrAl}^{Ni}$ shows a strong $Cr$ concentration dependence but a weak $Al$ dependence. Since the $Al$ content in the coating is so low ($< 2 \, \text{a/o}$), the profile in Fig. 71b essentially represents the diffusion of $Cr$ in a $Ni-20 \, w/o \, Cr$ alloy and the $Cr$ concentration profile in the $\gamma$ matrix is similar to that of pure $Ni$ coated in a $CrCl_2$-activated pack.

Figure 72 shows the optical micrograph of the cross-section of a $Ni-20 \, w/o \, Cr$ substrate coated at 1273 K for 25 hours in an $AlF_3$-activated pack containing a 90 $Cr$-10 $w/o \, Al$ masteralloy. As expected, the pack is strongly aluminizing and a two layer coating forms. Energy dispersive analysis of the outer layer reveals that it is $Al$-rich $\beta$-$NiAl$ with a two-phase $\alpha+\gamma$ inner diffusion zone. This morphology is similar to that obtained by Delanerolle and Seigle [67] who aluminized $Ni-Cr$ alloys in a aluminizing pack activated with $AlF_3$. Figure 73a shows the secondary electron image of the substrate shown in Fig. 72. The $Al$, $Cr$ and $Ni$ X-ray dot maps shown in Figs. 73b, c and d confirm that the outer region of the coating is rich in $Ni$ and $Al$ and devoid of $Cr$ while the lamellar phase in the inner diffusion zone is rich in $Cr$ with matrix rich in $Ni$ corresponding to the $\gamma$ phase. Since the pack contains a 90 $Cr$-10 $w/o \, Al$ masteralloy, it can be classified as a "low" $Al$ activity pack and so the $\beta$-$NiAl$ layer probably grew by the predominant outward diffusion of $Ni$. The $Ni$ depleted matrix has an average composition which was located in the two phase $\alpha+\gamma$ field resulting in the formation of the $\alpha$-$Cr$ phase.

Simultaneous chromizing-aluminizing of a high $Cr$ alloy such as $Ni-20 \, w/o \, Cr$ is important because even if the pack were aluminizing (as in the $AlF_3$ pack), incorporation of $Cr$ in the outer layer would be beneficial for hot corrosion resistance. This should be
Figure 72, Ni-20 w/o Cr coated in an AlF₃-activated pack containing a 90Cr-10 w/o Al masteralloy (1273°K, 25 hours, Ar atmosphere).
Figure 73. Ni-20 w/o Cr coated in AlF₃-activated packs containing a 90 Cr-10 w/o Al masteralloy (1273 K, 25 hours, Ar atmosphere)
accomplished by minimal Cr loss from the substrate. Therefore, Cr loss from the substrate would be reduced by maintaining aluminizing-chromizing condition rather than the current use of pure aluminizing conditions.

Since the CrCl$_2$-activated packs containing 95 Cr-5 w/o Al masteralloys tend to be chromizing and those containing 90 Cr-10 w/o Al tend to be aluminizing, a Ni-20 Cr substrate was coated in a CrCl$_2$-activated pack containing a 92½ Cr-7½ w/o Al masteralloy. Figure 74 shows the secondary electron image of the cross-section of a Ni-20 w/o Cr substrate coated at 1273 K for 25 hours in a CrCl$_2$-activated pack containing a 92½ Cr-7½ w/o Al masteralloy. The coating consists of a two-phase outer zone approximately 60 μm thick and containing fine second phase particles and a two-phase inner diffusion layer. The concentration profiles in the matrix of the outer layer and in the inner layer are indicated in Fig. 74b. The composition of the outer layer is in the β-NiAl phase field of the Ni-Cr-Al ternary phase diagram. The composition of the inner layer is predominantly in the ξ phase field (Fig. 74c).

Therefore, a small change in the Al content of the Cr-Al masteralloy results in a transition from chromizing to aluminizing conditions. The microstructures shown in Figs. 73 and 74 are similar to those obtained by Delanerolle and Seigle [68].

Figure 75 is a plot of weight-gain per unit area as function of time for a Ni-20 w/o Cr alloy coated in a CrCl$_2$-activated pack containing a 95 Cr-5 w/o Al masteralloy. The linear behavior indicates rate control by solid state diffusion. The rate constant $k_p$, calculated from the slope of this line is $2.5 \times 10^{-7}\text{gm}^2\text{cm}^{-4}\text{hr}^{-1}$. 
(a) Secondary electron image.

(b) Concentration (a/o) of Cr and Al as a function of distance into the substrate (µm).

Figure 74. Ni-20 w/o Cr coated in a CrCl₂-activated pack containing a 92\%Cr-7\%Al masteralloy (1273 K, 25 hours, Ar atmosphere).

(c) 1273 K isothermal section of the Ni-Cr-Al equilibrium diagram [65] showing the diffusion path corresponding to Figure 74 (b).
Figure 75. Weight gain per unit area ($\Delta m/A$) as a function of time ($\sqrt{t}$) for Ni-20 w/o Cr substrates coated in CrCl$_2$-activated packs containing a 95Cr-5 w/o Al master-alloy (1273°K, Ar atmosphere).
Figures 76 to 79 are concentration profiles (a/o) of Cr and Al as a function of distance into the substrate. The thickness of the outer \( \alpha \)-Cr layer increases and the inner diffusion zone increased as a function of time. The Al concentration at the outer layer remained fairly constant at approximately 3 a/o.

Figure 80 shows a plot of the thickness of the \( \alpha \)-Cr layer as a function of time. This linear behavior appears to be in accordance with the results of Mazille [43] for the chromizing of pure Ni.

4.5.2 Ni-base Superalloys

Rene 80 (60 Ni-14 Cr-9.5 Co-4 Mo-4 W-3 Al- 5 Ti- 0.17 C- 0.015 B- 0.03 w/o Zr) and IN 600 (Ni-15.8 Cr- 7.2 Fe- 0.2 Si- 0.2 Mg- 0.04 C) substrates were chosen as substrates. These alloys, with the exception of IN 600, are used in turbine blades and vanes and are subject to hot corrosion attack. Alloying additions of Cr mitigate hot corrosion attack [66]. Therefore chromizing-aluminizing Rene 80 should improve its resistance to low temperature hot corrosion.

IN 600 is used as heat exchanger pipe material for high-temperature, high-pressure aqueous systems and is resistant to stress corrosion cracking. Although the temperatures encountered are no higher than 550\(^\circ\) C, this substrate was chosen because it contains 7 w/o Fe. As discussed in the previous sections, the presence of Fe in the substrate could enhance the incorporation of coating elements such as Cr by undergoing exchange reactions with the Cr chloride.
Figure 76. Concentration (a/o) of Cr and Al as a function of distance into Ni-20 w/o Cr (1273 K, Ar atmosphere) 1 hour.
Figure 77. Concentration (a/o) of Cr and Al as a function of distance into Ni-20 w/o Cr (1273 K, Ar atmosphere) 4 hours.
Figure 78. Concentration (a/o) of Cr and Al as a function of distance into Ni-20 w/o Cr (1273 K, Ar atmosphere) 9 hours.
Figure 79. Concentration (a/o) of Cr and Al as a function of distance into Ni-20 w/o Cr (1273 K, Ar atmosphere) 16 hours.
Figure 80. Thickness of the α-Cr layer (μm) as a function of time (s/τ) for Ni-20 w/o Cr substrates coated in CrCl₂-activated packs containing 95Cr-5 w/o Al (1273 K, Ar atmosphere).
Figure 81 shows an optical micrograph of the cross-section of a Rene 80 substrate coated at 1273 K in an $AlCl_3/NaCl$-activated pack containing 95 Cr-5 w/o Al as masteralloy for 10 hours. A two-layer coating is observed. The outer layer is single phase, while the inner diffusion layer is two-phase with a lamellar morphology for the second phase. Figure 82a shows the secondary electron image for the coating and Figs. 82b-d show the X-ray dot maps for Ni, Cr and Al. The outer layer is rich in Al and Ni and the inner diffusion zone is Cr-rich. The compositions of the numbered regions in the secondary electron micrograph are indicated in the isothermal section of the Ni-Cr-Al phase diagram (Fig. 83). The outer region is in the single phase $\beta$ field, the lamellae in the inner diffusion zone are in the $\alpha$ phase field and the matrix is $\gamma$. A comparison of this microstructure with commercially available aluminide coating is made in the following.

Figure 84 shows the optical microstructure of a Rene 80 coupon coated in a pack of proprietary composition (General Electric’s Codep process). It consists of an Al-rich $\beta$-NiAl layer with the inner zone consisting of $\alpha+\gamma$ phases. The morphology of the two coated substrates are almost identical. However, the Cr content of the $\beta$-NiAl layer is higher in the chromized-aluminized coating (7-8 a/o) due to Cr deposition from the pack than in codep coating (2-3 a/o). The Cr in the codep coupon is the Cr from the substrate. The increased Cr in the outer diffusion layer is expected to enhance the hot corrosion resistance of the alloy.

The morphology of the two coatings mentioned above are compared to another commercially available coating - the AVCO 701 coating of the AVCO-Lycoming Co. Figure 85 shows an AVCO701 coating on an IN 713 substrate. The Al content (52 a/o) of the outer
Figure 81. Optical micrograph of the cross section of Rene' 80 coated in an AlCl₃/NaCl-activated pack containing a 95Cr-5 w/o Al master-alloy (1273°K, 10 hours, Ar atmosphere).
Figure 82. Rene 80 coated in an AlCl$_3$/NaCl-activated pack containing a 95 Cr-5 w/o Al masteralloy (1273 K, 10 hours, Ar atmosphere)
The positions of Nos. 5, 6, and 7 are marked on the ternary diagram above.

Figure 83. Isothermal section of Ni-Cr-Al phase diagram showing composition marked in the secondary electron image.
Figure 84. Optical micrograph of Rene' 80 sample coated with the General Electric 'Codep' process [70].
Figure 85. Optical micrograph of IN 713 sample coated with the AVCO-LYCOMING coating [70].
β-NiAl layer is higher than in the chromized-aluminized layer (41 a/o). The second phase particles contain 48.7 a/o of Al and 12.7 a/o of Cr. The morphology of this pack is typical of the high Al activity process (see Section 1.1.1). This process, like the codep, depletes the average Cr concentration of the substrate.

Figure 86 is an optical micrograph of the cross-section of a IN 713 coupon coated in a pack containing pure chromium and ammonium chloride as the activator. The coating consists of an α-Cr outer layer containing 89-92 a/o Cr. The microstructure is completely different from the aluminide coating described above.

Figure 87 shows the secondary electron image of an IN 713 substrate coated in an NH₄Cl-activated pack containing a 93 Cr-7 w/o Al masteralloy at 1050° C for 4 hours. The morphology is completely different from those observed in Figs. 82 through 86.

Compositional analysis reveals that the outer two-phase field has a second phase with a composition of 30 - 40 a/o Cr and 17 - 20 a/o Al with the matrix containing 18 Al - 5 a/o Cr γ-phase field) (Fig. 88). The second phase is expected to act as a reservoir of Cr and Al so that depeletion of the Cr and Al content of the matrix in forming an oxide scale can be compensated. This morphology and composition of the outer layer of the coating is therefore expected to be beneficial for low temperature hot corrosion resistance (due to the presence of Cr) and for oxidation and thermal cycling resistance (due to the presence of Al). The absence of a sharp interface between the outer two-phase layer and the internal single-phase layer is also expected to reduce the possibility of spalling of the oxide scale. The inner two-phase layer has a composition in the γ + γ' field.
Figure 86. Optical micrograph of IN 713 sample coated in pure Cr packs [70].
Figure 87. Secondary electron image of cross section through IN 713 substrate coated in NH₄Cl-activated pack containing 93Cr-7 w/o Al masteralloy (1323 K, 4 hours)[70].
<table>
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<th>LOCATION</th>
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<th>Cr</th>
<th>Fe</th>
<th>Co</th>
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</table>

Figure 88. Isothermal section of ternary Ni-Cr-Al phase diagram at 1273°K showing composition of points marked in Figure 87 [70].
Simultaneously chromized-aluminized Rene 80 and IN 600 coupons in packs activated by \( \text{CrCl}_2 \) and containing a 95 Cr- 5 w/o Al masteralloy were evaluated in low temperature hot corrosion environments as described below.

4.6 HOT CORROSION TESTS

Rene 80 and IN 600 were simultaneously chromized-aluminized in a pack containing 95 Cr- 5 w/o Al and a \( \text{CrCl}_2 \) activator for 25 hours. The coated coupons were preheated to 200° C and sprayed with a saturated sodium sulfate solution. The water evaporated, leaving the coupons coated with salt. A salt deposit of 3 \( \text{mg/cm}^2 \) was applied to the coupons in this manner. The coated coupons were exposed to an \( \text{SO}_2/O_2 \) atmosphere at 730° C for different exposure times. Figure 89 shows the uncoated, chromaluminized and codep coated coupons after 16 and 72 hours of hot corrosion attack in at 730° C. The uncoated alloy has been severely attacked and the corrosion product spalled. The corresponding microstructure is shown in Fig. 90.

The simultaneously chromized-aluminized coupons (\( \text{CrCl}_2 \)-activated pack containing 95 Cr - 5 Al masteralloy) did not appear to undergo severe corrosive attack (Figs. 89b and c). The microstructure of the corroded coupons (Figs. 91a and b) indicate that after 16 hours the outer layer of the coating which has a composition in the \( \alpha \)-Cr field is barely penetrated while exposure times of 72 hours resulted in the formation of pits in the outer layer while the coating was completely penetrated in some regions. This is attributed to two factors: non-uniformity of the Cr-Al coating and non-uniformity of applied salt spray. In the first instance, the coating is penetrated at the regions where it is very thin. From Luthra's proposed mechanism of type II hot corrosion, the sodium sulfate forms a eutectic liquid by
Figure 89. Rene' 80 coupons sprayed with Na₂SO₄ and exposed to a SO₂-O₂ atmosphere (0.1% SO₂) at 1003 K.
Figure 90. Optical micrograph of cross section of uncoated Rene 80 coupon corresponding to Figure 89 (a).
Figure 91. Secondary electron micrographs of cross section through chromized-aluminized coupon corresponding to Figures 89 (b) and (c).

(a) Exposed for 16 hours.

(b) Exposed for 72 hours.
Figure 92. Secondary electron micrographs of cross section through 'Codep' coupons corresponding to Figures 89 (d) and (e).
reacting with the $\text{NiSO}_4$ on the substrate surface. Therefore, if locally a large amount of salt was applied, it would attack the substrate immediately beneath it severely before the eutectic liquid covered the substrate completely.

The Codep™ coupon was pitted (Figs. 89c and d). The microstructures of the corroded coupons indicate that after 16 hours the outer layer of the coating which has a composition in the $\beta$-NiAl field ($< 3$ a/o Cr) is pitted (Fig. 92a) while exposure times of 72 hours resulted in penetration of the outer $\beta$-NiAl layer and the inner diffusion zone ($\gamma + \gamma'$).

The uncoated IN 600 underwent severe corrosive attack and the corrosion product spalled (Fig. 93a). The microstructure of the uncoated alloy is shown in Fig. 94. Na and S were detected indicating that some of the corrosion product still adhered to the alloy. The microstructures of the corroded coupons indicate that after 16 hours and 72 hours exposure times, there is no indication of pitting (Figs. 95a and b). Chemical analysis of the corroded substrate indicates that the surface composition is close to the substrate composition. This implies that the coating was probably corroded away even before 16 hours of exposure.
(a) Uncoated coupon exposed for 72 hours.

(b) Coated coupon exposed for 16 hours. [Coated in CrCl$_2$-activated pack containing a 95Cr-5 w/o Al masteralloy (1273°K, 25 hours, Ar atmosphere)].

(c) Coated coupon exposed for 72 hours. [Coated in CrCl$_2$-activated pack containing a 95Cr-5 w/o Al masteralloy (1273°K, 25 hours, Ar atmosphere)].

Figure 93. IN 600 coupons sprayed with Na$_2$SO$_4$ and exposed to a SO$_2$-O$_2$ atmosphere (0.1% SO$_2$) at 1003 K.
Exposed for 72 hours.

Figure 94. Optical micrograph of cross section through uncoated IN 600 coupon sprayed with Na$_2$SO$_4$ and exposed to SO$_2$-O$_2$ atmosphere (0.1% SO$_2$) at 1003°K [cf. Figure 93 (a)].
Figure 95. Optical micrographs of cross sections through simultaneously chromized-aluminized coupons sprayed with Na$_2$SO$_4$ and exposed to SO$_2$-O$_2$ atmosphere (0.1% SO$_2$) at 1003°C [cf. Figure 93 (b) and (c)].
CHAPTER V

SUMMARY AND CONCLUSIONS

GENERAL CONCLUSIONS

1. Simultaneous chromizing-aluminizing of Ni, Ni-20 w/o Cr and Ni-base superalloys is possible in chloride-activated packs with appropriate masteralloys.

2. The chromaluminized alloys show good to reasonable resistance against hot corrosion attack.

SPECIFIC OBSERVATIONS/CONCLUSIONS

1. Thermodynamic evaluation of the equilibrium partial pressures of gases in cementation packs with the SOLGASMIX program reveals that:

   • Comparable partial pressures of Cr and Al halides can be achieved in chloride-activated packs and not in fluoride-activated packs.

   • Unstable chloride activators such as CrCl₂, NH₄Cl and AlCl₃ generate higher partial pressures of the gaseous CrClₓ and AlClₓ species than the stable activators such as NaCl.

   • The partial pressures of gases in CrCl₂- and AlCl₃- activated packs are essentially the same in Ar and H₂ atmospheres. For NaCl-activated packs the
partial pressures of $CrCl_2$, $AlCl_2$ and $AlCl$ are lowered by three, two and one order of magnitude respectively in $H_2$ atmosphere relative to an $Ar$ atmosphere.

- The partial pressure of gases in $NaF$- and $AlF_3$- activated packs are the same in both $Ar$ and $H_2$ atmospheres.

2. Microstructural and compositional analyses of the coatings are summarized below:

- Pure $Ni$ can be simultaneously chromized-aluminized in a $CrCl_2$-activated pack containing a 95 Cr-5 Al masteralloy at 1273 K in a non-rotating pack under an $Ar$ atmosphere. The surface composition of the coated substrate is 40 Cr - 5 Al - 55 a/o Ni.

- $NH_4Cl$ is strongly chromizing with surface compositions of 92 Cr - 6 Al - 2 a/o $Ni$.

- Pure $Ni$ can be simultaneously chromized-aluminized in packs activated by complex activators such as $AlCl_3 / NaCl$ (2/1) (surface composition: 72 Cr - 11 Al - 17 a/o $Ni$) and $AlCl_3 / AlF_3$ (2/1) (surface composition: 36 Cr - 5 Al - 59 a/o $Ni$).

- Pure $Ni$ coated in a $CrCl_2$-activated pack containing a 92½ Cr - 7½ w/o Al masteralloy in an $Ar$ atmosphere for 25 hours has a surface composition of 58 Al - 2 a/o Cr. Therefore, even a small shift in the masteralloy composition has a significant effect on the coating composition.

- $Ni$ - 20 Cr coated in a $CrCl_2$-activated pack containing a 95 Cr - 5 w/o Al masteralloy for sixteen hours at 1273 K in a non-rotating pack under an $Ar$
atmosphere has a surface composition of $95 \text{Cr} - 3 \text{Al}$. A coating with this composition is expected to exhibit excellent resistance to hot corrosion attack.

- $\text{Ni} - 20 \text{Cr}$ coated in a $\text{CrCl}_2$-activated pack containing a $92\% \text{Cr} - 7\% \text{Al}$ masteralloy for 25 hours at 1273 K in a non-rotating pack under an $\text{Ar}$ atmosphere has an outer layer with a composition in the range 58 - 40 a/o Al and 2 - 10 a/o Cr. A coating with this composition is expected to exhibit good resistance to combined oxidation/hot corrosion attack.

- Rene 80 coupons coated in $\text{CrCl}_2$-activated packs containing a $95 \text{Cr} - 5 \text{Al}$ masteralloy for 25 hours develop a surface composition of $82 \text{Cr} - 2 \text{Al}$ which is expected to be resistant to hot corrosion environments.

- Rene 80 coupons coated in $\text{AlCl}_3 / \text{NaCl}$-activated packs containing a $95 \text{Cr} - 5 \text{Al}$ masteralloy for ten hours exhibit two-layer morphology with the outer layer having a composition in the $\beta$-$\text{NiAl}$ field and the inner, two-phase diffusion layer containing a Cr-rich second phase. This morphology is expected to be effective in providing combined oxidation/hot corrosion resistance.

3. A kinetic model for the simultaneous chromizing-aluminizing of $\text{Ni}$ proposes the existence of a depletion zone adjacent to the substrate. The thickness of the depletion zone is in the range 0.1 - 0.8 mm for packs containing different activators and a $95 \text{Cr} - 5 \text{Al}$ masteralloy. The thickness of the depletion zone is 0.5 - 4 % of the size of the pack and therefore the masteralloy is present in great excess. No global depletion therefore occurred.
4. Kinetic data for pure Ni and Ni - 20 Cr substrates coated in packs activated with CrCl$_2$ and containing a 95 Cr - 5 Al masteralloy indicate series diffusion in the pack and in the solid state is rate-limiting. The rate constants were determined to be $1.3 \times 10^{-6} \text{gm}^2\text{cm}^{-4}\text{hr}^{-1}$ for pure Ni and $2.5 \times 10^{-7} \text{gm}^2\text{cm}^{-4}\text{hr}^{-1}$ for Ni - 20 Cr substrates.

5. A finite element code was developed to predict diffusion profiles given the surface compositions and using diffusion data in literature. Excellent agreement between predicted and experimental profiles were obtained for pure Ni coupons coated in CrCl$_2$-activated packs containing a 95 Cr - 5 Al masteralloy.

6. Rene 80 coupons coated in CrCl$_2$-activated packs containing a 95 Cr - 5 Al masteralloy for 25 hours at 1273 K, were sprayed with a thin Na$_2$SO$_4$ salt film and exposed to a 0.1 % SO$_2$ / O$_2$ atmosphere at 730° C for 16 and 72 hours. The coupon exposed for 16 hours showed very little salt penetration while that exposed for 72 hours was penetrated at some points. Rene 80 coupons coated with General Electric's Codep™ process exhibited a pitted morphology (16-hour exposure). The coating was completely penetrated at the end of the 72-hour exposure. Uncoated Rene 80 was severely attacked and the corrosion product spalled.

7. IN 600 coupons coated in CrCl$_2$-activated packs containing a 95 Cr - 5 Al masteralloy for 25 hours at 1273 K were sprayed with a thin Na$_2$SO$_4$ salt film and exposed to a 0.1 % SO$_2$ / O$_2$ atmosphere at 730° C for 16 and 72 hours. The coating was completely penetrated even at 16 hours.
CHAPTER VI

FUTURE WORK

Suggestions for areas of future research are proposed below.

1. Extensive evaluation of the coated coupons is required under cyclic oxidation and hot corrosion conditions to verify the effectiveness of the coatings. Cyclic oxidation tests on coated Ni-base superalloy coupons are currently being carried out at the NASA Lewis Research Center, Cleveland, OH. Burner rig tests to evaluate the performance of coated Ni-base superalloy coupons in simulated gas turbine environments will be carried out at the General Electric Co., Evendale, OH.

2. Incorporation of reactive elements such as Y, Hf and Zr into the coating is expected to improve oxide scale adhesion and enhance cyclic oxidation resistance. A one-step coating procedure for the simultaneous incorporation of Y, Hf or Zr along with Cr and Al into the coating is therefore being developed.

3. Structural characterization of the simultaneously chromized-aluminized coupons via transmission electron microscopy would be useful in developing detailed mechanisms for the coating process.

4. Activators such as bromides and iodides tend to be strongly chromizing and therefore a reduction of Cr content of the masteralloy to achieve codeposition is possible. The use of these activators should be further investigated.
5. The effect of temperature, particularly an increase of coating temperatures, would be important in establishing the optimum temperature for achieving desired coating thickness.

6. Alternative coating systems such as Cr-Si and Al-Si would be very important to the coating process industry and one-step coating procedures to incorporate these elements simultaneously can be developed based on the principles described in this work.
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