New Methods to Deposit Nickel-Aluminide Alloys as High Temperature Protective Coatings on Stainless Steels

by

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Abstract

Nickel-Aluminide intermetallic alloys have drawn attention because of their interesting properties. They have long been used as coating materials for industrial and structural applications, where their functions have been to increase the lifetime of parts at high-temperature applications by enhancing not only mechanical properties such as high temperature tensile and compressive yield strength, high-temperature wear resistance, and fatigue resistance, but also by enhancing oxidation, and carburization resistance of parts at high temperature. Nickel aluminide coatings have been used extensively in gas turbines, turbocharger components, valves, and piston head of internal combustion engines, jet engines, furnaces and furnace assembly, and forging dies.

The present research focuses on developing novel methods to deposit nickel-aluminide intermetallic coatings on RA330 stainless steel. The basic aim has been to study the formation of different Ni-Al intermetallic coatings via several methods. These methods were identified to provide processes to coat complex geometries and develop the nickel aluminides. The thickness of the diffusion layers and intermetallics were controlled by post-diffusion treatment. All the coatings were characterized for their phase fractions, morphology, composition, microstructure, and adhesion to the substrate using XRD, SEM, EDS, EBSD, and optical microscopy and all methods were proven to be successful to develop one or more Ni$_3$Al and NiAl phases.
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Chapter 1 : Introduction

In this dissertation, stainless steel RA330 was selected for two purposes: 1) evaluate their performance under industrial cyclic carburization for times up to two years. 2) design several surface treatment methods to increase the lifetime of RA330 stainless steel under cyclic carburization.

The microstructural development of alloys during the prolong exposure in cyclic carburizing, surface treatments, and post-diffusion heat treatment will be presented and discussed.

1.1. Challenges in high temperature applications

High temperature alloys were widely used in many applications such as aerospace turbine blades, exhaust valves, heat exchangers, high temperature anti-corrosion applications, and fixture inside the high temperature furnace that are supporting the products. Many of the fixtures are consumed within 1 to 2 years of exposure in high temperature carburizing/oxidizing environments. According to IHEA, the sheer volume of the heat-treating industry is in the range of $65 to $75 billion-with the sale of heat treatment equipment alone being between $4.375 and $5.5 billion. The reliability and durability of these furnaces depend on the quality of their metallic components, usually made from austenitic heat resistant alloys. Iron-nickel based, and Iron-Nickel-Chromium based alloys are experiencing a variety of degradation mechanisms in these applications. As a result of the usage, furnace equipment undergoes fast carburization and thermal fatigue. These processes do not only impair the oxidation resistance, but also have a detrimental effect on rupture strength and cause declines in the values of expansion coefficient and conductivity that superimpose additional tensile stress on elements. This leads to premature cracking and as a consequence the life of the elements is profoundly reduced. For iron-based alloys, the primary reason for failure was the excessive carburization that leads to “metal dusting” and subsequent cracking. Therefore, the
industry was in need of alloys that have long service life. Developing technologies that can enhance the service life of the parts and fixtures at high temperature applications are valuable for commercial perspectives.

1.2. Objectives

The coatings that have shown the best protection against metal dusting and carburization are those based on ordered NiAl intermetallic alloys with BCB_B2 crystal structure, that behave as an Al source in order to develop protective Al<sub>2</sub>O<sub>3</sub>. In general, coatings must be dense and free of cracks and porosity. Aluminide diffusion coatings do not have adhesion problems and fulfil these criteria at a rather low cost. There are many commercial techniques employed today to aluminize the alloys to develop protective Al<sub>2</sub>O<sub>3</sub> scale such as pack-Aluminizing [1-4], Chemical vapor deposition (CVD) [5, 6], physical vapor deposition (PVD) [7], plasma transferred arc (PTA) [8, 9], high-velocity oxygen fuel (HVOF) [10-12], and Reactive spraying [13]. However, not all the aluminizing methods lead to formation of NiAl phase.

Current research focuses on developing alternative methods to deposit Ni-Al intermetallic on surface of RA330 stainless steel which are easier to control, and less expensive, and more suitable for parts with complex geometries. Ni-Al coatings in this work were prepared using several processes including pack aluminizing, electrophoresis, hot-dipping and several post-diffusion heat treatments.

1.3. References

Chapter 2 : Background

2.1. Background outline

- Metal dusting
  - Metal dusting mechanism
  - Carburizing of furnace alloys
  - Oxidation and breakdown of protective oxide in carbides
- Current Industrial methods to extend the service time
- Aluminizing

2.2. Metal Dusting

Metal dusting is a kind of corrosion phenomenon resulting from carbonaceous reaction. Natural gas such as methane (CH$_4$) will be reformed at the temperature of 1000°C or higher and partially oxidized to carbon dioxide, hydrogen and carbon monoxide gases and water, which constitute the synthesis gas environment. In the case of chromium steels and Ni-based alloys the corrosion product (coke) may also contain carbides and oxides. Then corrosion occurs when the temperature goes down to the range of 950°C to 350°C in carburizing atmospheres, containing CO and/or hydrocarbons, at carbon activities $a_C>1$ which means that the tendency for formation of graphite increases.

Iron, Nickel, Cobalt and other metals and alloys which dissolve carbon are sensitive to metal dusting corrosion. The carbon is diffuse into the metal surface from the atmosphere and dissolve in it. At carbon activity of greater than 1 ($a_C>1$) to oversaturation, the dissolution of the carbon in metal leading to growth of graphite which destroys the materials. In the case of iron and steels, MD leads to formation of cementite as an intermediate into which the graphite grows [1-6].
However, in the case of nickel and nickel-based alloys it causes the formation and direct inward growth of graphite [1, 4, 6-9]. For chromia-forming steels metal dusting starts locally, where the oxide scale fails, and leads to pitting and hole formation [3, 4, 9-11]. For Chromium and chromium-nickel steels, carburizing leads to formation of a carburized zone where internal carbides $\text{M}_{23}\text{C}_6$ and $\text{M}_7\text{C}_3$ precipitate before metal dusting starts.

Metal dusting occurs in carburizing atmospheres, mostly at intermediate temperatures 400-700°C. However, at high carbon activity ($a_C>1$) it is possible at any temperature (in equilibrium with graphite $a_C=1$) [4, 7, 8]. This type of corrosion would cause damage in the form of pits, notches, and cracks in metallic equipment leading to shortening the service time, high-cost maintenance, and serious safety issues. Many heat treatment industries reported that metal dusting corrosion causes expensive failures and damages of fixture parts, including racking poles, mash belt, fan blade etc. These failures were either catastrophic that leaded to the breakdown of the furnace or less catastrophic that caused a severe loss of materials, which required many repairs and replacements of various parts of the units [6].

In general, degradation due to metal dusting involves two steps, namely, the incubation period and the propagation. The incubation period is determined by the carbon activity in the gas phase, alloy chemistry, system pressure, and probably the exposure temperature. For the same exposure conditions, the incubation period for the onset of metal dusting is significantly greater for the Ni-base alloys when compared with that for Fe-base alloys.

2.3. **Thermodynamics of metal dusting**

Tendency to form graphite results in metal dusting phenomenon. At equilibrium with graphite ($a_C=1$), the Gibbs free energy of the process is equal to zero. Reduction of carbon monoxide and the Boudouard reaction (2) are the main carbon transfer reaction:
$$\Delta G = -RT \ln ac$$

\[
\begin{align*}
\text{CO} + \text{H}_2 & \leftrightarrow \text{H}_2\text{O} + \text{C} & (a_c)_1 &= K_1 \frac{P_{\text{CO} \cdot \text{H}_2}}{P_{\text{H}_2 \text{O}}} \log K_1 = \frac{7100}{T} - 7.496 & \text{Equation 1} \\
2\text{CO} & \leftrightarrow \text{CO}_2 + \text{C} & (a_c)_2 &= K_2 \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}} \log K_2 = \frac{8817}{T} - 9.071 & \text{Equation 2}
\end{align*}
\]

Activity of the carbon in these reactions is a function of temperature and the partial pressures of gas mixtures. When carbon activity is less than 1, formation of the graphite is not favorable thermodynamically. However, conversion and oxidation of gas is obtained at high temperatures which is not in equilibrium in the critical temperature range for metal dusting. For a non-equilibrium atmosphere, the values \((a_c)_1\) and \((a_c)_2\) are different. Under metal dusting condition it has been observed that according to reaction (2) \(a_c<1\), however, according to reaction (1) \(a_c>1\).

The kinetics of CO reduction reaction on metal free surface is faster than Boudouard reaction, therefore, effective carbon activity is value is closer to \((a_c)_1\) [12].

Also, severe metal dusting cases has been observed in mixture of natural gas (and other hydrocarbons). In such cases, high carbon activities may result from the reaction 3:

\[
\begin{align*}
\text{C}_x\text{H}_y & \leftrightarrow \frac{y}{2} \text{H}_2 + x\text{C} & a_c = \left(\frac{P_{\text{C}_x\text{H}_y}}{P_{\text{H}_2}^yK_3}\right) & \text{Equation 3}
\end{align*}
\]

There is a strong driving force for formation of graphite if carbon activity in all three reactions ((1), (2) or (3)) is greater than 1 \((a_c>>1)\). The carbon from the gas molecules should react to graphite and in fact that is the overall reaction which occurs in metal dusting and destroys the materials.

Another reaction to be considered is the oxidation of hydrocarbons:

\[
\begin{align*}
\text{C}_x\text{H}_y + x\text{H}_2\text{O} & \leftrightarrow x\text{CO} + \left(\frac{y}{2} + x\right)\text{H}_2 & \text{Equation 4}
\end{align*}
\]

by which the synthesis and reduction gas is produced. This reaction needs catalytic acceleration and is performed generally on Ni catalysts at temperatures > 700 °C. Its back reaction, the methanation of CO, may occur when metal dusting has produced fine metal particles, catalyzing
the methanation already at rather low temperatures. The methane formation can indicate the occurrence of metal dusting.

In addition to carbon activity, partial pressure of oxygen is also one of the most important factors in metal dusting and formation of oxides. The following reactions take place on catalytically active surfaces, such as metal free surfaces, at the temperature range of 350-900 °C by reaction steps of water-gas shift reaction which is non-equilibrium in process and reduction gases:

\[ \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{O}_2 \]  
Equation 5

\[ \text{O}_2 + \text{CO} \leftrightarrow \text{CO}_2 \]  
Equation 6

\[ \text{H}_2\text{O} + \text{CO} \leftrightarrow \text{CO}_2 + \text{H}_2 \]  
Equation 7

The schematic reactions in a CO–H\(_2\)–H\(_2\)O–CO\(_2\)–CH\(_4\) gas mixture can be illustrated by the schematic Figure 1.

![Schematic Figure 1](image)

Figure 1. Schematic representation of the partial surface reactions in carburization and metal dusting in a CO–H\(_2\)–H\(_2\)O–CO\(_2\)–CH\(_4\) gas mixture [5]

### 2.4. Carburizing of furnace alloys

Industrial reports have indicated that carburization and metal dusting are major failure mechanisms of high temperature corrosion caused by carbon transfer into metals and alloys. For Fe-Ni-Cr alloys high temperature carburization (T>800 °C) in carbonaceous atmospheres promotes formation of internal carbides and carbon enrichment. The carburization rate is determined by the presence of protective oxide scales, and the nickel and silicon content of the matrix, and carbon activity of the gas. The activity of carbon in gas in this process is less than unity, whereas its value is greater than unity for metal dusting process [3, 13]. In latter case, high carbon activity of the gas escalates the
tendency of graphite formation ($a_C = 1$) which leads to disintegration of the alloys and parts, either via formation of intermediate carbides (such as cementite) as in the case of low-alloy ferrous alloys or by direct inward growth of graphite as in the case of nickel alloys [6]. During carburization of Fe-Ni-Cr alloys at high temperature, carbon in atmosphere diffuses into the catalytic active surface and diffuses inward in metal matrix which causes precipitation of the metal carbides $M_{23}C_6$ and $M_7C_3$ ($M=Cr$, Ni, Fe). By more diffusion of carbon into the metal matrix and increasing the carbon content, $M_{23}C_6$ carbides transform into $M_7C_3$ carbides with higher carbon content and causing the formation of a two-zone diffusion layer with different precipitated carbides [8].

The carburization deteriorates the ductility and toughness by formation of carbides which increase the internal stresses due to thermal expansion coefficient and volume difference with matrix [8]. Therefore, during carburization, formation of cracks starts in the inner wall of tubes, see Figure 2, and propagate faster during the cooldown of the furnace leading to failure. The common alloys for carburization furnace and fixtures are HK40, HP40, Inconel 625, Alloy800, RA330, etc. with 17-25% Cr and 20-35% Ni at high temperatures form an outer spinel layer (Fe, Mn) $Cr_2O_4$ and an inner $Cr_2O_3$ layer. The carbon permeation through grown $Cr_2O_3$ layers is extremely slow because the solubility of C in such oxides is almost zero. The permeation occurs by diffusion of carbon-bearing molecules, though pores, channels of cracks of the oxide layer, thus carburization is negligible in the temperature range 800-1000°C, if an adherent, continues oxide scale had formed on the alloy.

2.5. Oxidation and breakaway of protective oxide in stainless steels

The most practical oxidation model is the Wagner oxidation model. In this model the rate of oxide layer formation is controlled by the outward diffusion of metallic ions and inward diffusion of oxygen ions in the oxide layer [14]. Figure 2 shows the illustration of the
oxidation rate dependency on diffusion of metallic and oxygen ions. Based on this model, the thickness of the oxide layer ($\Delta x$) can be estimated by determining the oxidation time ($\Delta t$) using equation (8).

$$\Delta x = K_p \sqrt{\Delta t}$$

Equation 8

![Diagram](image)

Figure 2. Wagner model for diffusion-controlled oxidation [15].

The oxidation phenomenon is a common but one of the most important issue when dealing with corrosion of alloys. Based on Nicholls and Hancock, a protective oxide layer should satisfy following requirements [16]:

- Thermodynamically stability of protective surface scale with uniform thickness
- Slow growth rate of protective surface scale
- Adherent surface scale
- High concentration of scale former

The metals and alloys will tend to be oxidized when exposed to air or environments containing oxygen. The oxygen partial pressure of the atmosphere and temperature determine the type of oxide layer grown on the surface of metal [17]. For high-temperature applications (T>600 °C), Cr$_2$O$_3$ and Al$_2$O$_3$ are the principal oxides used for the protection of metallic alloys [17].
However, at high temperature or long exposure time determining the durability of heat resistant alloys is problematic. The selective consumption of chromium protects all stainless steels from rapid oxidation by formation of a protective chromia scale. Chromia, $\text{Cr}_2\text{O}_3$, possess all required criteria for protective scales including slow growth rate. Chromia is a barrier against further oxidation owing to its very low diffusion coefficients for oxygen and metals, and then offer a high oxidation resistance [18]. Numerous investigations have reported that at high temperatures or after long-term exposures, the diffusion layer is a two-layer oxide scale composed of a dense and adherent inner sub-layer of $\text{Cr}_2\text{O}_3$ and an outer sub-layer of spinel type oxide $\text{MCr}_2\text{O}_4$ [19-22]. The formation of protective Cr-rich oxide scale, $\text{Cr}_2\text{O}_3$, depends on the chromium concentration at the alloy/oxide interface and also on the chromium diffusion coefficient in the metallic substrate from the core towards the interface. According to Evans et al. experiments, to form a protective layer for a Fe–20Cr–25Ni steel in the temperature range of 750 to 900 °C about 16 wt.% Cr is required at the alloy/scale interface [23]. However, the steel grain size [19, 23-28], the silicon content in the alloy [27, 29, 30] and the surrounding atmosphere [31] influence the Cr critical value for a given temperature. Decreasing the alloy grain size allows a quicker formation of a continuous chromia layer due to a faster effective diffusion of Cr in the alloy and to a smaller lateral growth distance required to form a continuous layer. Presence of silicon in the nominal composition of the steel induces the formation of silica at the alloy/oxide interface that acts as an additional diffusion barrier.

In water vapor [19–22] or carbon dioxide [32] containing atmospheres, the growth of chromia scale causes a greater depletion of Cr in the subsurface zone. The subsequent loss of chromium tends to convert the protective Cr-rich oxide, initially formed, into a poorly protective Fe-rich fast-growing oxide or spinel [33, 34]. Moreover, part of Cr can be either trapped in $\text{M}_{23}\text{C}_6$ or $\text{M}_7\text{C}_3$
carbides in carburizing atmospheres [35], or lost through \( \text{Cr}_2\text{O}_3 \) volatilization in gaseous \( \text{CrO}_2\text{(OH)}_2 \) (g) in water vapor containing atmospheres [36]. According to Huntz et al., for austenitic stainless steels, 18 wt.% of Cr is not sufficient to sustain the formation of chromia when temperature (or time) increases because lattice diffusion coefficients in face-centered cubic crystal structure (fcc-austenite) are smaller than the one in body-centered cubic crystal structure of ferritic stainless steel (bcc-ferrite) [20]. At high temperature (>850°C) in high oxygen partial pressure (\( \text{O}_2 \) or air), even if a thin chromia scale forms in the early stage of oxidation, the chromium concentration and diffusivity cannot feed the further growth of \( \text{Cr}_2\text{O}_3 \). Then, the nodular growth of iron oxides (spinel-like phase and hematite) takes place which induces a sudden increase of the oxidation rate. The phenomenon is usually called “breakaway oxidation”.

In various experimental conditions, breakaway oxidation of austenitic stainless steels gives rise to the inward growth of a complex oxide composed of a (Ni, Fe)-rich phase and of a spinel type oxide: in carburizing atmospheres [32, 37-39], in water vapor containing atmospheres [40-42] and in air at higher temperature [21]. In all cases, depletion of chromium in the subsurface alloy zone is the key factor leading to break-away oxidation. Depending on the experimental conditions, Ni-rich phase trapped in \( \text{FeCr}_2\text{O}_4 \) spinel oxide may be metallic or oxidized: (Ni, Fe, Cr)\(_3\text{O}_4 \) spinel oxide [33, 34], \( \text{FeNi}_3 \)[39], Ni–Fe solid solution [21, 40, 43, 44]. Some authors also report formation of a Cr-rich oxide layer at the interface with the substrate which can be \( \text{Cr}_2\text{O}_3 \)[38, 45] or \( \text{FeCr}_2\text{O}_4 \)[33, 44].

2.6. Current Industrial methods to extend the service time

The key to suppressing metal dusting is to stop the dissociation of the carbon source or subsequent carbon diffusion into the susceptible materials. There are several methods to succeed this purpose:
modifying the process conditions, surface poisoning, alloying, chemical, mechanical and laser treatments as well as diffusion coatings. Each method has advantages and drawbacks. Changes of process conditions are not an option due to the process requirements in most cases and the use of poisoning chemicals is still limited due to its interference with downstream processes. Newly developed alloys are sometimes not sufficiently resistant and expensive due to the large quantities involved. Mechanical and chemical surface treatments are not always applicable, and the lifetime of coatings is often limited by adhesion problems. There is thus a need to develop all these methods to challenge the metal dusting limits.

The protection for both Ni and Fe based alloys against MD by surface modification can be achieved in two ways. Firstly, the growth of a protective oxide (Cr₂O₃ or Al₂O₃) is enhanced. Secondly, the CO dissociation is minimized by specific metals present in high enough concentration, such as Cu (20 wt%), Sn and possibly Pt and Ag. Surface mechanical and laser treatments improve metal dusting resistance by increasing the rate of formation of the protective oxide by creating fast diffusion paths. Chemical treatments enhance the oxidation of the substrate surface, and thereby create a protective scale prior to exposure to the MD atmosphere.

Using coatings can provide many advantages: (1) no modification of processing conditions is required, (2) the surface treatment alternatives may not work for long exposures and are not applicable to all type of components, (3) existing alloys with good mechanical properties can be used and therefore the existing component manufacturing processes do not require modifications, (4) may allow the deposition of any suitable coating composition independently from those of the substrates and (5) can be repaired/reapplied in many cases. The various coating materials and deposition techniques that have been explored for this application, have advantages and disadvantages, and a number of factors must be taken into consideration when selecting the most
appropriate coating and deposition method for a specific component. Some of these factors are coating type and composition, substrate material, component size/weight and geometry, coating temperature, capacity for coating “in situ” and cost among others. The coatings that have shown the best performance are those based on NiAl intermetallics, that behave as an Al source in order to develop protective Al$_2$O$_3$. In general, coatings must be dense and free of cracks and porosity. Aluminide diffusion coatings do not have adhesion problems and fulfil these criteria at a rather low cost. On the other hand, this type of coatings degrades by coating substrate interdiffusion, which results in a reduction of the subscale Al content and therefore the coating lifetime will be decreased. The best alternatives for this type of coatings so far seem to be diffusion aluminides with some Cr, which helps to retard Al loss by inwards diffusion.

As already demonstrated with gas and aeronautic turbines, the use of coatings offer significant advantages for all industries in which metal dusting is an issue. Energy, as well as cost savings are directly and indirectly ensured: less expensive base materials can be used, the lifetime of components is significantly increased, less production interruptions due to component replacement can be achieved, among others.

There are various industrial coating processes being used to provide the surface protection. Based on the designed shape and application of the components, the coating processes will be selected. For instance, carburization resistant coatings may not be suitable for hot corrosion protection. Diffusion coatings are one the most commercial methods to protect the surface from corrosion and diffusion of interstitial elements such as carbon, oxygen, and sulfur. The most common constituent elements for diffusion coatings and their influences are given in Table 1 [46]. By controlling chemical composition, microstructure, and selection of manufacturing process, we can design a
coating that is tailored for specific applications. Table 2. lists some of the processes with typical coating thickness achieved.

Table 1. Elemental constituents of metallic coatings, their functions, and effects [46]

<table>
<thead>
<tr>
<th>Elemental Constituent</th>
<th>Beneficial Aspects</th>
<th>Detrimental Aspects</th>
</tr>
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<tr>
<td>Ni</td>
<td>Major constituent of substrate alloy. Provides strength.</td>
<td>Prone to destructive interaction with sulfur.</td>
</tr>
<tr>
<td>Co</td>
<td>Major constituent of substrate alloy. Provides microstructural stability and strength.</td>
<td>Prone to destructive interaction with sulfur.</td>
</tr>
<tr>
<td>Al</td>
<td>Constituent of substrate alloy. Major contributor to providing strength. Contributes to oxidation resistance.</td>
<td>Large concentration lowers melting point.</td>
</tr>
<tr>
<td>Ta</td>
<td>Enhances hot corrosion and oxidation resistance. Improves strength.</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>Enhances oxidation and type II hot corrosion resistance.</td>
<td>Large concentration leads to formation of brittle phases.</td>
</tr>
<tr>
<td>Hf, Y, Y2O3 oxides of other reactive elements</td>
<td>Improves adherence of alumina and chromia scales.</td>
<td>Large amounts are detrimental.</td>
</tr>
<tr>
<td>Pt</td>
<td>Improves oxidation and hot corrosion resistance.</td>
<td></td>
</tr>
</tbody>
</table>

2.7. Aluminizing

Aluminizing is one of the most common methods to protect the surface via combination of formation of protective surface scale and diffusion coatings and has been widely used in aerospace industry for decades and is well known as one of the best coating because of its excellent anti-corrosion properties. Aluminizing is aluminum metal diffuses into the alloy to increases the aluminum concentration at the part-surface. Typically, NiAl is formed. When the aluminized alloy is exposed to an oxidizing environmental high temperature environment, Al2O3 forms at the surface. This oxidation product is dense with low diffusivity and act to protect the alloy from oxidation. In addition, the Al2O3 oxidation products also produce an excellent barrier to carbon
absorption (i.e. carburization). Alumina was carried out at 1000°C to produce NiAl intermetallic compound, which acts as a reservoir of aluminum during high-temperature oxidation so that a protective layer of alumina is maintained on the surface of the component. The alumina provides good anti-corrosion properties because of its low solubility of carbon.

Aluminide coatings rely on the formation of FeAl and NiAl with B2 crystal structure on the surface of the component alloys. The major processes (Table 2. common aluminizing process and their parameters), by which the aluminide can be formed are:

- Metal spraying
- Cementation (Pack Aluminizing)
- Hot-Dipping
- Cladding
- Electrodeposition
- Vapor deposition

The aluminizing process effects on the microstructure and mechanical properties of the diffusion coatings which determine the mechanical properties of the coatings.

<table>
<thead>
<tr>
<th>Process</th>
<th>Temperature (°C)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cementation (Calorising)</td>
<td>850-950</td>
<td>25-1,000</td>
</tr>
<tr>
<td>Cladding</td>
<td>200-530</td>
<td>5-10% of the substrate</td>
</tr>
<tr>
<td>Hot dipping</td>
<td>700-750</td>
<td>10-75</td>
</tr>
<tr>
<td>Metal spray</td>
<td>Room temperature</td>
<td>50-500</td>
</tr>
</tbody>
</table>

2.8. References


Chapter 3: Experimental plan and Procedures

1.1 3.1. Experimental procedures

3.1.1. Selected alloy

RA330 is well known as the corrosion-resistant alloy offering an exceptional combination of strength and resistance to carburization, oxidation, and thermal shock. RA330 finds wide application in high temperature industrial environments where good resistance to the combined effects of carburization and thermal cycling is prime requisite. The chemical composition of RA330 samples is shown in table 1.

<table>
<thead>
<tr>
<th>wt.%</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Si</th>
<th>Cu</th>
<th>P</th>
<th>S</th>
<th>C</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>18.0</td>
<td>34.0</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
<td>Balance</td>
</tr>
<tr>
<td>MAX</td>
<td>20.0</td>
<td>37.0</td>
<td>2.0</td>
<td>1.5</td>
<td>1.0</td>
<td>0.03</td>
<td>0.03</td>
<td>0.08</td>
<td>Balance</td>
</tr>
</tbody>
</table>

All processes and aluminizing methods used in this work and their post heat-treatment processing have been given in table 2.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Post Processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclic Carburizing</td>
<td>12 months cyclic carburizing in an industrial carburizing furnace at 900 °C</td>
</tr>
<tr>
<td>Pack aluminizing</td>
<td>6 months and 24 months cyclic carburizing in an industrial carburizing furnace at 900 °C</td>
</tr>
<tr>
<td>Aluminum hot-dipping</td>
<td>36 hours post heat-treatment at 900 °C</td>
</tr>
<tr>
<td>Electrophoresis of Ni-Al composite</td>
<td>36 ours post heat-treatment at 900 °C</td>
</tr>
</tbody>
</table>

3.1.2. Cyclic carburization

Carburization processes were performed on normalized RA330 stainless steel and as-aluminized RA330 stainless steel. Austenitic stainless steel RA330 specimens, investigated in the present study, were cut out to rods with 0.5 in diameter and 5 in length.

RA330 stainless steel rod samples with 15 mm diameter and 150 mm length were aluminized using pack-aluminizing process at Bodycote Michigan site. The pack-aluminizing process was carried out in an industrial furnace in a static gas phase system at 1090 °C for 5 hours. Chromium
aluminum source material (70%Cr/30%Al) and ammonium fluoride granules were used in the system. The coating chamber was purged with argon to a dew point of -40 F or less was achieved, then the argon is shut off to the coating chamber (hence static system) and heating began.

To investigate the phase transformation and microstructure analysis of the reaction layer, the sample was cut, ground and polished perpendicular to the contact plane using standard metallographic methods.

Unaluminized and As-aluminized RA330 samples were welded to a holder basket and placed in carburizing furnace. One Unaluminized and two as-aluminized samples exposed to the cyclic carburizing environment for 12, 6 and 24 months respectively and experienced all steps of carburizing processes including quenching.

All exposed aluminized samples were cut, and mounted, and metallographic cross-sections were prepared by grinding and polishing to a 1 µm finish perpendicular to the contact plane to study the reaction layers. Then cleaned ultrasonically in a bath of ethanol and acetone and prepared for microstructure analysis.

3.1.3. Hot-Dip aluminizing

Six samples were cut, drilled, and ground using SiC grinding paper with 120, 320, and 600 grit then were cleaned by acetone, methanol, and DI water. All samples were weighed before and after dipping in aluminum. Ten samples were drilled and hung by a steel wire. Five samples were dipped in pure molten aluminum (99.9%) at 700 °C for 10 minutes and the other five samples were dipped in Al-20%Ni molten alloy at 720 °C for 10 minutes. To keep the temperature variation less than ±3 degree, the temperature of the molten aluminum was measured every two minutes. For determining the chemical composition of the molten metal bath before and after the dipping, two samples were prepared by casting a small amount of molten aluminum before and after the
hot dipping. These cast samples were water cooled and their chemical compositions were measured by OES.

The dipping process was also repeated for nickel plated samples in fresh new molten metal baths. Five pre-plated sample were dipped in pure aluminum and the other five were dipped in Al-20%Ni molten alloy. One sample from each experiment was collected as reference. All dipped samples were cleaned by acetone and ethanol prior to further characterization.

The weight of each sample has been measured by high accuracy electronic scales. Each sample was measured before and after every dipping process. Before each measurement, samples were cleaned in ultra-sonic machine by ethanol. The typical error range is within ±0.005g. Weight change was the combination inward diffusion of aluminum into the sample which leads to formation of a very thin diffusion layer and aluminum layer at the samples and outward diffusion of alloying elements such as Ni, Fe, and Cr into the molten metal. However, the thickness of the aluminum layer on surface of the samples and therefore the final weight of the sample was very sensitive to the angle and speed of the sample removal from the bath. Therefore, obtaining a
conclusive weight change analysis was problematic and not very comprehensive for this method of aluminizing.

3.1.4. **Co-deposition of nickel-aluminum composite (Electrophoresis)**

RA330 stainless steel substrates (cathodes) approximately 50x10x6 mm size were used as a plated area. Ni-Al composites were prepared by electrodeposition from nickel sulfamate bath. The bath composition is based on that of Guglielmi [1] and is similar to other commercial sulfamate baths. R-round nickels were used as the anode. Spherical aluminum particles of 50, 100, and 300 g/l with a mean diameter of 1 µm were added to the bath in order to form Ni-Al composite. Fig 1. Shows the feature of the as received Al particles viewed and analyzed using SEM and EDS. The process was carried out at 40, 50, and 60 °C and applied current densities were 1, 2, 5 and 8 A/dm². The PH of the solution was 3.8 and the stirring rates were 100, 150, and 200 rpm. After electrophoresis process, all the coatings were ultrasonically cleaned with DI water, and then dried for further characterization. Figure 3 Demonstrate the electrophoresis setup.

![Figure 3 Electrophoresis setup](image)

3.1.5. **Post Heat treatment Process**

Aluminum dipped samples were cleaned by acetone and ethanol, and then they were heat treated at 800 °C for 12, 24, and 36 hours. Al-Ni dipped, pre-plated samples, and electrophoresed samples
were heat treated at 800 °C for 24 hours. Furnace was heated up to before the samples were placed in. After heat-treating the samples, they were air-cooled. The system can be considered as semi-infinite diffusional system. The problem is to determine the distribution of the diffusivity substance at any time after the start of the experiment. The second Fick’s law can be solved by similarity variable technique, which converts the partial differential equation to ordinary differential equation.

3.2. Characterization Techniques

3.2.1. X-ray Diffraction (XRD)

Crystallography and phase analysis were conducted on a PANanalytical Empyrean 2 X-ray diffractometer (XRD) with Cu-Ka radiation at 45keV and 40mA. The phase percentage was also analyzed by Rietveld refinement technique. However, XRD analysis was only carried out for aluminum hot dipped and as-electrophoresed samples since most of the phases we are looking for in the samples are NiAl, FeAl, (Fe,Ni)Al, and (Fe, Ni)(Cr, Al) which the position of the identifying peaks are the same. Therefore, XRD analysis was not conclusive for phase identification and EBSD analysis coupled with EDS was used for identifying the phases.

3.2.2. Optical emission spectroscopy (OES)

Spectro optical emission spectroscopy (OES) analyzer was used to quantitatively measure the chemical composition of the RA330 stainless steel samples. The composition of the alloy was verified by OES.
3.2.3. **Optical microscopy**

Nikon optical microscope was used for measuring the thickness of the diffusion layers and characterization of microstructure. High temperature structural alloys have very high corrosion resistance. Therefore, electro-etching was used for sample preparations of RA330 samples. For this purpose, electro-etching was carried out in 10% oxalic acid for 30 seconds at 6Volt.

3.2.4. **Scanning electron microscopy (SEM)**

Secondary electron photomicrographs were obtained from all samples for high magnification characterization of microstructure using a JEOL-7000F scanning electron microscopy (SEM).

3.2.5. **Energy-dispersive X-ray spectroscopy (EDS)**

EDS point, line, and map analysis were used for chemical analysis of the samples at different location. EDS mapping was used to assist microstructure analysis and phase identification of the diffusion layers of the samples by EBSD.

3.2.6. **Electron backscatter diffraction analysis (EBSD)**

EBSD analysis was widely used for obtaining structural information about materials such as phases and orientations. In this study, EBSD technology has been used for phase identification and study the microstructural developments such as interface movement, phase transformation, precipitation, and carbon up take.

The structure and texture were studied using electron backscatter diffraction (EBSD) technique. samples were cut by low-speed saw and followed by mounting process to be prepared for EBSD analysis. Prepared samples were grinded from 200 grit to 1200 grit. Samples were polished by 1 micrometer alumina polishing powder then 0.3 micrometer, and at end they were polished by 0.05 micrometer alumina polishing powder. The last step for samples preparation is vibration polishing; Samples have been polished for 12 hours before EBSD investigation. In this study, EBSD coupled
with EDS was used as the major technique for characterizing, microstructure analysis, and phase identification.

3.3. References

Chapter 4: Case Study

4.1. Microstructure evaluation of RA330 stainless steel after 12 months cyclic carburization

4.1.1. Abstract

The high temperature corrosion resistant alloy RA330 is widely used for furnace fixtures in heat treatment furnaces. The present article is dedicated to study the anti-carburizing and anti-oxidation properties of RA330 and the microstructural characterization of the diffusion zone of RA330 austenitic stainless steels, subjected to a cyclic carburizing process and a subsequent quenching after each cycle for 12 months. The carburizing treatment forms chromium oxide layer at the metal-gas interface. However, thermal formation of chromium-carbides and graphite layer compromise the sustention of the protective oxide layer. The purpose of this paper is to explore the microstructural evaluation and phase transformations in RA330 stainless steel after 12 months cyclic carburization in an industrial carburization furnace at 920° C was investigated. Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and Electron Backscatter Diffraction (EBSD) were applied to characterize the different layers of the diffusion zone. The thermodynamic predictions of stable phases were in agreement with the experimental results. Although the chromium expected to protect the surface by formation of chromium oxide, however the concentration of chromium was insufficient to sustain the continuous protective chromia, hence formation of the FeCr$_2$O$_4$ spinel type oxide, Cr$_7$C$_3$ and Cr$_{23}$C$_6$ carbides occurred.
4.1.2. Introduction

High nickel and chromium alloys have been commonly used as heat-treatment furnace materials and fixtures that have a long service life and reduced heat capacity [2-7]. However, the use of high nickel content alloys for long periods of time at temperatures above 800 °C requires the application of protective coatings to prevent surface degradation phenomena such as metal dusting, oxidation, carburization, sulfidation, and hot corrosion [6-10].

Carburization and metal dusting are two types of corrosion often occurring on austenitic Fe-Ni-Cr alloys in carburizing atmospheres at high temperature. The mechanisms of the above two corrosion modes have been widely studied [11-15]. Exposure of these alloys to gas mixtures with carbon activity (ac) less than 1, reduces their mechanical properties by formation of the internal alloy carbides [12]. On the contrary, metal dusting frequently occurs in gas mixtures with ac≥1. In case of metal dusting, surface of the exposed sample replaces by mixtures of carbides, carbon coke and metal particles [12].

Formation of a protective oxide layer at the surface is one of the convenient methods to prevent the carbon attack. These oxide layers should be contentious and have slow growth rates. Cr$_2$O$_3$ is the protective oxide layer forms in austenitic Fe-Ni-Cr alloys [11, 16-20]. However, at high temperatures due to evaporation and formation of volatile hydroxide species it does not offer effective protection. In addition, chromium may react with carbon and form stable carbides in alloys exposed to gas mixtures with high carbon activities. This will result in the depletion of chromium in a subsurface alloy zone and suppress the formation of external Cr$_2$O$_3$ scales.

At early stage of carburization, austenitic stainless steels are protected from rapid interdiffusion of interstitial elements such as oxygen and carbon by the selective consumption of chromium which leads to the formation of a continuous protective Cr$_2$O$_3$ scale with low growth rate [11, 19, 20].
Numerous investigations have been conducted to study the formation of chromium oxide scales on steels and alloys. These studies concluded the oxide layer is in fact a two-layer oxide composed of a dense inner sublayer of Cr$_2$O$_3$ and an outer sublayer of spinel type oxide FeCr$_2$O$_4$, chromite [21-26]. The phase responsible for the surface protection is Cr$_2$O$_3$ since its low diffusion coefficient for oxygen [25, 26]. The formation of protective Cr-rich oxide scale, Cr$_2$O$_3$, depends on two main criteria: (i) the concentration of the chromium at the interface of stainless steel and oxide and (ii) on the diffusion coefficient of chromium in the metallic substrate from the core towards the interface. According to Evans et al. experiments [27], about 16 wt.% in Cr is required at the alloy/scale interface to form a protective chromium oxide layer in the temperature range from 750 to 920 °C for a Fe–20Cr–25Ni steel. However, stainless steel grain size highly effects on the critical chromium concentration to form a protective layer for a given temperature, and the surrounding atmosphere [22, 28-33].

Decreasing the grain size leads to rapid formation of a continuous chromia layer due to a faster diffusion of Cr in the alloy and to a smaller lateral growth distance required to form a continuous layer. In atmospheres containing water [22, 34-37] or carbon dioxide [19, 38, 39], the growth of Cr$_2$O$_3$ scale accelerated which leads to a greater depletion of Cr in the subsurface zone. At both atmospheres, the subsequent chromium loss tends to replace the protective initially formed Cr-rich Cr$_2$O$_3$ oxide with a nonprotective fast growing oxide, chromite [26]. According to Huntz et al., 18 wt.% of Cr in austenitic stainless steel is not enough to sustain the formation of Cr$_2$O$_3$ scale at elevated temperature (>850 °C or time). Then, the growth of iron rich oxides (spinel-like phase and hematite) takes place which accelerates the oxidation rate and leads to breakaway oxidation [23]. Breakaway oxidation of austenitic stainless steels increases the inward growth of a two-layer
oxide composed of chromia and chromite in carburizing atmospheres [26, 38, 39], in wet atmospheres [8, 40, 41] and in air at higher temperature [24].

The aim of this paper is to investigate the evolution of the RA330 microstructure after 12 months cyclic carburization. EBSD phase mapping allows to evidence an alteration of the composition from \( \text{Cr}_2\text{O}_3 \) to \( \text{FeCr}_2\text{O}_4 \) linked to a loss of protectiveness of the Cr-rich oxide scale formed at the interface with the substrate.

### 4.1.3. Materials and Methods

#### 4.1.3.1. Materials preparation

Carburization processes were performed on normalized RA330 stainless steel. The samples investigated in the present study were cut out to rods with 0.5 in diameter and 5 in length. This steel was selected for its widespread use in high temperature applications, for example heat-treat furnace and gas turbine components (where it is used because it has superior properties at high temperatures like thermal fatigue and creep resistance). The chemical composition of the RA330 is given in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIN</td>
<td>18.0</td>
<td>34.0</td>
<td>1.0</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Balance</td>
</tr>
<tr>
<td>MAX</td>
<td>20.0</td>
<td>37.0</td>
<td>1.5</td>
<td>0.08</td>
<td>2.0</td>
<td>0.03</td>
<td>0.03</td>
<td>1.0</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Stainless steel rod sample with 8.25 in\(^2\) surface area was welded to the bottom of a holder basket and placed in an industrial carburizing furnace to be exposed to the carburizing environment and experience the industrial carburizing cycles of heating followed by quenching for 12 months. Each carburizing cycle was performed in carburizing furnace at 900 °C that followed by rapid cooling. After the experiment, the 12-month exposed sample was cut and mounted, and metallographic
cross-sections were prepared by grinding and polishing to a 1 µm finish perpendicular to the contact plane to study the reaction layers. Then ultrasonically cleaned in a bath of ethanol and acetone and were prepared microstructure analysis.

4.1.3.2. Characterization

Microstructure analysis and phase identification of the reaction zone were performed using SEM, EDS, and EBSD coupled with EDS chemical analysis and the Powder Diffraction File PDF-4 (release 2018) published by ICDD. Thicknesses of the reaction zones were measured using an optical microscope, which was equipped with an image analysis software. SEM was performed using JEOL 7000F Equipped with the field emission gun, and energy dispersive x-ray spectroscopy (EDS) system and an Oxford EBSD system. EBSD was used to study and identify the crystallographic structure and reaction phases. Quantitative thermodynamic analysis also performed using EDS chemical composition, the Powder Diffraction File PDF-4 (release 2018) published by ICDD, and Thermo-Calc package.

4.1.4. Results

The results from 12-month exposure experiments are given in Figures 1-8. Figure 1 shows the microstructure of RA330 stainless steel samples before and after 12 months exposure to the carburizing furnace obtained by optical microscopy. Fig. 1 clearly shows exposure to the carburizing environment caused formation of oxide layer at outer surface and extensive precipitation of carbides at the grain boundaries of the base metal. Figures 2-4 are the SEM micrographs of the exposed sample at the surface, 450 µm distance from the surface, and diffusion zone at lower magnification respectively. It can be seen that the average thickness of the diffusion zone is 810 µm. Note that figs 1 and 2 are displayed at different magnifications. These SEM micrographs shows that diffusion zone consists of at least three different parts. SEM micrographs
indicate that the diffusion layer is continuous but is thickness varies along the baseline and consists of at least three types of reaction layers, which differ in microstructure and gray level. Fig. 1 shows at least three types of reaction layers at the surface of the carburized sample in different magnifications. The average thickness of the continuous surface layer is 10 µm. The average thickness of the second layer, which consists of two phases, is 200 µm.

Figure 1 Optical photomicrographs of RA330 stainless steel (a) before, and (b) After 12 months exposure to carburizing furnace

Figure 2 SEM cross section photomicrographs of 12-month exposure at the surface area.
Figure 3 shows the third layer consists of two phases which their fraction changes by distance from the surface. The second phase, which is darker in gray scale and is formed at grain boundaries of the matrix phase, is varies in size and shape. Figure 4 represents the locations of different areas at diffusion zone which selected for further characterization.

Figure 3 SEM cross section photomicrographs of 12-month exposure at the surface area

Figure 4 selected characterized areas
Figures 5-8 compile representative results obtained from EBSD and EDS measurements for this sample condition at different locations shown in figure 4. Figure 5 shows an EBSD phase mapping result merged with EBSD band-contrast data (in grayscale) and EDS map analysis obtained for surface of the 12-months exposed sample. This figure clearly shows that the oxide layer at the surface of the 12-months exposed sample consists of chromite (aqua blue) and Cr$_2$O$_3$ (green) which chromite phase accounts for the majority of the oxide layer at the surface. The oxide layer is continuous and has thickness of 5-20 µm. Graphite and austenitic stainless steel appear in dark blue (Graphite) and red, respectively. To further investigate this oxide thin layer at the surface of the carburized sample, the chemical composition of the reaction area at the surface measured by EDS. Complementary to the EBSD results, two different Cr average concentrations of 70 Wt.% and 45 Wt.% corresponds to two different chromium oxides at the surface. The oxide phase at vicinity of the graphite which is the dominant phase at the oxide layer is separated from the steel substrate by discontinuous thin oxide layer with higher Cr content. The outer oxide with lower Cr content was identified by automated EBSD to have different crystal structure to thin oxide layer at the interface with steel and to have similar crystal structure as steel. SEM micrograph of the sample at the surface, figure 5, also indicates the chromium oxide layer despite being continuous is not a protective layer and it does not adhere to the steel completely.

Figure 6 shows the SEM micrographs taken at position 2. The microstructure of the third layer of diffusion zone, with thickness of 250-300 µm, consists of chromium oxide (dark shades in SEM micrograph) in austenitic (Fe-Fcc) matrix. EBSD phase mapping result merged with EBSD band-contrast data (in grayscale) indicate chromium oxides regions consist of Cr$_2$O$_3$ (green) and chromite (aqua blue). However, the latter is the dominant phase in oxide phases in this layer and
chromite was only observed to be formed at the close distance to the surface and by distancing from the surface it disappears.

The chemical composition of the reaction layer measured by EDS. Coincide with EBSD result, detection of two oxides with different Cr concentrations at close distance from the interface is evident of presence of two different chromium oxides. The calculation of precise phase fractions was not applicable since the regions with removed oxides are frequent (Black areas in EBSD map).
However, by distancing from the surface the chromite phase fraction decreases and reaches to zero at middle of the third layer.

Figure 6 EBSD analysis of unaluminized RA330 after 12-month exposure at position 2 (surface)

SEM micrograph in Figure 7 also reveals that there is a fourth zone at diffusion layer which is next to the oxide/stainless-steel interface. Carbides (dark gray) were formed and distributed in different sizes and shapes across the austenitic stainless-steel matrix (Light gray). EBSD result indicates the
only present carbide is Cr$_3$C$_7$ at the area in close distance of the third layer interface. Figure 7 represents results obtained from SEM and EBSD phase mapping result merged with EBSD band-contrast (in grayscale) obtained for exposed sample at location 3. The microstructure of the sample at this location features similarity to the microstructure of the austenitic matrix close to the third zone interface.

The SEM micrograph shows the carbides (dark gray features) are formed in different sizes, shapes, and number density in austenitic stainless-steel matrix (light gray). The EBSD results clearly shows these carbides were formed at grain boundaries, twins, and other defects of austenite. However, unlike the location 2, EBSD determines two different carbides at location 3 which are identified as Cr$_7$C$_3$ and Cr$_{23}$C$_6$ in dark blue and aqua blue, respectively. The Figure 7 also indicates
that by distancing from the surface the phase fraction of precipitated carbide decreases, and the
grain size of the base metals increases.

Figure 8 shows the SEM and EBSD mapping result merged with band-contrast image. The average
size and the number density of the carbides in the austenite at location 4 is smaller in compare to
the carbides at location 3. EBSD mapping identified carbides as Cr$_{23}$C$_6$ (Aqua blue) which are
formed at grain boundaries and other defects in austenite.

![Figure 8 EBSD analysis of RA330 after 12-month exposure at position 5 (Core).](image)

4.1.5. Discussion

Isopleth diagram of RA330 stainless steel with carbon mass percentage is shown in figure 9. Based
on figure 10, theoretically, exposure of RA330 stainless steel to carburizing atmosphere results in
formation of chromium carbides which their stoichiometries change with amount of diffused
carbon over time. At lower carbon content Cr$_2$C$_6$ is more stable than other stoichiometries since its free energy of formation is lower than others, however, increasing exposure time or/and temperature reduces the stability of this phase thus by further diffusion of carbon over time and increase in carbon content, other stoichiometries such as Cr$_7$C$_3$ and then Cr$_3$C$_2$ become more stable.

Figure 9 Isopleth diagram of RA330 vs carbon mass percentage

Current experiment has been carried out on under carburizing and oxidizing environment. For better understanding of phase transformations during the carburization under this condition, trinary phase diagram of RA330 with mass percentage of oxygen and carbon has been demonstrated in figure 10. In contrast to pure carburizing atmosphere exposure (Figure 9), formation of the Cr$_2$O$_3$ layer was theoretically predicted during exposure in the carburizing/oxidizing atmosphere (Figure
10) and presence of the carbon doesn’t have any major effect on formation of chromium oxide, corundum.

Figure 10 trinary phase diagram of RA330 vs mass percentage of carbon and oxygen at 900 °C.

Figure 10 trinary phase diagram of RA330 vs mass percentage of carbon and oxygen at 900 °C.
During the exposure of stainless steel to the carburizing-oxidizing atmosphere, oxygen in the gas reacts with chromium in the alloy forming chromia layer which in turn may react with carbon forming carbide according to the equation:

$$7\text{Cr}_2\text{O}_3 + 6\text{C} = 2\text{Cr}_7\text{C}_3 + 10.5\text{O}_2$$ (1)

According to Kinniard, the carbide $M_7\text{C}_3$ rich in Fe may equilibrate with graphite directly, so that $\text{Cr}_3\text{C}_2$ is neglected in equation (1) [42]. According to Grabke, the solubility of carbon in $\text{Cr}_2\text{O}_3$ at 1000 °C is below 0.01 ppm [43]. Therefore, carbon should not be able to permeate efficiently through dense $\text{Cr}_2\text{O}_3$ scales. Therefore, the formation of continuous and compact external layers of $\text{Cr}_2\text{O}_3$ is expected to be very helpful for developing a good resistance to carbon attack. By increasing oxygen content, the chromium carbides in phase diagram experiencing a left shift. In other words, increase in diffusion of oxygen and carbon leads to reduction in stability of $\text{Cr}_{23}\text{C}_6$ and stabilizes $\text{Cr}_7\text{C}_3$ and then $\text{Cr}_3\text{C}_2$ and $\text{Cr}_7\text{C}_3$ carbides can be stable at lower carbon content.

Although under carburizing and oxidizing atmosphere, $\text{FeCr}_2\text{O}_4$ Spinel forms at all oxygen contents, but the presence of carbon causes delay in formation of spinel at low diffused oxygen content (less than 0.012 %wt. oxygen).

The average thickness of the diffusion zone of the 12-months carburized RA330 stainless steel in this study is 810 µm. Based on analysis on location 1-4 of figure 3, the diffusion zone consists of five major layers: (1) graphite, (2) $\text{Cr}_2\text{O}_3 + \text{FeCr}_2\text{O}_4$, (3) austenite+$\text{Cr}_2\text{O}_3$, (4) austenite+$\text{Cr}_7\text{C}_3$, (5) austenite+$\text{Cr}_{23}\text{C}_6$. Since the sample was cooled down rapidly at the end of each cycle, theoretical thermodynamic calculations can be used using Thermo-Calc software with TCFE9 database to predict the isopleth diagram and equilibrium phases for each location on figure 4. The isopleth of location 1 is shown in figure 11. Complementary to the experimental EBSD results, the surface area at carburizing temperature consists of $\text{Cr}_2\text{O}_3$ (Corundum), austenite (FCC_A1), chromite
(Spinel), graphite, and slightly orthorhombic SiO$_2$ (Tridymite). However, in contrary with the theoretical results, SiO$_2$ phase was not detected in experimental characterization which can be explain by the fact that the volume fraction of SiO$_2$ at the surface is less than 0.24 mass fraction). The spinel phase consistently makes up the largest fraction in the oxide layer that forms at the surface of the exposed RA330 caused by interdiffusion between oxygen and carbon and RA330 stainless steel during the carburization process.

According to Wagner analytical model, the critical mole fraction of Cr of the bulk alloy, N$_{Cr^*}$, needed for the transition from the internal to the external formation of Cr$_2$O$_3$ scales for binary Fe–Cr alloys [44]. However, it must be considered that despite Wagner’s theory this experiment was done under mixed gas atmosphere. Thus, the Wagner’s approach cannot be applied to this experiment without modifications. One possible reason is that diffused carbon in the alloy can produce a precipitation of carbides, thereby reduces the chromium content available for the outward diffusion in the alloy to form a protective Cr$_2$O$_3$ scale. In addition, the presence of carbon in the gas mixture tends to reduce the degree enrichment of chromium in the region of the internal oxidation due to a mechanism, associated with the simultaneous internal oxidation by two oxidants resulting in a larger critical concentration requires for the transition between its internal and external oxidation.

The presence of oxygen generally reduces the corrosion rates with respect to the case of pure carburization due to the formation of discontinuous chromium in selected regions but was never sufficient to prevent the formation of internal carbides. During the mixed gas carburization process, the oxidation proceeds through an outward cationic diffusion of chromium which the substrate provides required Cr to the protective oxide scale via grain boundaries than at the steel grain centers due to slow lattice diffusion compared to grain boundary diffusion. At the center of
the underneath alloy grains, the chromium activity becomes insufficient and then \( \text{Cr}_2\text{O}_3 \) layer locally loses its protective feature which results in fast outward iron diffusion and inward oxygen diffusion leading to the formation of two-layer oxide which consists of protective \( \text{Cr}_2\text{O}_3 \) (corundum) and non-protective \( \text{FeCr}_2\text{O}_4 \) (a type of spinel called chromite). According to Liu and Shen the presence of even chromium content of 21% is still insufficient for a complete protection in the present mixed gas atmosphere [45]. Therefore, the critical chromium contents needed to sustain the protective oxide layer at the surface of the RA330 stainless steel exposed to the carburizing (mixed gas) atmosphere are significantly larger than the chromium content of this alloy.

During exposure of RA330 stainless steel to the carburizing atmosphere used in this study, both carbon and oxygen reacted with the metal substrates forming simultaneously carbides rich in chromium and chromium oxide on the surface. Carbon diffusing inwards reacted with the alloy forming the stable carbides \( \text{Cr}_7\text{C}_3 \) and \( \text{Cr}_{23}\text{C}_6 \). These reactions produced a depletion of chromium in a subsurface zone, so that the chromium content left in solution in the alloy was no longer enough to sustain the formation of protective and continuous external \( \text{Cr}_2\text{O}_3 \) scales. Therefore, the fraction of the external surface covered by \( \text{Cr}_2\text{O}_3 \) was very low due to its reduced chromium content. The lateral growth of the protective oxide phase was blocked by the formation of carbides, Fe-rich oxide, and graphite.
According to SEM and EBSD phase analysis, location 1 in figure 4 contains layer 2 (chromia+chromite), layer 3 (chromia+austenite), layer 4 (austenite+Cr$_7$C$_3$) of the diffusion zone. Isopleth of the exposed sample at location 2, figure 12, predicts the presence of Cr$_2$O$_3$, Austenite, graphite, and M$_7$C$_3$, SiO$_2$, and FeCr$_2$O$_4$ which is in good agreement with the experimental EBSD phase mapping results. The absent of SiO$_2$ phase in experimental results and EBSD analysis can be explained by the fact that the theoretical and experimental weight fraction of this phase in this area is negligible.

The isopleth of location 3 is demonstrated in figure 13. According to Figure 13 and chemical composition of the area, presence of two chromium carbides, Cr$_{23}$C$_6$ and Cr$_7$C$_3$, in the austenitic matrix was predicted. This prediction is in agreement with experimental results and EBSD analysis.
(figure 7) suggesting this location is located at the interface of layer 4 (austenite+Cr$_7$C$_3$) and layer 5 (austenite+Cr$_{23}$C$_6$) of diffusion zone.

By distancing from the exposed surface, the carbon content decreases and suggests that the carbon carbide stoichiometry with lower carbon content is more likely stable. According to the SEM micrographs and EBSD phase mappings, the carbide sizes and concentration of carbon in carbides decrease by distancing from the surface and carbides transforms from Cr$_7$C$_3$ to Cr$_{23}$C$_6$. This transition is predicted by comparing isopleths of location 3 and 4 in figures 13 and 14, respectively.
Location 4 on figure 4 is located in layer 5 of the diffusion zone. EBSD analysis of this location identified austenite, Cr$_{23}$C$_6$, and negligible amount of Cr$_7$C$_3$ as the present phases. Chromium carbides are mainly precipitated at the grain boundaries, twinnings, and other defects of the austenitic matrix (figure 8). The results of phase prediction of location 4 (figure 14) coincides with experimental results and characterizations. Based on this plot, the phase fraction of Cr$_7$C$_3$ phase is negligible in comparison to Cr$_{23}$C$_6$ and this area mostly contains austenite and Cr$_{23}$C$_6$. A negligible amount of MnSiO$_3$ is predicted to be presence in this area which can explains the absence of this phase in experimental results.
In the present case, Internal carburization occurred in the sample exposed to the carburizing atmosphere, so that it was not able to form continuous external oxide scales. Therefore, the chromium concentration of 18.7 wt.% is still insufficient for a complete protection. As a result, more chromium is needed for a complete prevention of the carbon attack by forming continuous external chromia scales.

Addition of elements such as Al to binary Fe–Cr alloys will help to increase the volume fraction of internal oxide, thus reducing the critical content of Cr needed for the transition. For ternary Fe-Cr-Al systems the effective volume fraction of internal oxide to be used is given by the sum of the corresponding values for the less-reactive element and the most reactive element.

4.1.6. Conclusion

Austenitic RA330 stainless steel was cyclically carburized at 900 °C carburizing furnace for 12 months. The average thickness of the diffusion zone was measured 810 µm and it consists of five
layers: (1) graphite, (2) Cr$_2$O$_3$+FeCr$_2$O$_4$, (3) Cr$_2$O$_3$+austenite, (4) Cr$_7$C$_3$+austenite, (5) Cr$_{23}$C$_6$+austenite. The experimental EBSD phase mappings were in good agreement with the theoretical thermodynamic predictions. The presence oxygen and of chromium oxide layer had only a slight effect on the corrosion behavior of RA330 due to the formation of a surface layer of graphite, carbide, and non-protective Fe-rich spinel type oxide. Also, the occurrence of the grain growth in substrate, reduces the outward diffusion rate of chromium which assists the formation of carbide, Fe-rich oxides, internal oxidation. The critical chromium content needed for the transition from the internal to the external oxidation for Fe-Ni-Cr alloys, exposed to the carburizing-oxidizing atmosphere, and for sustaining the protective oxide is larger than the chromium content of RA330, therefore, addition of the oxygen in the carburizing mixed gas is not very effective. However, the addition of any elements such as aluminum which could promote the formation of external oxide and induce the presence of continuous oxide scales is beneficial.

4.1.7. References


4.2. Cyclic carburization of aluminized RA330 stainless steel

4.2.1. Abstract

Austenitic stainless steel RA330 is a high temperature corrosion resistant alloy which is widely used as furnace alloys and fixtures in heat treatment industries. In this study the anti-carburizing and anti-oxidation properties of aluminized RA330 has been investigated. Aluminizing is an effective method to enhance the high temperature oxidation and carburization resistance of nickel-based alloys. This paper focuses on performance of aluminized RA330 under industrial mixed gas carburization furnace environment for 6 months and two years. The oxide properties, oxide stability, and microstructure analysis of the samples at aluminum coating and substrate at high temperatures will be presented. In addition, the preliminary analysis of microstructure of as-aluminized RA330 will be presented. These samples were characterized using optical and scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), and electron backscatter diffraction (EBSD). It was found that the aluminized stainless steel RA330 exhibited better carburization and oxidation resistance in comparison to unaluminized alloys.
4.2.2. Introduction

Extending the service life of heat-treating furnace alloys and fixtures is one of the highest demands in heat-treating industries and other high temperature applications. These alloys are typically manufactured using Ni-based alloys. However, Stainless steel alloys whose chemical composition is selected to achieve the required mechanical performance and creep resistance, even if this caused limited anti-corrosion and anti-oxidation properties are widely used as a more economic substitute in high temperature anti-corrosion applications such as fixtures inside the high temperature furnace [46]. As a result, without the use of protective surface treatments, these degradation mechanisms could lead to catastrophic failures, resulting in complete system shutdown. Many of the fixtures fail within one years of exposure in high temperature carburization atmospheres [40, 47].

Furnace fixtures operate in severe environment. Iron-nickel based, and Iron-Nickel-Chromium based alloys are experiencing a variety of degradation mechanisms [8, 10, 48, 49]. The corrosion products are mainly graphite, chromium carbide, and oxides. For RA330 alloy, the primary reason for failure was the excessive carburization that leads to “metal dusting” and subsequent cracking [15, 50-52].

Extending the service life for high temperature structural alloys is the goal for many heat treaters. Aluminizing is a coating that has been widely used in aerospace industry, especially in turbine blade applications [9, 53]. It is also known that carbon has very low solubility in alumina. In that case, aluminizing could be a good method for protecting high temperature structural alloys. The protection is achieved by enriching the surface layer of the aluminum through diffusion mechanisms. Aluminum element reacts with the substrate material to form secondary phases and the intermetallic that act as a reservoir of scale formers during the service life [7].
This work is focused on the development of a better understanding of the effects of carburization on these alloys and coatings.

4.2.3. Materials and Methods

4.2.3.1. Materials preparation

In this study, RA330 austenitic stainless steel was selected as the main substrate alloy. RA330 is well known as the corrosion-resistant alloy, offering an exceptional combination of strength and resistance to carburization, oxidation and thermal shock. RA330 finds wide applications in high temperature industrial environments where good resistance to the combined effects of carburization and thermal cycling is prime requisite. The chemical composition of RA330 alloy is given in table 1.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIN</td>
<td>18.0</td>
<td>34.0</td>
<td>1.0</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Balance</td>
</tr>
<tr>
<td>MAX</td>
<td>20.0</td>
<td>37.0</td>
<td>1.5</td>
<td>0.08</td>
<td>2.0</td>
<td>0.03</td>
<td>0.03</td>
<td>1.0</td>
<td>Balance</td>
</tr>
</tbody>
</table>

RA330 was aluminized to improve its carburization resistance and oxidation resistance. The aluminizing process was carried out in a static gas phase system at 1090°C for 5 hour Chromium aluminum source material (70%Cr/30%Al) and ammonium fluoride granules were used in the system. The coating chamber was purged with argon until a dew point of -40F or better was met, then the argon is shut-off to the coating chamber (hence static system) and heating begins.

As fabricated and aluminized samples were exposed in an industrial gas carburizing furnace. The samples investigated in the present study were cut out to rods with 0.5 in diameter and 5 in length. Stainless steel rod samples with 8.25 in² surface area was welded to the bottom of a holder basket and placed in an industrial carburizing furnace to be exposed to the carburizing environment and
experience the industrial carburizing cycles of heating followed by quenching for 6 months and 24 months. Each carburizing cycle was performed in carburizing furnace at 875-925 °C and carbon potential of approximately 0.7% that followed by rapid cooling. After the experiment, the 6 and 12-month exposed sample was cut and mounted, and metallographic cross-sections were prepared by grinding and polishing to a 1 µm finish perpendicular to the contact plane to study the reaction layers. The samples were ultrasonically cleaned in a bath of ethanol and acetone to be ready for microstructure analysis.

4.2.3.2. Characterization

Microstructure analysis and phase identification of the reaction zone were performed using SEM, EDS, and EBSD coupled with EDS chemical analysis and the Powder Diffraction File PDF-4 (release 2018) published by ICDD. Thicknesses of the reaction zones were measured using an optical microscope, which was equipped with an image analysis software. SEM was performed using JEOL 7000F Equipped with the field emission gun, and energy dispersive x-ray spectroscopy (EDS) system and an Oxford EBSD system. EBSD was used to study and identify the crystallographic structure and reaction phases. Quantitative thermodynamic analysis also performed using EDS chemical composition, the Powder Diffraction File PDF-4 (release 2018) published by ICDD, and Thermo-Calc package.

4.2.4. Results

4.2.4.1. As-aluminized RA330

The results of microstructure analysis of the as-aluminized sample are given in Figures 1-3. Fig.1 and Fig. 2 are the SEM micrographs and EBSD coupled with EDS map analysis of the as-aluminized sample at the coating and diffusion zone and Fig. 3 is the SEM micrographs of the
substrate at the middle and center of the sample. The average thickness of the diffusion layer is 100 µm. The SEM micrographs in Fig. 1 indicates that the diffusion zone is consists of at least four multiphase reaction layers. Figure 1 shows the first layer of the diffusion zone is a thin oxide layer at outer surface of the sample. The second layer, next to the oxide layer toward the coating-substrate interface, consists of two phases: dark precipitated phase in a gray base phase. The size and volume fraction of the second phase are not consistent throughout the second layer and they decrease by distancing from the outer surface. This layer accounts for most of the diffusion zone and its average thickness is 64 µm.

Third layer with the average thickness of 6 µm consists of at least three phases: a) extremely dark (black) phase with almost a random morphology, b) the light gray phase (silver), and c) the rough gray phase similar to the main phase in the second layer. The fourth layer of the diffusion layer which is located at the coating/substrate interface is the second major layer with thickness of 30 µm. This layer consists of two different needle-shape phases in a third smooth base phase. The
first needle shape phase is smooth light gray phase which has the similar microstructure to the silver phase in the third layer, and the second needle shape phase is a rough gray phase.

Figure 2 compiles the representative results obtained from EBSD and EDS measurements of the as-aluminized sample. Fig. 2a shows an EBSD phase mapping merged with EDS mapping obtained for as-aluminized sample. Fig. 2a clearly shows that the \( \alpha_2 \) phase (orange) accounts for the majority of the reaction layer. Austenitic RA330, chromium carbide, and sigma phase appears in green, red, and dark blue, respectively. The chemical composition of the reaction layer measured by EDS along the line indicated by the yellow arrow in Fig. 2b. Complementary to the EBSD result, the Al concentration of 860 cps corresponds to the \( \alpha_2 \) phase as the dominant component. The light green (needle shape) and light blue phases in Fig. 2a near the interface with the steel were identified by automated EBSD to have similar structure as \( \alpha_2 \) phase. EBSD map analysis is not able to distinguish the light blue and light green as two separate phases since they both share the same crystal structure and group name, and constituting elements of Al, Ni, and Fe. However, EBSD results merged with EDS measurements could distinguish the later phases. Fig. 2c shows the EDS map analysis of the sample.
Figure 2. EBSD analysis coupled with EDS map, EDS map, and EDS line profiles for the major elements at different layers formed by pack aluminizing.
Fig. 2c clearly shows that nickel is the major constituent elements in the needle shape phase (green phase in fig. 2.a) and iron concentration is very low in compare with nickel and aluminum concentrations. The other two phases near the steel/coating interface (the light blue and dark blue phases in Fig. 2a) have higher iron concentration, however, they have different crystal structures and chemical compositions. The phase with lower chromium concentration and higher amount of iron has the same crystal structure as the needle phase and $\alpha_2$ phase.

Fig. 3 shows SEM micrographs taken after aluminizing process from the core of the steel substrate. The SEM micrographs shows the typical austenitic stainless-steel microstructure which includes various austenitic twin. However, there is an imaginary line which separates the substrate stainless steel into two regions: a) a region on interface side which has higher average grain size, and b) the region near the core of the sample with considerably finer average grain size.
4.2.4.2. 6-month exposure

Fig. 4 represents the cross-sectional SEM micrographs of the pre-aluminized sample which exposed to industrial carburizing furnace for 6 months. Fig. 4 shows the average thickness of the reaction zone is 80 µm and consists of several different layers. The carburizing of RA330 occurs at 900 °C has caused carbon deposition at the surface of the sample and formation of various cracks in the coating toward the steel/coating interface (Fig. 5 a-b). The average thickness of the deposited
graphite at the surface is measured 8 µm. Next to the graphite layer (layer #1), there is a thin layer of oxide layer with average thickness of 2 µm.

![SEM cross section photomicrographs of 6-month exposed aluminized sample at the surface](image)

Figure 4. SEM cross section photomicrographs of 6-month exposed aluminized sample at the surface

Figure 5 c-d represents the higher magnification of the reaction zone at the vicinity of the interface. It is obvious from fig. 5c and 5d that in compare with as-aluminized sample (Fig. 1), carburizing treatment for 6 months caused an increase in precipitation and size of chromium carbide phase at substrate but did not affect significantly the phase fraction of the carbide at the coating. The average thickness of the α-phase (layer #2) is 57 µm. The reaction zone at the vicinity of the interface shows similarity to the reaction zone of the as-aluminized sample, however, there is an extra layer at the heat-treated sample which has a coarsened microstructure with coexist of two phases of α₁+ α₂. The average thickness of this layer is 4 µm (layer #2’).
The two-phase microstructure is also observed at regions in the vicinity of the cracks at the third layer of the reaction zone. Complimentary with as-aluminized sample, the third layer with average thickness of 23 µm consists of small carbides (dark gray islands) in a matrix phase (light gray). The fourth layer of the reaction zone, which is located exactly at the RA330/coating interface consists of at least two different phases. The EBSD phase analysis merged with EDS and bond contrast measurements and EDS map analysis of the sample are shown in Fig. 6. EBSD results confirm the sigma phase (green) and α₂ (bright red) are constituent phases of the fifth layer of reaction zone. Chromium carbides (brown) are mostly precipitated at grain boundaries of the substrate or formed in a matrix of α₂ phase at the fourth layer of reaction zone.
Figure 6. EBSD coupled with EDS map analysis of 6-month exposed aluminized sample at the surface.

On account of the facts that \( \alpha, \alpha_1, \) and \( \alpha_2 \) phases have same BCC crystal structure and their bond contrast are very low, EBSD results alone cannot distinguish these three phases. However, merging
EBSD results with EDS measurements provides the opportunity of differentiating these phases. α-phase (purple) is the major phase at the second layer where most of the cracks are located. The average grain size of the α-phase is considerably larger than grains at other part of the reaction zone.

![Figure 7. SEM cross section photomicrographs of 6-month exposed aluminized sample at core](image)

Fig. 7 shows the SEM micrographs of RA330 substrate at the core of the sample (the furthest distance from the surface). The substrate is austenite as the main phase containing austenitic twins and carbide particles as the secondary phase. The average size of the precipitated chromium carbides in the substrate is 500 nm which has been experienced growth in compare with as-aluminized sample.

### 4.2.4.3. 24-month exposure

The microstructure of the pre aluminized sample after 24 months exposure is presented in Figures 8-10. Fig. 8a and 8b are the SEM cross-section micrographs of the sample at different magnifications and Fig. 8c and 8d are SEM micrographs of the sample at higher magnification at different locations of the reaction zone. The average thickness of the reaction zone is 90 µm and various cracks are formed at the surface toward the substrate/coating interface.
Figure 8. SEM cross section photomicrographs 24-month exposed aluminized sample at the reaction zone
For the 6-months exposure sample, all cracks were propagated not further than layer 2 of the reaction zone. However, for the 24-months exposure sample, it was observed that most of the surface cracks were propagated further than reaction zone and reached the interface. Also, there are some cracks at the surface which propagated in layer two of the reaction zone parallel to the interface, however, the number of these cracks is much lower than the number of cracks which were grown perpendicular to the interface. Similar to 6-months exposed sample, microstructure of the reaction zone of the 24-month exposed sample consists of different layers (Fig. 3b).

Fig. 8 indicates that there are at least four different layers: 1) the outer oxide layer, 2) a dual-phase layer (with spinodal like microstructure) and is the thickest layer of the reaction zone with average thickness of 48 µm. 3) the two-phase layer containing a second phase islands (carbides) in the matrix of a rough phase. The average thickness of this layer is 28 µm and the secondary phase islands have random sizes, shapes, and distributions, and 4) a layer consists of a smooth phase with a small phase fraction of secondary phase which has the same microstructure as the matrix phase at the third layer. The average thickness of this layer is 14 µm.

EBSD results merged with EDS measurements and EBSD map analysis merged with bond contrast are shown in Fig 9a and 9b, respectively. Coincide with SEM microstructure predictions, primarily EBSD results indicates the second and third layers both have BCC crystal structure but different lattice parameters. At the third layer, carbides islands are distributed randomly in a continuous BCC phase. The fourth layer is mostly made of sigma phase with a few islands of a precipitated phase with the same crystal structure of main phase of third and second layers. Merging EBSD results with EDS measurements provides the more accurate results and more information regarding the microstructure of the reaction zone. The second layer consists of two lamellar phases of $\alpha_1 + \alpha_2$
with BCC crystal structures and main phase in second layer and the small, precipitated island in second layer is $\alpha_2$.

Figure 9 (a) EBSD phase analysis merged with EDS and bond contrast, and (b) EDS measurements merged with bond contrast of 24-month exposed aluminized sample at the reaction zone
Most carbides on substrate are precipitated at grain boundaries of RA330 substrate and at the substrate/coating interface, shown in Fig. 10 and Fig. 9, respectively. The average size of carbides at substrate is 1.25 µm.

![Figure 10 EDS map analysis of 24-month exposed aluminized sample at the core (Base metal)](image)

4.2.4.4. Crack analysis

Post carburizing heat treatment of the aluminized samples results in formation and growth of surface cracks at reaction zone. It has been observed that after 6 months exposure to carburizing environment, only a few propagated passed the reaction zone and reached to the interface. Majority of the cracks were growing only within the third layer of the reaction zone (Fig. 11). EDS measurements alumina was formed at the surface of the cracks and protected the sample from further oxidation and carburization. For the longer cracks which have passed the third layer and reached the substrate, chromium oxide formed at the surface of the cracks due to lack of aluminum contents in these regions. However, it can be observed that there are some linear regions parallel to the surface and interface at the third layer/fourth layer and coating/substrates which are affected by post carburization process, consisting of chromium carbides and alumina phases.
Figure 12 (a)-(d) SEM cross section photomicrographs of surface defects of 6-month exposed aluminized sample at the surface, (e),(f) EDS map measurements (c) and (d), respectively.

Figure 12d also confirms the phase separation around the cracks at second layer of the reaction zone ($\alpha \rightarrow \alpha_1 + \alpha_2$). EDS map analysis (Fig. 12f) indicates the phase that is formed like a grain boundary (the light gray phase on Fig. 12d) has high iron concentration and inside the grains, both $\alpha_1$ and $\alpha_2$ are coexisted. The nickel concentration at the vicinity of the cracks at the reaction zone
is higher. The third layer which is consists of α₂ and chromium carbide has lower aluminum concentration at the vicinity of the cracks since aluminum content of α₂ has been used for formation of alumina at the surface of the cracks.

SEM micrographs of the 24-months exposed sample at areas closed to the surface cracks are shown in Fig. 13. The quantity, the length, and the thickness of the cracks in 24-months exposed sample are higher in compared to 6-month exposed sample. In 24-months exposed samples, the majority of the cracks passed the second layer and reached the interface and the substrate. Branching the main cracks caused the formation of new cracks at reaction zone and substrate which propagate in different directions from the main cracks. The microstructure of the 24 months exposed sample at the vicinity of the crack shows similarity to those for 6 months exposed sample. however, in comparison with the microstructure of the 6 months exposed sample, the precipitated chromium carbides at the substrate, at the vicinity of the alumina at the crack surface, and affected areas are thicker.

EDS measurements of a crack at the reaction zone of the 24-months exposed sample are shown in Fig. 14. The studied crack has propagated through the substrate/coating interface. Alumina has been formed at the surface of the crack at second and the third layer of the reaction zone, however, due to insufficient aluminum concentration at the fourth layer of the reaction zone, the phase fraction of only chromium carbides at the crack’s surface increases dramatically in comparison with alumina.
Figure 13 SEM cross-section micrographs of 24-month exposed aluminized sample at reaction zone

Chromium carbide precipitates at in vicinity of the contentious alumina layer at the crack’s surface at the third layer and by getting closer to the interface, the amount of precipitated chromium carbides increases until they form a continuous carbide layer next to the alumina layer at the third layer/fourth layer interface and completely covers the crack’s surface at fourth layer of the reaction zone.
Figure 14 EDS map analysis of the surface crack of 24-month exposed aluminized sample
Also, phase separation was occurred at the second layer of the reaction zone from next to the outer thin layer of alumina at the surface to the third layer of the reaction zone. \((\alpha_2 \rightarrow \alpha_1 + \alpha_2)\). Figure 15 represent the EDS measurements of the area in the vicinity of the cracks at the surface.

Figure 15. EDS map analysis of the surface crack of 24-month exposed aluminized sample (Higher magnification)
4.2.5. Discussion

The reaction zone of the as-aluminized sample contains four layers of (1) a thin alumina layer at surface, (2) $\alpha_2$-(Fe, Ni) Al phase with bcc crystal structure, (3) $\alpha_2$ (bcc) and carbides, and (4) sigma phase, $\alpha_1$ (BCC), and $\alpha_2$ (BCC) at the coating/substrate interface. Exposure of the aluminized RA330 stainless steel to industrial carburizing environments causes variations in microstructure of the reaction zone which differs by exposed time. In addition to increase in the thickness of the third layer, by increasing the time of the exposure to 6 months and 24 months, the fraction of the carbides at this layer increases. The fraction of the $\alpha_1$ and $\alpha_2$ phase at the fourth layer decreases by extending the exposure time so that $\alpha_1$ disappears completely after 6 months of exposure.

Phase decomposition of $\alpha_2$-(Fe,Ni)Al occurs mainly at the second layer of the exposed sample in saturated $\alpha_2$ phase and by increasing the time of the exposure, the thickness of the affected area increases so that in the 24 months exposed sample the $\alpha_2$ phase in second layer is completely decomposed to $\alpha_1$ and $\alpha_2$. This breakdown was also observed at the fourth layer of the reaction zone, however, by being co-existed with sigma phase, the phase fraction of these later phases decreases by increasing the time of exposure.

The coarsening growth kinetics of the $\alpha_2$ precipitates, in general, has followed the modified LSW theories for diffusion-controlled coarsening [54-57]. At the second layer of the 24 months exposed sample, $\alpha_1$ precipitates in matrix of $\alpha_2$. At the beginning of precipitation, it is expected to have a coherent interface between these two phases since their lattice parameter is very similar. Over the course of time, the precipitates become aligned with the matrix. A further exposure time causes aging and promotes the increase in size of precipitates.

Phase decomposition of $\alpha_2$-(Fe,Ni)Al into $\alpha_2$-(Ni,Fe)Al and $\alpha_1$-(Fe) has been studied in detail by Bradley, Kiuchi, Tylor, and Hao et. al [58-61]. The miscibility gap in Fe-Ni-Al system results in
the breakdown of a high temperature bcc phase $\alpha_2$ into two bcc phases of $\alpha_1$ (Fe-rich disordered bcc phase) and $\alpha_2$ (intermetallic NiAl-rich ordered bcc phase) with B2 (CsCl) crystalline structure. The miscibility gap in the broad bcc phases extends from the Fe corner to the NiAl in Fe-Ni-Al system. Fig. 16 shows the phase diagram of Fe-Ni-Al system. According to the ternary diagram, shown in fig. 16, the precipitation reaction can take place in two ways [60, 62]:

$$\alpha_2 \rightarrow \alpha_1 + \alpha_2$$

or

$$\text{BCC}_B_2 \rightarrow \text{BCC}_A_2 + \text{BCC}_B_2 \ #2$$

(1)

$$\alpha_1 \rightarrow \alpha_1 + \alpha_2$$

or

$$\text{BCC}_A_2 \rightarrow \text{BCC}_A_2 + \text{BCC}_B_2$$

(2)

That is, the supersaturated solid solution of either the BCC_B2 ($\alpha_2$) or BCC_A2 ($\alpha_1$) phase can produce a mixture of the disordered ferrite $\alpha_1$ and the ordered intermetallic $\alpha_2$ phase. Ordered intermetallic phases with BCC_B2 crystal structure can promote an increase in the mechanical strength and thus a better performance at high temperature, however, formation of ordered $\alpha_1$ (ferrite Fe) may weaken the mechanical properties of $\alpha_2$ at service temperature and become a media for nucleation and propagation of cracks in $\alpha_2$ matrix. Additionally, according to the EBSD measurements, it is expected to have a coherent interface between these two phases since their lattice parameter is very similar, and thus EBSD results alone are enough to distinguish between these two phases. Merging EBSD data with EDS measurements provided the conclusive results to accurately identify all phases at the reaction zone.
Figure 16: (a) pseudo-binary phase diagram of Fe-Ni-Al system. Dotted line shows the miscibility gap calculated by the regular solution model [62], (b) Three-dimensional illustration of miscibility gap in Fe-Ni-Al [62], and (C) Trinary diagram of Fe-Ni-Al system at 900 °C.
All samples in this study contain considerable amount of chromium. Addition of chromium causes some changes in Fe-Ni-Al ternary system. Fig. 17 shows the calculated pseudo-ternary Fe-Ni-Al phase diagrams with the addition of 1 wt.%, 2 wt.%, 3 wt.%, and 7 wt.% Cr. Generally, by increasing chromium content, the two-phase region of BCC_A2 and BCC_B2 shrinks at first but for nickel content of higher than 25 wt.% it expands. In other words, addition of chromium promotes the increase of coarsening resistance by either its dissolution into the ferrite matrix or precipitates. In Fe-Ni-Al alloys with higher amount of nickel (higher than 25 wt.%). Addition of chromium depresses the coarsening resistance and promotes the formation two-phase (BCC_A2 + BCC_B2 or α1 + α2) region. Since chromium has an extended solubility in austenite and ferrite phases, it is expected that the diffusion in α1 and α2 phases in Fe-Ni-Al-Cr system would be faster than that in the other systems since the melting temperature of α1 and α2 phases drops by increasing the dissolved chromium content. This can be explained by a general rule that the atomic mobility in some phases is increased by an alloying element which lowers the melting temperature. Precipitation or growth of the chromium carbides due to exposure of the aluminized sample to carburizing environment causes decrease in dissolved chromium in α1 and α2 phases and thus the decrease in atomic mobility of these phases and it slows down the diffusion.

Phase breakdown in 6 months exposed sample occurred in saturated α2 which its aluminum content in lower than Ni and Fe. This means that Al-low side of the phase can remain stable if the extra Ni atoms are accommodated either by occupying the Al-sites (NiAl and FeAl antisites) or creating vacancies at the Al-sublattice (VAl). For α2 phase with high nickel content (+25 wt.%), the dissolved chromium accelerates saturation and decomposition of α2 phase, however, for alloys with lower nickel content, dissolved chromium delays the α2 breakdown. The nickel content of α2 phase at the second layer of the 6-month exposed sample is at the edge of the critical point (~24.5 wt.%).
which makes it very sensitive to a local chemical composition fluctuation. A small increase in Ni content would lead to breakdown of the $\alpha_2$ phase. This can be seen at the vicinity of the boundary of second and third layer of reaction zone which forms a thin layer of dual phase region of $\alpha_1 + \alpha_2$ at the boundary of second and third layers.

Figure 17 Isothermal phase diagram of pseudo-ternary Fe-Ni-Al-Cr system for (a) 1 wt.% Cr, (b) 2 wt.% Cr, (c) 3 wt.% Cr, and (d) 7 wt.% Cr.
By increasing the time of exposure from 6 months to 24 months, the thickness of the third layer composed of $\alpha_2$ with high nickel content (+50 wt.%) increases from 23 $\mu$m to 28 $\mu$m. Subsequently the thickness of the second layer which is completely decomposed to $\alpha_2$ and $\alpha_1$ decreases.

Additionally, exposure to the industrial carburizing environment induces surface cracks in variety of sizes and by increasing the time of the exposure, the number density of these cracks, their widths, and their lengths increase. By formation of the cracks, $\alpha_2$ acts as an aluminum reservoir for alumina. Aluminum in $\alpha_2$ phase migrates to the surface cracks to form alumina and protect the coating. Migration of the aluminum atoms from $\alpha_2$ phase creates vacancies at the Al-sublattice ($V_{Al}$).

$\alpha_2$ phase at second layer of 6-months exposed sample (before phase breakdown) is Al-low part of (Fe,Ni)Al-B2 phase. Diffusion of the aluminum to cracks surface adds Al-sublattice vacancies ($V_{Al}$) to already existent $V_{Al}$ and/or antisites Fe$_{Al}$ and Ni$_{Al}$. Bradley and Tylor inferred that on the Al-low side, the presence of vacancies leads to a reduction in lattice parameter since the smaller Ni atoms occupy the Al-sublattice ($r_{Ni} = 1.24 \text{ Å}$ and $r_{Al} = 1.43 \text{ Å}$)[]. Formation of the dual-phase regions ($\alpha_1+\alpha_2$) at vicinity of the cracks for 6 months exposure sample can be explained by the fact that increase in density of vacancies and reduction in lattice parameter would lead to stability of $\alpha_2$, $\alpha_2$ dual phase, atom mobility, and diffusion in the $\alpha_2$ phase and they accelerate the decomposition of the phase into $\alpha_1 + \alpha_2$.

### 4.2.6. Conclusion

Carburizing pack-aluminized RA330 stainless steel causes formation of a multilayer reaction zone. The reaction zone has 4 layers consists of: 1) a thin alumina layer at the outer surface, 2) $\alpha_2$ phase (in as-aluminized and 6-month exposed samples) or $\alpha_1$+ $\alpha_2$ (in 24 months exposed sample), 3) $\alpha_2$ phase and carbides, and 4) sigma phase and $\alpha_2$ phase.
Addition of alloying elements like chromium in the samples used for this study (> 25 wt.% Ni in the coating) accelerates the decomposition of the $\alpha_2$ phase to $\alpha_2$ (Ordered BCC_B2) and $\alpha_1$ (disordered BCC_A2) phases at the second layer of the reaction zone. This phase decomposition may weaken mechanical properties of the coating at the high temperatures by formation of $\alpha_1$ phase in spinodal-like microstructure.

By increasing the time of exposure, the number density of the cracks, their width, and their lengths increases. The migration of aluminum from ordered $\alpha_2$ phase to crack surface and formation of protective alumina layer causes increase in Al-sublattice vacancies and subsequently, they would increase diffusion and acceleration in $\alpha_2$ decomposition.

Surface aluminizing can extend service life of RA330 austenitic stainless steel by formation of a multilayer reaction zone which its ordered $\alpha_2$ phase provides aluminum reservoir for formation of protective alumina layer at the surface and crack’s surface and also by enhancing mechanical properties of the coating at high temperature by formation of $\alpha_1$ phase.

4.2.7. References

Chapter 5: Hot-Dipping Process

5.1. Microstructural Evaluation of Hot-Dip Aluminizing of RA330 Austenitic Stainless-Steel

5.1.1. Abstract

Austenitic stainless steel RA330 is a high temperature corrosion resistant alloy which is widely used as furnace alloys and fixtures in heat treatment industries. Aluminizing is an effective method to enhance the high temperature oxidation and carburization resistance of nickel-based alloys. This paper focuses on evaluation of the final microstructures of as-dipped aluminized and post heat-treated aluminized RA330 stainless steel. In addition, the preliminary analysis of microstructure of as-aluminized RA330 will be presented. These samples were characterized using optical and scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), and electron backscatter diffraction (EBSD). It was found that Fe$_2$Al$_5$, Fe$_4$Al$_{13}$, and Cr$_7$Al$_{45}$ intermetallic phases were formed at reaction zone of the as-dipped sample, however, heat treatment caused the dissolution of all Fe-Al, Cr-Al intermetallic phases existing prior to heat-treatment and formation
an ordered $\alpha_2$ phase with BCC which enhances the mechanical properties of the aluminized RA330 at elevated temperatures.

5.1.2. Introduction

Extending the service life of heat-treating furnace components and fixtures is one of the highest demands in heat-treating industries and other high temperature applications. These alloys are typically manufactured using Ni-based alloys. Nickel aluminides and iron aluminides because of their high melting point (1911 K), compact crystal structure, and excellent corrosion resistance at high temperature, are potential candidate for high-temperature applications. Stainless steel alloys are widely used as a more economic substitute in high temperature anti-corrosion applications such as fixtures inside the high temperature furnace. As a result, without the use of protective surface treatments, degradation mechanisms could lead to catastrophic failures, resulting in complete system shutdown. Many of the fixtures fail within one year of exposure in high temperature carburization atmospheres [1, 2].

Hot-dip aluminizing is one of a versatile and economical techniques to aluminize steel. Hot-dip aluminized steels are produced by immersing steel substrates into a molten Al or Al-Si bath, followed by post heat-treatment to alloy the Al coating over the steel substrate through interdiffusion of aluminum, iron, and other alloying elements and formation of Fe-Al intermetallic phases. A thin aluminum oxide layer formed on top of the coating is believed to act as a diffusion and thermal barrier, enhancing the corrosion and thermal resistance [3-5]. The first study on Fe-Al alloys as coating alloys was investigated by Heumann et al. by hot dip aluminized pure iron sample [4]. They observed a brittle intermetallic compound with irregularly grown columnar shape elongated along its orthorhombic [001] directions [6, 7] forms as the major phase in the reaction layer below the aluminum oxide layer which is nowadays known as the $\eta$-Fe2Al5 layer. The
chemical composition of this irregularly grown phase at the interface of Fe substrate composition was attributed to stoichiometry of bulk Fe2Al5 sample measured by Schubert [8].

The nature of these intermetallics including η-Fe2Al5 determines the mechanical and physical properties of the final product, such as oxidation and carburization rates, mechanical properties, and corrosion resistance [9, 10]. Therefore, designing the dipping process to obtain the favorable final microstructure to satisfy the properties of the part is critical. However, an unambiguous identification of the final microstructure of as-dipped parts is a difficult essential for designing the aluminizing process for different applications. Although, characterize and understand these phases has been subject of extensive investigation in past decades [9-22], there is still a fair amount of confusion on the composition and microstructure of the final product.

The Fe–Al binary system is one of the basic and important binary systems from which vast practical Fe-based alloys have stemmed. The body-centered cubic solid solutions that are stable over a wide range of the Fe rich portion have garnered extensive attention in various structural and functional applications [23-27]. Intermetallic compounds in the Al-rich portion have also played a key role in the surface coating of steels, of which one practical application is hot-dip aluminized and Al-added galvanized steels. Aluminized steels are used practically as alternatives to galvanized steels because of their superior heat and oxidation resistance [28].

The η-phase (Fe2Al5) is known to play an essential role in aluminized steels, because the η phase is the main constituent phase in the coating layers of aluminized steels and it instantaneously forms on the steel substrate of steels. A precise understanding of the phase stability and mechanical properties of the η phase is therefore indispensable to better design aluminized and Al-added galvanized steels.
Nowadays the term of ‘Fe2Al5’ is commonly used to indicate the η-phase [7, 29, 30] however, the term with integer stoichiometry incorrectly suggests a well-defined composition and the name Fe2Al5+x is more accurate to address η-phase. Several models have been put forth by researchers to predict first phase nucleation and subsequent phase formation [49-51]. Burkhardt et al. demonstrated that with sparsely occupied 4b and 8f Al sites, the η-phase (Cmcm space group) with orthorhombic crystal structure is partially disordered [31]. Burkhardt suggested a structure model for η-phase based on diffraction data from a single crystal specimen result in a formula Fe2Al5.6 corresponding to 73.7 at.% Al [31]. However, recent research of this phase are not entirely consistent with the refinement by Burkhardt et al [31]. Recently, Becker et al. modified the existing model by reporting that not only Al but also Fe atoms occupy the c-axis chain sites in the η phase [32, 33], unlike the expectation from the crystal structure model by Burkhardt et al. [15]. Van Alboon et al. was the first who provided experimental evidence obtained from atom probe tomography measurements which support existence of high Al contents (> reported homogeneity range) in η-phase at low temperatures [34]. Very recently, a few research groups have independently provided experimental evidence for formation of low-temperature ordering structures that have crystal structures based on the η phase [30, 33, 35-37]. On the Al-rich side of the solubility range, a η'-Fe3Al8 phase was identified to form in alloys around the 72.7 at. % Al. Its monoclinic crystal structure was identified from electron microscopy and selected area electron diffraction (SAED) data [35] and refined on the basis of powder X-ray diffraction (P-XRD) data [33]. Moreover, it appears from some other reported SAED patterns [38, 39] that beside η' at least three low-temperature long-range ordered phases, η", η"m, and η"m, exist and from theoretically considered superstructures [30, 40, 41].
Eggeler et al. reported formation of another thin layer that separates the \( \eta \)-phase at the interface of hot-dipped Fe sample from the top aluminum layer which is now known as \( \theta \)-phase [42]. Based on Grin et al. [43] and Black et al. [44], the actual stoichiometry of the monoclinic \( \theta \)-phase with space group C2/m is Fe4Al13, however, the term of “FeAl3” has been commonly used for addressing \( \theta \)-phase in the coating literature [45-48] and references of binary phase diagrams [49]. It is also known that carbon has very low solubility in alumina. In that case, aluminizing could be a good method for protecting high temperature structural alloys. The protection is achieved by enriching the surface layer of the aluminum through diffusion mechanisms. Aluminum element reacts with the substrate material to form secondary phases and the intermetallic that act as a reservoir of scale formers during the service life [7].

While the objective of this research is developing and growing aluminide intermetallic phases as aluminum sources for contentious formation of alumina (diffusion barrier) on the surface of high nickel content steel, the focus of the present work is to characterize the microstructure evolution of austenitic RA330 stainless steel after hot-dip aluminizing and post heat-treatment processes. By the consistent analysis of information from experimental data such as the composition and crystal structure, combined with EBSD phase analysis, unambiguous conclusions have been obtained about the intermetallic phases that appear in hot-dip aluminized RA330 steel.

5.1.3. Materials and Processes

The hot dip aluminizing process were performed on normalized RA330 stainless steel. The samples investigated in the present study were cut out to rods with 0.5 in diameter and 5 in length. This steel was selected for its widespread use in high temperature applications, for example heat-treat furnace and gas turbine components (where it is used because it has superior properties at
high temperatures like thermal fatigue and creep resistance). The chemical composition of the RA330 is given in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIN</td>
<td>18.0</td>
<td>34.0</td>
<td>1.0</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Balance</td>
</tr>
<tr>
<td>MAX</td>
<td>20.0</td>
<td>37.0</td>
<td>1.5</td>
<td>0.08</td>
<td>2.0</td>
<td>0.03</td>
<td>0.03</td>
<td>1.0</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Stainless steel rod specimens with 8.25 in² surface area were ground using SiC grinding paper with 120, 320, and 600 grit then were cleaned by acetone, methanol, and DI water. Three of the specimens were drilled, hanged by stainless steel wires and hot dipped into the pure aluminum bath. The chosen alloy for experiment has high nickel content thus at the experiment temperature, 900 K, it is still austenite.

Drilled samples were hanged by a wire and dipped in pure molten aluminum (99.9%) at 900 K for 10 minutes. The thickness of the casted coat on the RA330 parts is not perfectly homogeneous and it is changing from one case to another. A lot of factors like speed of removing parts from the furnace, size, and geometry of the parts, etc. affect the thickness of the coatings. Aluminum transported rapidly to the surface, forms intermediate phase layers with the base alloy. The growth rates of intermediate layers are controlled by the interdiffusion of aluminum and base alloy components, (Iron, Nickel, and chromium) through the coating layers.

The samples were sectioned, and the coatings were metallographically prepared. Coating-substrate assemblies were analyzed in the as-plated condition with samples mounted in cold-setting epoxy and prepared using standard metallographic techniques. For cross-sectional analysis, grinding was conducted with successively finer silicon carbide papers from 120 to 600 grit. Polishing steps included 6 and 1 µm diamond pastes, 0.3 mm alumina suspension, and 0.05 mm colloidal silica. The layers thickness was estimated by the microscopic methods. The surface morphology and microscopic cross-section studies of the coatings were carried out using a scanning electron
microscope (JOEL 7000F) provided with a digital system of the image recording. Quantitative chemical analysis of the coatings was determined by means of energy dispersive X-ray method (EDS). Electron backscatter diffraction methods (Oxford), EBSD, were also used for phase analysis and microstructure examination of the deposited and heat-treated samples using phase information based on ICDD card standards (2000).

5.1.4. Results

Optical micrographs in figure 1 illustrate the overall microstructure of the reaction product at 670 °C after 10 minutes. The aluminum and stainless steel interface is easily recognizable. The interface layer has a cellular-dendritic characteristics, where the coarsened dendrites have overlapped and formed a massive block of intermetallic phase at the interface. It is evident in figure 1, it is almost impossible to distinguish different phases within the interface layer and therefore, the SEM micrographs are presented in figure 2 to clearly show the formation of at least two phases at the interface layer.

Figure 1 Optical image of as-dipped aluminized RA330 stainless steel

Figure 2 shows SEM cross section photomicrographs of the sample hot dipped at 670 °C for 600 seconds (10 minutes). Based on figure 2, the diffusion zone consists of 5 different layers. The first layer of the diffusion zone is a thin oxide layer at outer surface of the sample. The second layer,
next to the oxide layer toward the coating-substrate interface, consists of two phases: light gray needle like precipitated phase in a medium dark gray aluminum matrix.

By distancing from the outer surface, the phase fraction of the precipitated phase increases at first but at close distance from the interfacial layer decreases. The third layer is located between the two-phase layer aluminum matrix (layer 2) and interfacial zone (layer 4 and 5). At this layer, the amount of light gray precipitated phase is negligible, however, two different larger island-shape phases in two different shape types and size are present. Figures 2(c) and 2(d) show a magnified views of the rectangular area in Figure 2(b). It is clear that the interfacial layer can be divided into two layers: (a) layer 4: a tongue-like morphology toward the aluminum at the interface with
average thickness of 3-5 µm and (b) layer 5: a coarsened cellular-dendritic characteristics morphology with thickness of 9-13 µm, despite the fact that the contrast between these two phases is very small and makes it very difficult to distinguish them on optical microscopy or even on scanning electron microscopy at lower magnifications. Figure 3(a) shows a magnified views of red rectangular zone in figure 2 (b). The component distribution along the cross sectional scanning line is shown in Figure 3(b). The chemical compositions of layer 4 and layer 5 exhibit clear differences. The layer 5, near RA330 stainless steel, has a lower Al content than layer 4 and its Al content increases by distancing from the interface. while Al contents decreases by closing distance to interface in layer 5, Ni and Fe contents increase which causes higher amount of nickel in compare with chromium in this layer. In contrary to layer 5, the chromium content at layer 4 is higher than nickel content despite the chromium contents in both layers are very similar.

Based on EDS analysis and measurements, phase identification was performed to identify the phase microstructures of the layers 1-4 in Figure 3(b). Table 2 represents the chemical compositions of layer 4 and layer 5 obtained by taking account of ZAF correction of EDS measurements.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Chemical Composition (atomic%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>4</td>
<td>79.7</td>
</tr>
<tr>
<td>5</td>
<td>72.2</td>
</tr>
</tbody>
</table>

Based on composition profiles and EDS results, the interfacial microstructures are composed of $\theta$-Fe$_4$Al$_{13}$ (FeAl$_3$) as the dominant phase of interface zone at vicinity of Aluminum and the tongue-like $\eta$-Fe$_2$Al$_{5+x}$ phase (Fe$_2$Al$_5$) as minor phase at interface generated by the solid/liquid diffusion couple between solid RA330 stainless steel and liquid aluminum, according to Fe-Al phase diagram [50].
In order to more accurately identify the interfacial intermetallic phases, further crystallographic information was obtained by EBSD phase mapping merged with EDS measurements.

Figures 4 and 5 compile the representative results obtained from the SEM, EBSD, and EDS phase mapping results merged with EDS measurements and band-contrast (in gray scale) of as-dipped aluminized RA330 stainless steel specimen at two different magnifications. The low magnification EBSD, Figure 4, shows three minor phases formed in aluminum coating: (a) \((\text{Fe,Cr,Ni})\text{Al}_9\) phase (pink color) with monoclinic crystal structure and \(\text{P21/c}\) space group forming thought the aluminum coating matrix, (b) an Island-shape chromium aluminide phase (orange color) with monoclinic crystal structure and \(\text{C2/m}\) space group at vicinity of the interfacial zone, and (c) small island-shape \(\text{Fe}_4\text{Al}_{13}\) phase with monoclinic structure and \(\text{C2/m}\) space group.

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In Figure 3, EDS map analysis of as-dipped aluminized RA330 stainless steel:

- **2**: \(\text{Al} \text{(FCC)}\)
- **3**: \(\text{Al} \text{(FCC)}\)
- **4**: \(\theta\text{-Fe}_4\text{Al}_{13}\)
- **5**: \(\eta\text{-Fe}_2\text{Al}_5\)

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**Figure 3.** EDS map analysis of as-dipped aluminized RA330 stainless steel
Figure 4: (a) EBSD map analysis merged with bond contrast and (b) EDS Map analysis of as-dipped aluminized RA330 stainless

Figure 5 shows the interfacial zone at higher magnification. Generally, the EBSD mapping results of interfacial layer formed in liquid/solid reaction appears to be in good agreement with the microstructure that EDS measurements suggested which indicates the diffusion zone consists of 5 layers: 1) a thin alumina layer at surface, 2) a thick aluminum coating with (Ni,Fe)Al₉ precipitates, 3) a layer of aluminum matrix with Cr₇Al₄₅, Fe₄Al₁₃ and (Ni,Fe)Al₉ phases, and a two-layer interfacial zone (layer 4 and 5).
The two intermetallic layers at interface formed in solid/liquid reaction at the interface, namely, a porous non-uniform layer bordering the aluminum coating (green color, layer 4) and a tongue-like grown layer immediately adjacent to the RA330 stainless steel (Red color, layer 5).
The layer 4 of diffusion zone (green color), as EDS phase analysis predicted, is $\theta$-Fe$_4$Al$_{13}$ with monoclinic crystal structure and C2/m space group. However, the most noticeable difference between the EBSD and EDS results is the characteristic of the first layer of interfacial zone at vicinity of the stainless steel (red color phase, layer 5). Based on EBSD map analysis, the crystal structure of layer 5 which grown toward aluminum is monoclinic crystal structure which is similar to the $\theta$-Fe$_4$Al$_{13}$ phase. These results are in contrary with the EDS phase analysis that based on chemical composition characterized this phase as $\eta$-Fe$_2$Al$_{5+x}$ with orthorhombic crystal structure. Also, the grains of this tongue-like phase are longer but narrower than $\theta$-Fe$_4$Al$_{13}$ phase. As figure 5 shows, the bottom of Cr$_7$Al$_{45}$ phase (Orange color), formed in layer 3 of diffusion zone is covered with small amount of two different phases: (a) (Fe,Ni,Cr)Al$_{19}$ and (b) CrAl$_5$ ($\eta$-(Fe,Cr)$_{25}$Al$_{129}$).

5.1.5. Discussion

In the present investigation, the RA330 stainless steel was immersed into a molten aluminum bath maintained at 670°C. At the instant two events are expected to occur where the RA330 stainless steel contacted the molten Al: (a) solidification of liquid aluminum on the surface of the stainless steel due to rapid cooling and (b) dissolution of alloying elements from stainless steel base metal due to outward diffusion of elements to establish equilibrium. As the heat transfer continues, a part of the solidified Al layer remelts. This melting is the result of solute transport across the interface rather than thermally driven melting. Such melting has been reported to occur during welding of dissimilar metals by Chatterjee et. al [50]. Dissolution or melting occurs because the composition at the interface is far from equilibrium. Furthermore, because the dissolution process continues, a concentration profile develops at the interface. The concentration of alloying elements at a particular distance from the solid/liquid interface is defined by two factors: (a) the rate of solute
enrichment because of the dissolution process and (b) the rate of solute reduction from the interface because of the diffusion process.

In this study, despite Immersing stainless steel into molten aluminum develops the concentration profile of Fe, Cr, Ni, and Al ahead of the solid/liquid interface, the concentration profile of Ni has not been taken into account at first to slightly simplify the investigation. However, the effect of nickel concentration will be discussed later in this paper. Figure 8 shows the ternary phase diagram of Fe-Cr-Al in absent of nickel at 670 °C. At the Al-rich side of the ternary phase diagram, by diffusion Fe and Cr, two-phase equilibrium of Cr$_7$Al$_{45}$ + Liquid Al formed. Fe and Cr has limited solubility in liquid Al at 670 °C and by further diffusion of Fe and Cr, three-phase equilibrium of Fe$_{4}$Al$_{13}$ + Cr$_7$Al$_{45}$ + Liquid Al is established.

Figure 8. Al-Cr-Fe ternary phase diagram at 680 °C
A schematic concentration profile ahead of the stainless steel substrate is shown in Figure 9. $C_m$, $C_s$, and $C_\infty$ are metastable concentration (at interface), equilibrium concentration, and concentration far from the interface, respectively. Higher concentrations (higher than the equilibrium concentration) of elements are expected because the system is under nonequilibrium conditions. Because the liquid Al is supersaturated with elements, a strong driving force for nucleation of intermetallic phases exists. The process of nucleation of solid particles from the melt is a complex phenomenon because the energy barrier associated with the nucleation is required to be overcome by supersaturation of liquid with respect to Fe, Cr, or Ni. The higher the supersaturation, the better the chance of survival of newly born nuclei. Therefore, it is likely that a greater number of fine nuclei form near the interface.

Notably, not only thermodynamic aspects but also kinetics plays a critical role in the nucleation and growth of intermetallic phases. The $\eta$-Fe$_2$Al$_5$ phase enthalpy is more negative than that for the $\theta$-Fe$_4$Al$_{13}$ phase [10], which indicates that the interatomic bonds in $\eta$-phase are stronger than those
in θ-phase. Kinetically, the η-phase is more strongly favored because of its open structure and lower ΔHf.

The solidification temperature of the intermetallic phases is greater than 680°C, and they are expected to nucleate and attempt to grow. Theoretically, only nucleation of Fe₄Al₁₃ and Cr₇Al₄₅ phases are expected to occur in the liquid aluminum at solid/liquid interface according to the ternary equilibrium diagram in absence of nickel, figure 8. By assuming dipping process is in equilibrium, the final microstructure of the region 1 is predicted to include Fe₄Al₁₃, Cr₇Al₄₅, and aluminum with slight amount of Fe and Cr solutes. The volume fractions of these phases in final microstructure are predicted to be 0.14, 0.24, and 0.62, respectively.

It is well known that among five intermetallic compounds exist in the Fe-Al binary system, usually only two, namely η-Fe₂Al₅⁺ₓ and θ-Fe₄Al₁₃ (or FeAl₃), form intermetallic layers during interaction of iron and its alloys with aluminum, however, there are some ambiguities in formation of η-phase, where the reaction temperature is below the lowest eutectic temperature (655°C) in the Al-Fe system [9]. In this study, in addition to formation of θ and Cr₇Al₄₅ phases which were also theoretically predicted, another phase was observed at solid/liquid interface at region 1. The chemical composition of this phase obtained from EDS analysis is similar to that of the η-Fe₂Al₅ phase at process temperature, however, the crystal structure of this phase obtained by EBSD is closer to monoclinic than orthorhombic which is crystal structure of η-Fe₂Al₅ phase. This occurrence can be explained by the recent modification of Fe-Al phase diagram at low temperatures. Figure 10 represent the most recent Fe-Al modified phase diagram by Homanda et al. [37].

Air Cooling of as-dipped aluminized stainless steel specimen causes temperature and cooling rate profiles ahead of the interface. The region at immediate vicinity of the base metal/aluminum
interface experiences a lower cooling rate which allows a slow path through low temperature transformation range which results in the formation of low-temperature ordering structures that have monoclinic crystal structures. However, at regions further away from the interface (region 2), cooling rate is higher and the microstructure of the cooled coating at this region is similar to the microstructure of the coating at hot-dipping temperature. In the other words, at time of dipping, η- and θ- phase forms at the liquid/solid interface, however during the cooling processes, η-phase transform to low temperature ordering structures that have monoclinic crystal structures which causes the incoherency between the EDS and EBSD results.

![Image of Fe-Al phase diagram](image-url)

Figure 10 Experimentally determined Fe-Al phase diagram: (a) overall view and (b) enlarged low-temperature section.

The unit cell dimensions of θ- and η- phases and unit cell dimensions and atomic coordinates of low-temperature η-phase derivatives which have been used for phase characterization are given in table 3 and table 4, respectively.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Monoclinic</th>
<th>Orthorhombic</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ-Fe₄Al₁₃ [51]</td>
<td>C2/m (12)</td>
<td>Cmcm (63)</td>
</tr>
<tr>
<td>Space group</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>15.4965</td>
<td>7.6559</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.0526</td>
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<td>c (Å)</td>
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<td>4.2184</td>
</tr>
<tr>
<td>β (deg.)</td>
<td>107.694</td>
<td></td>
</tr>
<tr>
<td>η-Fe₂Al₅ [31]</td>
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<td>b (Å)</td>
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<tr>
<td>c (Å)</td>
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<tr>
<td>β (deg.)</td>
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</table>
Despite characterizing the monoclinic crystal structure of this phase, results obtained from EBSD analysis merged with EDS was not conclusive for determining which low temperature η-derivatives (η’, η’") this phase accurately belongs to.

<table>
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<td>Fe1</td>
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<td>0</td>
<td>0</td>
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</table>

For investigating the effect of nickel content in final microstructure of the as-dipped stainless steel, the trinary diagrams of Fe-Cr-Al with four different Ni content have been illustrated in figure 11. At Al-rich corner of the ternary phase diagrams, nickel enrichment causes extend in the stability range of multiphase regions (blue circle) at vicinity of Al-Cr line which make them to be stable at higher Al content. In other words, addition of nickel causes multiphase regions with Ni and Cr wt.% <30 shift toward Al corner of the ternary phase diagram (shift to down and right).
Theoretically, immersing austenitic RA330 stainless steel in pure aluminum and migration of Ni alongside of Fe and Cr atoms at 680 °C result in formation of FeNiAl₉ phases in addition to liquid aluminum with Fe, Ni, and Cr solutes, Fe₄Al₁₃, and Cr₇Al₄₅ phases which are already predicted to form in absence of Ni. Thus, a multi-phase equilibrium of liquid aluminum, Cr₇Al₄₅, Fe₄Al₁₃, and FeNiAl₉ with phase fractions of 0.54, 0.26, 0.15, 0.05 at region 1 is expected to occur in the liquid state at 680 °C.

Even though the quantitative phase predictions are differed from the experimental results, the theoretical prediction is relatively in agreement with the experimental results of microstructure analysis of the region 1. The differences between the experimental microstructure and theoretical prediction are the presence of unpredicted CrAl₅ phase in final microstructure, and formation of...
η-phase at the immediate vicinity of the liquid/solid interface which, as discussed before, results in formation of low-temperature ordering structure during the solidification.

The formation of an intermetallic aluminide layers at the solid/liquid interface affects the concentration profile of the area ahead of the aluminide layer. The formation of intermetallic phases at interfacial zone at region 1, reduces the supersaturation which causes the dissolution to continue. The dissolved elements that do not participate in the nucleation of intermetallic phases migrate away from the interface. By distancing from the interface, the concentration of Ni, Fe, and Cr elements decreases.

Aluminum base in region 1 (third layer of diffusion zone) and region 2 (second layer of diffusion zone) has a continuous gray Al matrix (figure 2), in contrast with the bright Al-based intermetallic phases. The details of these features are shown in the SEM micrographs presented in figure 2, and EDS measurements and EBSD map analysis in figures 3-5. Intermetallic phases forming during aluminum hot-dipping of steels can be classified two categories based on their morphologies: polygonal intermetallic phases and acicular intermetallic phases. SEM–EDS analysis indicates that polygonal morphology corresponds to the Cr-Al intermetallic phase such as Cr$_7$Al$_{45}$ and acicular morphologies correspond to an Fe-Al intermetallic phases such as of Fe$_4$Al$_{13}$, Fe$_2$Al$_5$, and FeNiAl$_9$. These phases are present in the aluminum matrix throughout third layers of diffusion zone (end of region 1). As it can be seen in figure 4, there are several spherical nano-size precipitates within the Cr$_7$Al$_{45}$ phase which correspond to twining around the (001) planes of this phase [52].

Theoretically, at further distance from solid/liquid interface in liquid state at 680 °C, Cr$_7$Al$_{45}$ phase with negligible volume fraction of 0.006 is the only intermetallic phase dispersed in aluminum base at region 2. However, experimental microstructure analysis results obtained by EBSD-EDS indicate the only intermetallic that formed in region 2 is FeNiAl$_9$ which distributed in liquid.
Theoretical and experimental disagreement can be the result of nonequilibrium nature of dipping process. There are several factors related to experiment design that may alter the final microstructure and distribution and concentration of alloying elements of the hot-dipped sample, such as furnace type (induction or resistance), bath volume to specimen size, specimen removal speed, position of the sample in bath, etc.

5.1.6. Conclusion

In this study, hot-dip aluminizing austenitic stainless steel developed a five layers of reaction zone: (1) a thin alumina layer at the surface of the sample, (2) (Fe,Ni,Cr)Al₉ precipitates in aluminum matrix which contains the majority of the diffusion layer, (3) a multiphase layer with aluminum, (Fe,Ni,Cr)Al₉ precipitates, island-shape phase of Al₄₅Cr₇, and CrAl₅ phase formed at immediate boundary of Al₄₅Cr₇ islands and aluminum, (4) a porous layer of (Fe,Cr,Ni)₄Al₁₃ with monoclinic crystal structure next to layer 5, and (5) a continuous layer of tongue-shape monoclinic phase which is derivative of η-phase crystal structure at immediate vicinity of liquid/solid interface.

During hot dipping process, at the close distance from the stainless steel/coating interface, two different Fe-Al intermetallic phases formed: a) Fe₄Al₁₃ (θ-phase) with monoclinic crystal structure which typically forms during the hot dipping process of stainless steel and (b) Fe₂Al₅ (η-phase) with orthorhombic crystal structure which transforms into derivative of η-phase with monoclinic crystal structure after air colling the as-aluminized sample.

5.1.7. Reference

$Fe$ and Al$_5$Fe$_2$: First
–
NIUM MELTS BETWEEN 670 AND 800 degree C.


5.2. Evaluating the effect of Post Heat treatment on Hot-Dip Aluminized RA330 Austenitic Stainless-Steel Microstructure

5.2.1. Abstract

Austenitic stainless steel RA330 is a high temperature corrosion resistant alloy which is widely used as furnace alloys and fixtures in heat treatment industries. Aluminizing is an effective method to enhance the high temperature oxidation and carburization resistance of nickel-based alloys. This paper focuses on evaluation of the final microstructures of as-dipped aluminized and post heat-treated aluminized RA330 stainless steel. In addition, the preliminary analysis of microstructure of as-aluminized RA330 will be presented. These samples were characterized using optical and scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), and electron backscatter diffraction (EBSD). It was found that Fe$_2$Al$_5$, Fe$_4$Al$_{13}$, and Cr$_7$Al$_{45}$ intermetallic phases were formed at reaction zone of the as-dipped sample, however, heat treatment caused the dissolution of all Fe-Al, Cr-Al intermetallic phases existing prior to heat-treatment and formation an ordered α$_2$ phase with BCC which enhances the mechanical properties of the aluminized RA330 at elevated temperatures.
5.2.2. Introduction

Heat-treating furnace components and fixtures alloys are typically manufactured using Ni-based alloys [1-4]. Nickel aluminides because of their high melting point (1911 K), compact crystal structure, and excellent corrosion resistance at high temperature, are potential candidate for high-temperature applications [5, 6]. Application of stainless steel alloys is a more economic substitute for nickel base alloys in high temperature and anti-corrosion applications such as fixtures inside the high temperature furnace. However, without protective surface treatments, degradation mechanisms such as metal dusting could lead to catastrophic failures and resulting in complete system shutdown.

Hot-dip aluminizing has long been successfully used to form an aluminum coating on the surface of steel substrate to enhance the service property of base steels [7-9]. As surface of the base metal contacts the aluminum melt during the hot-dipping process, Al diffusés into steel to form intermetallic alloys. Due to crystal structures of these intermetallics and their high aluminum content, these intermetallics possess attractive high temperature properties such as thermal erosion resistance, corrosion resistance, and oxidation resistance. Oxidation of the aluminum layer on the surface of steel base, leads to formation of a thin protective alumina layer at the outer surface of the coating which protects the base metal and other layers of the diffusion zone.

The current work was one of a series study of surface modification of austenitic stainless steels to improve the properties such as resistance to high temperature oxidation and anti-aluminum corrosion by surface modification and coatings. This paper reports the effect of post heat-treatment on microstructure of hot-dip aluminized RA330 stainless steel.

5.2.3. Materials and Processes

The hot dip aluminizing process were performed on normalized RA330 stainless steel. The samples investigated in the present study were cut out to rods with 0.5 in diameter and 5 in length. This steel was selected for its widespread use in high temperature applications, for example heat-treat furnace and gas
turbine components (where it is used because it has superior properties at high temperatures like thermal fatigue and creep resistance). The chemical composition of the RA330 is given in Table 1.

5.2.3.1. Table 1: chemical composition of RA330 samples

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
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<td>0.04</td>
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<td>-</td>
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<tr>
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<td>Balance</td>
</tr>
</tbody>
</table>

Stainless steel rod specimens with 8.25 in² surface area were grinded using SiC grinding paper with 120, 320, and 600 grit then were cleaned by acetone, methanol, and DI water. Specimens were drilled, hanged by stainless steel wires and hot dipped into the pure aluminum bath. The chosen alloy for experiment has high nickel content thus at the experiment temperature, 900 K, it is still austenite.

Drilled samples were hanged by a wire and dipped in pure molten aluminum (99.9%) at 900 K for 10 minutes. The thickness of the casted coat on the RA330 parts is not perfectly homogeneous and it is changing from one case to another. A lot of factors like speed of removing parts from the furnace, size, and geometry of the parts, etc. affect the thickness of the coatings. Aluminum transported rapidly to the surface, forms intermediate phase layers with the base alloy. The growth rates of intermediate layers are controlled by the interdiffusion of aluminum and base alloy components, (Iron, Nickel, and chromium) through the coating layers. Hot-dipping process was followed by post heat-treatment of as-dipped samples in commercial resistance furnaces at 900 °C for 36 hours.

The samples were sectioned, and the coatings were metallographically prepared. Coating-substrate assemblies were analyzed in the as-plated condition with samples mounted in cold-setting epoxy and prepared using standard metallographic techniques. For cross-sectional analysis, grinding was conducted with successively finer silicon carbide papers from 120 to 600 grit. Polishing steps included 6 and 1 µm diamond pastes, 0.3 mm alumina suspension, and 0.05 mm colloidal silica.
The layers thickness was estimated by the microscopic methods. The surface morphology and microscopic cross-section studies of the coatings were carried out using a scanning electron microscope (JOEL 7000F) provided with a digital system of the image recording. Quantitative chemical analysis of the coatings was determined by means of energy dispersive X-ray method (EDS). Electron backscatter diffraction methods (Oxford), EBSD, were also used for phase analysis and microstructure examination of the deposited and heat-treated samples using phase information based on ICDD card standards (2000).

5.2.4. Results

The results from as-dipped and 36 hours post heat-treatment at 900 °C are given in figure 6 and figure 7. Figure 6 shows the SEM micrographs of as-dipped and heat-treated sample at different magnifications. SEM micrographs indicate that the diffusion zone with the average thickness of 45 µm, is continuous but its thickness varies along the baseline and consists of at least four different reaction layers, which differ in microstructure and gray level. First layer is oxide layer at outer surface of the heat treated sample. The second layer, next to the oxide layer consists of precipitated carbides at the grain boundaries of the matrix phase. The size and volume fraction of the second phase are not consistent throughout the second layer and they decrease by distancing from the outer surface. This layer accounts for most of the diffusion zone and its average thickness is 34 µm. At higher magnification, there is an extra layer at the heat-treated sample which has a coarsened microstructure with coexist of two phases of $\alpha_1 + \alpha_2$. The average thickness of this layer is 1.5 µm (layer #3). The fourth layer with average thickness of 5 µm has microstructure with coexist of carbides in matrix of a base phase. The fifth layer of the diffusion layer which is located at the immediate coating/substrate interface is the second major layer with thickness of 9 µm. This layer consists of a needle-shape phase in a second smooth base phase.
Figure 7 compiles representative results obtained from EBSD and EDS measurements for heat-treated aluminized sample. Figure 7a shows the EBSD phase mapping merged with EDS mapping obtained for heat treated aluminized sample. Based on this figure, the diffusion zone of as-dipped RA330 consists of 5 different layers. The first layer of the diffusion zone is a thin oxide layer at outer surface of the sample. The second layer, next to the oxide layer toward the coating-substrate interface, consists of two phases: light gray needle like precipitated phase in a medium dark gray aluminum matrix. The diffusion zone after post heat treatment also consists of 5 layers. Figure 7a confirms the sigma phase (green) and \( \alpha_2 \) (bright red) are constituent phases of the fifth layer of the reaction zone. Chromium carbides (dark blue) are mostly precipitated at grain boundaries of the substrate or formed in a matrix of \( \alpha_2 \) phase at the fourth layer of reaction zone. On account of the facts that \( \alpha, \alpha_1 \), and \( \alpha_2 \) phases have same bcc crystal structure and their bond contrast are very low, EBSD results alone cannot distinguish these three phases. However, merging EBSD results with EDS measurements provides the opportunity to differentiate these phases. \( \alpha \)-phase (orange) is the major phase at the second layer where most of the cracks are located. The average grain size of the \( \alpha \)-phase is considerably larger than grains at other part of the reaction zone. Austenitic RA330, chromium carbide, and sigma phase appears in Yellow, dark blue, and green respectively. The chemical composition of the diffusion zone measured by EDS along the line indicated by the yellow arrow in Figure 7c. Complementary to the EBSD result, the Al concentration of 600-700 cps corresponds to the \( \alpha_2 \) phase as the dominant component. The light red (needle shape) phase near the interface with the steel at fourth layer and light red matrix phase in third layer of diffusion zone and orange base phases in third layer (Figure 7a) were identified by automated EBSD to have similar structure as \( \alpha_2 \)-phase.
Coincide with SEM microstructure predictions, primarily EBSD results indicates the second and third layer’s base phase have BCC crystal structure but different lattice parameters. EBSD map analysis is not able to distinguish the light red and orange phases as two separate phases since they both share the same cubic crystal structure and group name, and constituting elements of Al, Ni, Cr, and Fe.
Figure 7 EBSD analysis coupled with EDS map, Eds map, and EDS line analysis of the major elements of 36-hour heat-treated hot-dipped aluminized sample at 900 °C
However, merging EBSD results with EDS measurements provides the more accurate results and more information regarding the microstructure of the reaction zone. EBSD results merged with EDS measurements could distinguish the later phases.

Figure 7b shows the EDS map analysis of the sample. Fig. 7b clearly shows that nickel is the major constituent elements in the needle-shape phase in fourth layer’s base phase (light red phase in figure 7a) and iron and chromium concentrations are very low in compare with nickel and aluminum concentrations. The other phase of fourth layer, near the steel/coating interface, (green phase in Figure 7a) has higher iron and chromium concentration and have tetragonal crystal structures with P4_2/mnm space group.

Crystal structure of the base phase, \( \alpha_2-(\text{Ni,Fe})\text{Al} \), in third layer of diffusion zone has also bcc crystal structure with nickel and aluminum as its main components. The second layer consists of \( \alpha-(\text{Fe,Ni,Cr})\text{Al} \) phase with bcc crystal structures and cubic \( \text{Cr}_{23}\text{C}_6 \) precipitates with Fm\( \text{m} \)m space group.

### 5.2.5. Discussion

In compare with as-dipped aluminized RA330 stainless steel, heat treating aluminized sample leads to dissolution of \( \theta-, \eta-, \text{Cr}_7\text{Al}_{15}, \text{CrAl}_5, \text{FeNiAl}_9 \) intermetallic phases at diffusion zone and microstructure evolution of reaction zone of the sample. The reaction zone of the heat treated sample contains four layers of (1) a thin alumina layer at surface, (2) \( \alpha-(\text{Fe, Ni})\text{Al} \) phase with bcc crystal structure, (3) \( \alpha_2 \) (bcc) and \( \alpha_1 \) (bcc), (4) \( \alpha_2-(\text{Fe, Ni}) \) and carbides, and (5) sigma phase and \( \alpha_2 \) (bcc) at the coating/substrate interface. Also, heat-treatment of hot-dipped aluminized RA330 stainless steel caused an increase in volume fraction of and size of chromium carbide precipitates at the coating (figure 6).
Phase decomposition of $\alpha_2$-(Fe,Ni)Al occurs mainly at the third layer of the heat-treated sample in saturated $\alpha_2$ phase. The coarsening growth kinetics of the $\alpha_2$ precipitates, in general, followed the modified LSW theories for diffusion-controlled coarsening [10-13]. At the third layer of the heat-treated sample $\alpha_1$ precipitates in matrix of $\alpha_2$. At the beginning of precipitation, it is expected to have a coherent interface between these two phases since the lattice parameter of these is very similar. Over the course of time the precipitates become aligned with the matrix. A further exposure time causes aging and promotes the increase in size of precipitates.

Phase decomposition of $\alpha_2$-(Fe,Ni)Al into $\alpha_2$-(Ni,Fe)Al and $\alpha_1$-(Fe) has been studied in detail by Bradley, Kiuchi, Tylor, and Hao et. al. [14-18] The miscibility gap in Fe-Ni-Al system results in the breakdown of a high temperature bcc phase $\alpha_2$ into two bcc phases of $\alpha_1$ (Fe-rich disordered bcc phase) and $\alpha_2$ (intermetallic NiAl-rich ordered bcc phase) with B2 (CsCl) crystalline structure. The miscibility gap in the broad bcc phases extends from the Fe corner to the NiAl in Fe-Ni-Al system. Fig. 12 shows the phase diagram of Fe-Ni-Al system. According to the ternary diagram, shown in fig. 13, the precipitation reaction can take place in two ways [14, 17]:

\[
\begin{align*}
\alpha_2 & \rightarrow \alpha_1 + \alpha_2 & \text{or} & & \text{BCC}_B2 & \rightarrow \text{BCC}_A2 + \text{BCC}_B2 \ #2 \\
\alpha_1 & \rightarrow \alpha_1 + \alpha_2 & \text{or} & & \text{BCC}_A2 & \rightarrow \text{BCC}_A2 + \text{BCC}_B2
\end{align*}
\]

That is, the supersaturated solid solution of either the BCC$_B2$ ($\alpha_2$) or BCC$_A2$ ($\alpha_1$) phase can produce a mixture of the ferrite $\alpha_1$ and the ordered intermetallic $\alpha_2$ phase. Ordered intermetallic phases with BCC$_B2$ crystal structure can promote an increase in the mechanical strength and thus a better performance at high temperature, however, formation of ordered $\alpha_1$ (ferrite Fe) may weaken the mechanical properties of $\alpha_2$ at service temperature and become a media for nucleation and propagation of cracks in $\alpha_2$ matrix.
Figure 12 (a) pseudo-binary phase diagram of Fe-Ni-Al system. Dotted line shows the miscibility gap calculated by
the regular solution model [14], (b) Three-dimensional illustration of miscibility gap in Fe-Ni-Al [14], and (C)
Trinary diagram of Fe-Ni-Al system at 900 °C.

All samples in this study contain considerable amount of chromium. Addition of chromium causes
some changes in Fe-Ni-Al ternary system. In general addition of chromium promotes the increase
in coarsening resistance by either its dissolution into the ferrite matrix or precipitates by for Fe-
Ni-Al alloys with higher amount of nickel (higher than 25 wt.%), addition of chromium depresses
the coarsening resistance and promotes formation two-phase (BCC_A2 + BCC_B2 or $\alpha_1 + \alpha_2$)
region [Chapter 4]. Since chromium has an extended solubility in ferrite phases, it is expected that the diffusion in $\alpha_1$ and $\alpha_2$ phases in Fe-Ni-Al-Cr system be faster than that in the other systems since the melting of $\alpha_1$ and $\alpha_2$ phases drop by increase in dissolved chromium content. This can be explained by a general rule that the atomic mobility in some phases is increased by an alloying element which lowers the melting temperature.

Precipitation or growth of the chromium carbides due to exposure of the aluminized sample to carburizing environment causes decrease in dissolved chromium in $\alpha_1$ and $\alpha_2$ phases and thus the decrease in atomic mobility of these phases and slows down the diffusion.

Phase breakdown occurred in saturated $\alpha_2$ which has low aluminum content in compare with Ni and Fe. This means that Al-low side of the phase can remain stable if the extra Ni atoms be accommodated either by occupying the Al-sites ($\text{Ni}_{\text{Al}}$ and $\text{Fe}_{\text{Al}}$ antisites) or creating vacancies at the Al-sublattice ($V_{\text{Al}}$). For $\alpha_2$ phase with high nickel content (+25 wt.%), the dissolve chromium accelerates saturation and decomposition of $\alpha_2$ phase, however, for alloys with lower nickel content, dissolve chromium delays the $\alpha_2$ breakdown. The nickel content of $\alpha_2$ phase at the second layer of the heat-treated sample is at the edge of the critical point (~24.5 wt.%) which makes it very sensitive to a local chemical composition fluctuation. A small increase in Ni content, the $\alpha_2$ phase breakdown occurs. This can be seen at the vicinity of the boundary of second and third layer of reaction zone which forms a thin layer of dual phase region of $\alpha_1 + \alpha_2$ at the boundary of second and third layers. Therefore, any increase in diffusion of Ni and chromium from the substrate into coating leads to break down of the $\alpha_2$ phase at the second layer of the diffusion zone. In other words, increase in heat-treatment time or temperature can accelerate the phase break down in second layer of the diffusion (reaction) zone.
Shinohara et al. pointed out that the precipitation of the $\sigma$ phase was a diffusion-controlled phase transformation in 25% Cr-20% Ni stainless steel, and that the Cr atom had an important effect on the acceleration of the precipitation rate of the $\sigma$ phase [19]. $\alpha_2$ phase with ordered body centered cubic and sigma phase with tetragonal crystal structure coexist at the immediate interface with stainless steel, fifth layer. When the Cr content is higher than 25 wt.%~30 wt.%, the $\sigma$ phase precipitate via phase transformation of $\delta \rightarrow \sigma$ ($\delta$-ferrite to $\sigma$ phase) at temperature between 600°C and 1000°C [20-22]. Heat-treating aluminized stainless steel causes increase in Ni, Cr, and Fe content of the fifth layer of the reaction zone which leads to enrichment of the Cr to $\sim$39 wt.% and occurrence of $\delta \rightarrow \sigma$ phase transformation. The contents of Cr of $\delta$-ferrite decreased and the Ni contents increased simultaneously after the $\sigma$ phase precipitated which leads to formation of $\alpha_2$ phase which of rich in Ni and Al.

**5.2.6. Conclusion**

Post heat treatment of as-aluminized sample completely transforms microstructure of the aluminized sample. All Fe-Al and Cr-Al intermetallic phases has been dissolved in reaction zone after heat-treatment. Heat-treating as-aluminized RA330 stainless steel causes formation of a multilayer reaction zone. The reaction zone has 5 layers consists of consists of five different layers: (1) a thin layer of alumina at the outer surface of the sample, (2) chromium carbide precipitations in matrix of ordered $\alpha_2$-(Fe,Ni)Al with BCC_B2 crystal structure, (3) a thin dual phase layer of ordered $\alpha_2$-(Ni,Fe)Al (BCC_B2#2) and disordered $\alpha_1$-(Fe) (BCC_A2), (4) a layer consists of carbide precipitates in matrix of saturated $\alpha_2$ phase, and (5) a layer at the immediate interface of stainless steel/coating consists of sigma phase and $\alpha_2$ rich in nickel and aluminum.

Increase in alloying element contents like chromium in the samples used for this study (> 25 wt.% Ni in the coating) accelerates the decomposition of the $\alpha_2$ phase to $\alpha_2$ (Ordered BCC_B2) and $\alpha_1$.
(disordered BCC_A2) phases at the second layer of the reaction zone. This phase decomposition may weaken the high temperature mechanical properties of the coating by formation of α_1 phase in spinodal-like microstructure.

Increase in the heat-treating time or temperature and consequently Cr and Ni enrichment of α_2 phase due to diffusion, saturates α_2 phase and accelerates decomposition of α_2.

Surface aluminizing can extend service life of RA330 austenitic stainless steel by formation of a multilayer reaction zone which its ordered α_2 phase provides aluminum reservoir for formation of protective alumina layer at the surface and crack’s surface.

5.2.7. Reference

Chapter 6: Co-Deposition of Ni-Al Composite Coating

6.1. Electrophoresis of Nickel-Aluminum Alloys on RA330 austenitic stainless steel

6.1.1. Abstract

Ni-Al Intermetallic alloys are widely considered as coatings to extend the lifetime of components for high-temperature applications. In this study, Ni-Al composite coatings were co-deposited by electrophoresis process on RA330 austenitic stainless steel. The influence of naphthalene tri-sulfonate acid additive on the processing parameters on Al wt.% of composite was investigated. The results show that the presence of naphthalene tri-sulfonate acid changes texture coefficient of \( TC_{(200)} \) and \( TC_{(111)} \) and it alters the preferred orientation and texture of the co-deposited coatings. Naphthalene tri-sulfonate acid also has caused a shift in Al wt.% of the coating to higher current density. The maximum Al content in composite, 16.5 wt.%, obtained at 3A/dm\(^2\), 50 °C, 200 g/l Al load in electrolyte, and 150 rpm stirring rate.
6.1.2. Introduction

Intermetallic alloys are widely considered as coatings to extend the lifetime of components for high-temperature applications, in particular, for gas turbines, jet engines, and furnace fixtures and alloys. Although Ni-Al intermetallics (γ’-Ni$_3$Al and β-NiAl) have excellent mechanical properties and corrosion resistance at high temperature, Aluminum contents of these intermetallic alloys act as reservoir for formation and maintenance of protective alumina layer at the surface of the components. Therefore, the higher aluminum content of intermetallics is preferable. Ni$_3$Al intermetallic alloys have attracted considerable attention because of their great potential for high-temperature structural applications due to high strength at the elevated temperature, low density, and excellent resistance to high temperature corrosion [1-3]. NiAl intermetallics are the most attractive among all Ni-Al intermetallics due to good physical properties, ease of production, and low cost [4, 5]. Although low ductility and toughness of NiAl below its brittle-to-ductile temperature is a critical drawback of NiAl in structural applications, micro alloying NiAl with γ’-Ni$_3$Al and/or γ-Ni has been produced moderately tougher Ni-Al materials. However, it results in increase in density, decrease in melting point, oxidation resistance, etc. Therefore, the ratio of these phases is a critical parameter in every specific application. There are several methods to obtain Ni-Al intermetallic alloys [3, 6-10]. Electrodeposition has the merits of simple processing and ease of fabrication, low expense, high productivity, and good compositional control. Electrodeposited composite coatings consisting of a metal matrix dispersing second-phase particles are frequently used as protective coatings for diverse purposes, such as wear resistance, solid lubrication, corrosion, and dispersion hardening [11-13]. However, electrodeposited composites with good resistance to high temperature oxidation have been less investigated.
The aim of this project is developing a practical method for various industries such as heat treatment industries to produce Ni-Al intermetallic coating at low cost and ease of control of the final phase structure by heat-treating co-deposited Ni-Al composite coating. For this purpose, electrophoresis process is used to deposit the Ni-Al composite on RA330 stainless steel. Commercial electroplating baths contain different additives such as wetting agents (surfactants), brightening agents, leveling agents and etc. to enhance and modify morphology, mechanical, and physical properties of the coatings. Therefore, deposition from lab made electrolyte may not lead to the same results as commercial baths. Naphthalene tri-sulfonate acid is a typical organic additive used in commercial electroplating baths for enhancing mechanical properties of the deposits such as increasing hardness, producing internal compressive stress (not tensile), and increasing tensile strength of the deposits. In this study, the influence of naphthalene tri-sulfonate acid additive in nickel sulfamate bath on the electrodeposition parameters on chemical composition of the Ni-Al composite coating is investigated.

6.1.3. Experimental procedure

RA330 stainless steel substrates (cathodes) were used as a plated area. Ni-Al composites were prepared by electrodeposition from nickel sulfamate bath. For this purpose, two nickel plating baths have been prepared. The compositions of plating baths are shown in Table 1. All the bath components were mixed in 1.5 litter of deionized water. Spherical Aluminum powders (99.99%) with mean diameter of 2 µm were added to the bath and held in suspension by agitation of the bath using a magnetic stirrer at 150 rpm. Figure 1 shows the feature of the as received Al particles viewed and analyzed using SEM and EDS.
Table 1 Bath composition of nickel baths studied

<table>
<thead>
<tr>
<th>Bath</th>
<th>Bath constituent</th>
<th>Additive</th>
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| A    | Nickel sulfate (NiSO₄·6H₂O): 427 g/l  
   Nickel chloride (NiCl₂·6H₂O): 6 g/l  
   Boric acid (H₃BO₃): 37.5 g/l | - |
| B    | Nickel sulfate (NiSO₄·6H₂O): 427 g/l  
   Nickel chloride (NiCl₂·6H₂O): 6 g/l  
   Boric acid (H₃BO₃): 37.5 g/l | naphthalene tri-sulfonate acid: 25 ml/l  
   C₆H₈O₉S₃ |

RA330 austenitic stainless steel was chose as the cathode. Surface preparation before deposition is an important factor and can be achieved by mechanical and electrochemical methods. The procedure adopted was removal of surface scales using mechanical polishing to get a smooth surface, degreasing with trichloroethylene. The substrate was prepared by mechanical polishing on abrasive paper (Struers, P 800, SiC) and using diamond pastes (Struers, DP grain size: 9 µm), and chemical etching in HCl solution (v/v 1:1) for 5 min. Then the cathode’s surfaces were prepared by deposition of thin layer of nickel using Wood’s nickel strike electro-deposition. This layer provides a flash coating of nickel onto hard-to-plate metal with a common electroplating setup. An effect of metal powders sedimentation on the coatings morphology or chemical composition was not observed.

The coatings were deposited on RA330 austenitic stainless steel substrates with dimension of 50x10x6 mm placed parallel to the vessel wall (Pyrex® glass cell). The cell volume was 2 litters. Deposition was carried out in the vessel containing 1.5 L of the electrolyte. R-round nickels were served as a counter electrode. The pH of the bath was adjusted to 3.8 ±0.1 using drops of H₂SO₄ (CP 101 Elmetron pH-meter).

After preparation of sulfamate bath, different loads of 20 g/l, 50, 100, 200, 300, and 400 g/l of commercially pure aluminum powder (99.5%) were added to the baths. Based on quantitative image analysis, the mean particle diameter was 1 µm. The suspensions were sonically treated for
30 minutes prior to deposition processes to avoid excessive agglomeration of the aluminum powder in the baths. Zeta potential of the aluminum particle in the bath was measured (Malvern Zetasizer Nano ZS). Figure 1 shows the feature of the as received Al particles viewed and analyzed using SEM and EDS.

Figure 2 shows the schematic diagram of the experimental setup. For investigating the effect of electrodeposition parameters on the quality and microstructure of the composite coating, the codeposition process was carried out at 30, 40, 50, and 60 °C, applied current densities of 1, 2, 3, 5 and 7 A/dm². After electrophoresis process, all the coatings were ultrasonically cleaned with DI water, and then dried for further characterization.

![Figure 2](image)

**Figure 2 (a)** Schematic diagram of the experimental setup and (b) co-deposited composite coating [14]

Adhesion of the nickel deposits obtained in the presence and absence of additives from the nickel baths was tested by subjecting the plated specimens to standard tape test (ASTM D3359). The deposits from both baths were found to withstand the bend test, showing that the adhesion of the deposits to the base metal were very good in all cases.

The samples were sectioned, and the coatings were metallographically prepared. Coating-substrate assemblies were analyzed in the as-plated condition with samples mounted in cold-setting epoxy
and prepared using standard metallographic techniques. For cross-sectional analysis, grinding was conducted with successively finer silicon carbide papers from 120 to 600 grit. Polishing steps included 6 and 1 µm diamond pastes, 0.3 mm alumina suspension, and 0.05 mm colloidal silica. The coating microstructure and particle distribution were found to be the same in the planar and cross-sectional orientations. The layers thickness was estimated by the microscopic method. The surface morphology and microscopic cross-section studies of the coatings were carried out using a scanning electron microscope (JOEL 7000F) provided with a digital system of the image recording. Quantitative chemical analysis of the coatings was determined by means of energy dispersive X-ray method (EDS).

Microstructural investigations of the coatings were conducted by XRD method using PANalytical Empyrean x-ray diffractometer (X’Pert model) with Cu Kα-radiation (1. 54056 Å) at 30mA and 40 kV. monochromatized by a graphite monochromator. The diffraction patterns were registered using “step-scanning” in the angular range from 30° to 100°. Registered XRD patterns were the basis of qualitative and phase analysis. Qualitative phase analysis was carried out based on ICDD card standards (2000). Electron backscatter diffraction methods (Oxford), EBSD, were also used for phase analysis and microstructure examination of the deposited and heat-treated samples.

6.1.4. Results and Discussion

6.1.4.1. Ni-Al co-deposition mechanism

Although the co-deposition mechanism of particles has not been fully understood, there are several models developed to explain the co-deposition mechanism and effect of processing parameters such as the Guglielmi’s model, the Celis et al., and the trajectory model [15-19]. According to previous studies, the co-deposition behavior was closely related with the surface characteristic of the co-deposited particles [20, 21]. Measuring zeta potential is a method to determine the surface potential...
characteristic of the particle in a specific environment. Zeta potential is defined as the electrical potential at the interface of solid particle and electrolyte. It is related to the surface charge of the particle, adsorbed interface layers, and the composition of the electrolyte. Table 2 shows the zeta potential of the aluminum particles in nickel sulfamate baths with pH of 3.8. Zeta potential of the aluminum particles was measured to be very close to the Al₂O₃ particles in the solution which is in agreement with other studies [20, 22]. This can be explained by formation of a thin amorphous Al₂O₃ around the Al particle in the solution which changed the surface characteristic of the Al particles in the electro-co-deposition bath and made the Al particles to be similar to ceramic particles during the co-deposition process.

<table>
<thead>
<tr>
<th>Zeta potential /mV</th>
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<tbody>
<tr>
<td>Aluminum particles in electrolyte solution A</td>
</tr>
<tr>
<td>Aluminum particles in electrolyte solution B</td>
</tr>
<tr>
<td>Al₂O₃ particles in electrolyte solution A</td>
</tr>
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According to all suggested mathematical models, variation of bath compositions and electroplating parameters leads to change in mass transfer rate of Ni ions and Al particles. Therefore, aside from zeta potential, the amount and distribution of particles are related to electrodeposition parameters including particle characteristics (shape, size, concentration (g/l), and surface charge), electrolyte composition (additives, surfactant type and concentration), pH and applied current (direct or pulsed current and current density), temperature, current density, and bath agitation [18, 23-26].

### 6.1.4.2. Structure properties and texture

The additives and processing parameters have a complex relationship in terms of their influence on the deposition mechanism [18, 19, 27]. Commonly organic additives used for industrial nickel plating, are aromatic sulphones or sulphonates to modify the surface morphology, structure, crystal size and physical properties such as hardness and wear resistance of the metal deposits.
Naphthalene tri-sulfonate acid is a building block agent which is commonly used as an additive in electroplating baths for modification of the physical properties of the deposited coating. In addition to altering the physical properties of the electrodeposited coating, the naphthalene tri-sulfonate acid also affects the microstructure, chemical composition, and influence of electrodeposition parameters. Figure 3 shows the X-ray diffraction patterns of the as-deposited Ni-Al composites with different Al loads obtained at the current density of 3 A/dm$^2$ at 50 $^\circ$C from baths A and B. All the deposits are crystalline in nature and have face-centered cubic structure. Figure 3a shows that the pure nickel electrodeposited has the typical nickel deposition texture with observed (111), (200) and (220) planes but the (200) plane was more predominant peak, and the other peak intensities were smaller. Similar observations have been made by others [28, 29]. Absorption of atomic or and molecular hydrogen and nickel hydroxide to the cathode surface leads to the formation of (200) preferred texture in pure nickel deposits. As Al particle load increases in the bath A, the intensity of the (200) and (111) planes decrease and increases, respectively. Consequently, as Al particle loading exceed to 100 g/l, the preferred orientation of the co-deposited composite coating was suppressed by (111) planes. Al loading in bath has not any significant effect on the intensity of other nickel peaks, such as (220) and (311) peaks.

Figure 3b shows the X-ray diffraction patterns for the bath B with additive for different Al loadings. As it was demonstrated in figure 3b, three planes Ni (111), Ni (200), and Ni (220) have the main intensity and it confirms that these three planes compose the most surface area of coatings. However, in contrary with the bath A, the intensity of the (111) planes in the electrodeposited coating from bath B is higher than (200) and (221) planes and the preferred orientation of the pure nickel is (111). As the Al loading increased, the preferred orientation of (111) was suppressed. For the coating with 50 g/l Al load, the normalized intensity of nickel peak
(111) was higher than any other nickel peaks which shows that (111) is the preferred orientation like pure nickel. With further increase in the Al particle loading up to 200 g/L, the Ni–Al coating preferred orientation slightly shifts to (200). The Al peaks were also observed with increase of the Al particle loadings. The results of XRD confirms addition of Al particles to the deposited coating leads to the texture evolution from (111) plane to predominant (200) plane for bath B which changes the preferred orientation of the coating.

![XRD pattern](image)

Figure 3 XRD pattern of the Ni-Al composite coatings for different Al loads (a) No additive, (b) with additive

According to the following reactions, ionization of the boric acid leads to formation of two cations in the co-deposition of Ni–Al composites which were absorbed by aluminum particles in electrolyte:

\[
\text{B(OH)}_3 + \text{H}_2\text{O} \leftrightarrow \text{[B(OH)4]}^- + \text{H}^+ \\
\text{Ni}^{2+} + \text{[B(OH)4]}^- \leftrightarrow \text{Ni[B(OH)4]}^+ 
\]

The Al microparticles in the bath could adsorb the Ni\(^{2+}\) and Ni[B(OH)4]\(^+\) cations, and then the adsorbed cations are attracted to the growth center carrying with Al microparticles, which will
shield the growth center from the cations of the electrolyte and prohibit grains from further growth. Since a thin layer of Al$_2$O$_3$ forms around the Al particles, the ionic transport of the Al particles in bath decreases. As a result, the active surface area of the cathode decreases. The reduction of Ni$^{2+}$ ions adsorbed on Al particles forms an electric conductive layer all over the Al particles. The applied electric field can be concentrated on these weakly adsorbed Al particles since they act as the moving interface between nickel and the solution. Nucleation rate of nickel is enhanced at these Al particles due to higher local current density. Thus, enhanced nucleation and inhibited growth of nickel on Al microparticles lead to the formation of fine grains [30]. In this study, the presence of naphthalene tri-sulfonate acid in bath B alters the common texture of pure nickel deposition texture from (200) to (111) planes. Therefore, by adding aluminum particles, recrystalization occurs at the preferred orientations of (111) in Bath A and (200) in bath B. However, the inhibitor species is not enough to affect the electrocrystallization of all grains. Therefore, the relative intensity of the (200) and (111) peaks are still significant in bath A and bath B, respectively.

Details of the texture evolution of Ni-Al composite coatings was examined using XRD analysis (figure 4). According to the XRD pattern of co-deposited Ni-Al composite with different Al load (figure 3), all deposits display three main Bragg diffraction peaks indexed as the (111), (200), and (220) planes of the face-centered cubic (FCC) crystal structure. By comparing the XRD spectra, an apparent change in the crystallographic structure is observed in both baths according to the intensities of the (111) and (200) diffraction peaks. This means that the Al load plays a critical role in controlling the Ni (111) and (200) peak intensities. In contrast, the significant drop in the intensity of the Ni (220) peak just after introducing Al particles to the Ni matrix, shows little change in Ni-Al composite coatings. This phenomenon implies that the crystallographic
orientation was not randomly orientated, but grains grew in specific orientations and were significantly influenced by Al particle load.

The relationship between the Al load and the $\text{TC}_{(hkl)}$ is described in Figure 4a. As seen in figure 4a, the (200) texture coefficients decreased and the (111) texture coefficients increased with increasing Al particle load in Bath A. It seems that introducing Al particle to nickel matrix inhibited the grain growth of primary grains usually oriented in (200) planes in Bath A and provided nucleation sites for the growth of new oriented grains. Qu et al. pointed out that the of nickel electro-crystallization was a highly inhibited process and the (200) texture mode was considered to be the result of a bath free from any additives and other extras. However, it is to be completely free from inhibiting species. Existence of some chemical species such as hydrogen and nickel hydroxide are unavoidable in the bath. On the other hand, some additives are intentionally added to the baths to enhance the mechanical and physical properties of the electroplated coatings in commercial electrodeposition baths. Existence of naphthalene tri-sulfonate acid in bath B causes the change in preferred orientation of pure deposited coating to (111) crystalline planes, as indicated by the intensive (111) line and a high value of $\text{TC}_{(111)}$. Thus, increasing the presence of Al particles in bath leads to decrease in the strong (111) texture and increase in the (200) texture coefficients (figure 4b).

The slip plane of a face-centered cubic (fcc) lattice is the (111) plane, a crystallographic plane whose atomic density is highest than any other plane. Consequently, any additives that alters the planar density of deposited nickel to (111) planes, enhances the mechanical properties of the deposited nickel. (200) planes have lower planar density than that of the (111) planes in the fcc structure.
The hardness of the composite coatings at 50 °C with the predominantly (200) planes is lower than when the prefer orientation of the deposited coating is Ni (111) plane. Addition of Al particles or presence of naphthalene tri-sulfonate acid in bath A enhances intensity of (111) planes and consequently it should increase the hardness of deposited coatings. Besides the negative effect of the presence of the low density (200) planes with low hardness, a reason for increasing microhardness of the Ni-Al composite coatings with rising Al particle load (>100 g/l) can be explained by composite grain sizes, which was explained by Susan et. al [9]. As it was shown in figures 5-7, by increasing the Al particle load, the deposited Al content in the coating increases, which as explained before, can be followed by grain size refinement.

### 6.1.4.3. Al particle load and current density

The surface morphology and cross-section images of Ni-Al coatings co-deposited for different Al particle loads in bath B are presented in figure 5. As seen in figure 5a, the coating deposited at 20 g/l shows regular morphologies of nickel electrodeposited coating, a mixed structure of truncated pyramids and cauliflower shapes (colonized structure). Figure 5a shows the surface of coatings deposited with 20 g/l Al particle load with more pronounced cauliflower-like structures and deep
crevices outlining groups of smaller substructures that are visible over the entire surface. With increase of the Al particle loadings, the probability of the Al particles absorbing on the growing coating surface has increased. However, when the Al particle load in bath increases, the coating has become more compact, the surface roughness of the composite reduced, and distribution of Al particles in Ni matrix has become more homogeneous. The micro-crevices between different grains gradually have disappeared as indicated by Figure 5e, and the grains are separated by clear boundaries. Figure 5b, d, and f show the cross-sectional SEM images of Ni coatings deposited for 20, 100, 200 g/l Al particle loads in bath B.

Figure 6 shows EDS map analysis of the composites from bath B for different Al particle loads. As seen, the final composition of the co-deposited composite coating is a function of the aluminum load in the electrodeposition bath. Increase in Al particle load from 20 g/l to 200 g/l leads to increase in Al content of composite from 5.5 wt.% to 16.5 wt.%). According to EDS cross-section map analysis of these coatings (Figure 6), the dark spots on figure 5 are the results of co-deposited particles agglomerated in bath. Increase of Al load in electrolyte has reduced the particle agglomeration, enhanced the distribution of particles in nickel matrixes, and reduced the distance between the neighbor scattered particles providing homogenous composite with enhanced properties. The thickness of the coating was uniform with an average value in the range of 150-180 µm based on more than six profile measurements at different positions.
Figure 5 SEM surface micrograph of Ni-Al co-deposited from bath B with (a) 20 g/l Al, (c) 100 g/l Al, and (e) 200 g/l Al load and SEM cross-sectional image of (b) 20 g/l Al, (d) 100 g/l Al, and (f) 200 g/l Al load.
The Al particle content in the deposits as a function of Al particle loadings in bath A and B are plotted in Figure 7. The Al particle content showed a direct relationship with the increase of Al particle loading in bath. The isoelectric point (IEP) of Al$_2$O$_3$ is pH 9 [31] which is larger than the pH of the plating suspension in this study (pH = 3.8). Theoretically, the particle surface should be positively charged in an aqueous solution of pH = 3.8. As it was already discussed, there is a thin amorphous Al$_2$O$_3$ layer forms around the Al particle in the bath which changed the surface characteristic of the Al particles in the electro-co-deposition bath and make the Al particles behave similar to ceramic particles (Al$_2$O$_3$) during the co-deposition process.

The results shown in figure 7 correspond well to the Celis et al. model [18, 19] because the model was developed for co-deposition of electrically ceramic particles. Since the zeta potential
calculation indicated that a thin layer of Al$_2$O$_3$ forms on the surface of the Al particles, this model can explain the variation of the Al wt.% of composite coating by current density. This model predicts a maximum in particle weight percent at low current density (charge transfer overvoltage) and then a gradual decrease in volume percent at higher current densities (concentration overvoltage). Although, the data in Figure 7a show a similar trend to that predicted by the Celis et al. model, but a strong maximum is not shown, perhaps because very low current density coatings were not deposited and other differences in the codeposition systems. At current densities higher than about 2 A/dm$^2$, Figure 6a shows that the codeposition process may already be in the concentration of overvoltage regime and, therefore, volume percent is relatively insensitive to current density. For pure Ni coatings, the concentration overvoltage current density is higher, approximately 25 A/dm$^2$ [32]. It may be speculated that the Al bath additions decrease the current density for concentration overvoltage effects. Alternatively, the local current density near Al particles may be increased relative to the overall Ni matrix deposition.

Many parameters influence the surface charge of the particles. Fink and Prince in 1928 noted the importance of the surface charge and stated that a positive surface charge enhances codeposition, because the particles are electrostatically attracted to the cathode [33]. This results was confirmed
by Tomaszewski et al., who found that the negatively charged silica particles transported to the cathode less than the positively charged $\text{Al}_2\text{O}_3$ particles [34]. He suggested that particles may obtain a positive surface charge by adsorption of metal ions and $\text{H}^+$ ions depends on their isoelectric point (IEP) [35]. Kariapper and Foster noticed that increasing metal ion concentration or presence of additives such as TEPA or EDTA changed the amount of adsorbed metal ions [36]. Consequently, they assumed that the promoting effect on codeposition of these additives is derived from the fact that they enhance metal ion adsorption.

Based on Smoluchowski’s equation, which explains the relation between velocity ($\theta_E$) of a charged particle moving in an electric field (E), as the electric field intensifies, the velocity of the charged particle also increases. This means that as the electric field increases, the amount of precipitated particles in the coating also increases [37]. Many articles have reported that the particle content of deposit is drastically changed when the current density is modified [38-41].

In this study, It was seen that Al particles in bath B also show similar behavior. Addition of naphthalene tri-sulfonate acid to the electrolyte (bath B), transformed the behavior of composition of deposition with current intensity. As seen in figure 7b, we can find that by increasing current density in the range of 1 – 3 A/dm², aluminum weight percent of the composite coating increases. However, at higher current density than 3 A/dm² the deposition of Al will decrease with the rise in current density. It may be caused by the smaller electro-chemical equivalent of aluminium (0.093 mg/c) than that of nickel (0.304 mg/c), which will lead to a faster increase of deposition speed of Al in compare to Ni as the current density increases. When the current density reached to 3A/dm², the Al content of coating has been as large as 16.5 wt.%. As a result, a slivery deposit film with a strong adhesive force is covered on the surface of plate at this moment. However, at 3 A/dm², co-deposition process may already be in the concentration overvoltage regime and,
therefore, Al weight percent decreases with current density after experiencing a maximum. It may be speculated that the Al particle load decreases the current density for concentration overvoltage effects. under this condition, fewer particles are embedded in the coating. Alternatively, the local current density near an Al particle may be increased relative to the overall Ni matrix deposition. Low current density (< 1 A/dm²) yields extremely slow plating rates and it was not considered in the present study. The results for Bath B shown in figure 7b correspond well to the Celis et al. model.

6.1.4.4. Deposition temperature

The experimental results for the effect of temperature on chemical composition of the Ni-Al composite coatings for bath A and bath B are plotted in figure 8. According to previous studies on the effect of temperature on final composition of the co-deposited composite, it seems that the effect of temperature varies for different co-deposition systems [26, 42, 43]. In this study, The effect of co-deposition temperature on the chemical composition of composite coatings has been investigated by preparing the co-deposition at 30, 40, 50, and 60 °C. Although the variation of temperature slightly changes the final composition of the composite deposited from bath A (figure 8a) and bath B (figure 8b), however, the effect of temperature on composition of Ni-Al composite is more notable for coating deposited from bath B. As Figure 8b shows, the Al content of composite coating deposited from bath B decreased when the temperature increases beyond 50 °C. The decreasing trend after a critical temperature value may also be due to the decrease in the current efficiency of nickel deposition at higher temperatures. The curve has a Gaussian form like the curve of Al with a maximum temperature at 50 °C. Increasing temperature, which leads to reduce in polarization, and may influence the cathode current effectiveness of the deposition of metals [44].
At any given pH value, Zeta potential drops by increasing temperature, which also indicates proton desorption from the surface [45, 46]. Generally, the increasing temperature causes a shift of the isoelectric point (IEP) to lower values. At the IEP, the net charge of the particles becomes zero, and they stop migrating. Therefore, the ability of the corporation into a deposition and the range of stability of positive particles are decreased, which are not favorable for electrophoresis. As the maximum incorporation of each particle appears at a specific temperature, particles under such conditions should have positive surface charges up to that temperature and negative surface charges beyond that temperature. These results show that increasing temperature beyond 50 °C does not favor particle adsorption.

![Graph of Effect of Temperature for bath A and bath B](image)

Figure 8 Effect of co-deposition parameter (a) temperature and (b) stirring rate on Al content of composite obtained from bath B

### 6.1.5. Conclusion

The purpose of this study was understanding the effect of additive on the processing parameters and the composition of Ni-Al composite coating. Some conclusions could be drawn as followed:

- Presence of naphthalene tri-sulfonate acid additive in electrodeposition bath alters the texture and preferred orientation of the deposited nickel from (200) planes to (111) planes.
• Addition of aluminum particle loads in bath gradually changed texture coefficient of the co-deposited composite coatings. Contrary to bath A that TC\text{200} decreased and TC\text{111} increased by increasing Al particle load, TC\text{200} and TC\text{111} values of coatings deposited from bath B (contain additive) increased and decreased, respectively.

• Increasing Al load in electrolyte reduced the agglomeration and enhanced the distribution of the Al particles in Ni matrix.

• Regardless to presence of naphthalene tri-sulfonate acid additive, increase in Al particle load in electrolyte leaded to increase in Al wt.% of co-deposited composite.

• Although, coatings deposited from both baths obeyed Celis et al. model, presence of naphthalene tri-sulfonate acid additive changed the effect of current density on chemical composition of the co-deposited coatings. For bath A, Al wt.% of the composite decreased with rising the current density. However, addition of tri-sulfonate acid to bath (bath B) shifts the maximum wt.% to a higher current density, and after experiencing a maximum value at 3 A/dm², Al wt.% has then decreased with increase of current density.

• The effect of temperature on both baths are small. However, in presence of tri-sulfonate acid, the effect of temperature on Al wt.% has become more notable. There is an optimum temperature (50 °C) for electro-co-deposition process of Ni-Al composite, deposited from bath B, to obtain the maximum wt.% of Al in composite. There is no noticeable change in Al wt.% of the composite deposited from bath A with temperature variation.

6.1.6. References


6.2. Microstructure evaluation of heat-treated co-deposited Ni-Al composite coating

6.2.1. Abstract

An electrodeposited alumina-forming Ni–Al composite having Ni matrix with uniform distribution of Al particles was heat-treated in a conventional resistance furnace at 900 °C for four hours, leading to diffusion of aluminum and nonuniform distribution of aluminum in composite. As the result of the heat-treatment and consequently the non-uniform distribution of Al throughout the coating, $\gamma$-Ni, $\gamma'$-Ni$_3$Al and $\beta$-NiAl phases are formed throughout the composite coating and NiO, NiAl$_2$O$_4$, Al$_2$O$_3$ phases are formed at the surface of the coating. This investigation will be helpful to assess the ability of the co-deposited Ni—Al composite coating to increase the service life of alloys and parts at high temperature application.
6.2.2. Introduction

As is known, electrodeposition has the merits of simple processing and ease of fabrication, low expense, high productivity, and good compositional control. Electrodeposited composite films consisting of a metal matrix dispersing second-phase particles are frequently used as protective coatings for wide applications, such as solid lubrication and dispersion hardening [1-3]. However, there are only a few investigations on the electrodeposited composites for high temperature applications [4-10]. The second component in the metallic base of the composite coating enhances service life and high temperature resistance of the metallic base by reducing the growth rate and improving mechanical properties of protective thermally grown oxide (TGO) layer at high temperature [10, 11]. The most typical TGOs are chromia (Cr₂O₃) and alumina (Al₂O₃) by developing oxidation-resistance coatings via co-electrodeposition of metallic composites rich in Cr, Al and alumina particles [12-14]. Despite TGO-forming Ni–Al composites were obtained by the electrophoresis of micron-sized aluminum particles in a nickel matrix and by Susan et. al [12], however, there are not extended data on the oxidation and carburization resistance of the electrodeposited composites at high temperature.

In this work, an as-deposited, alumina-forming Ni–Al was heat-treated in conventional resistance furnace, and the microstructure and oxidation of the composite coating after the post heat-treatment were investigated. This result will be helpful to assess the ability of the co-deposited Ni—Al composite coating to increase the service life of alloys and parts at high temperature application.

6.2.3. Experimental procedure

RA330 stainless steel substrates (cathodes) has been used as a plated area. Ni-Al composites were prepared by electrodeposition from nickel sulfamate bath. For this purpose, nickel sulfamate bath
with the following composition has been used: 427 ml/l nickel sulfamate (NiSO$_4$.6H$_2$O), 37.5 g/l boric acid, 6 g/l nickel chloride (NiCl$_2$.6H$_2$O), 25 ml/l naphthalene tri-sulfonate acid additive. All the bath components were mixed in 1.5 litter of deionized water. Spherical Aluminum powders with mean diameter of 1 µm were added to the bath and held in suspension by agitation of the bath using a mechanical stirrer of 150 rpm. Figure 1 shows the feature of the as received Al particles viewed and analyzed using SEM and EDS.

| Table 1 Bath characteristics and operating conditions for electrolytic co-deposition |
|---------------------------------|---------------------------------|
| Type of deposit                 | Ni + Al                         |
| Bath composition                | Nickel sulfate (NiSO$_4$.6H$_2$O): 427 g/l |
|                                 | Nickel chloride (NiCl$_2$.6H$_2$O): 6 g/l |
|                                 | Boric acid (H$_3$BO$_4$): 37.5 g/l |
|                                 | 25 ml/l naphthalene tri-sulfonate acid: C$_{10}$H$_8$O$_9$S$_3$ |
|                                 | 200 g/l Al particle             |
| Anode/cathode pretreatment      | 10% sulfuric acid in water, 30 s |
| Anode area/cathode area         | 2/1                             |
| Anode to cathode distance       | 45 mm                           |
| pH                              | 3.8 (start of plating)          |
| Temperature                     | 50 °C                           |
| Current density                 | 3 Adm$^2$                       |
| Agitation                       | 150 rpm                         |
| Thickness of deposit            | 140–180 µm                      |

The surface of samples was prepared by deposition of thin layer of nickel using Wood’s nickel strike electrodeposition. This layer provides a flash coating of nickel onto some hard-to-plate metal with a common electroplating setup. An effect of metal powders sedimentation on the coatings morphology or chemical composition was not observed. The pH of the bath was adjusted to 3.8 ±0.1 using drops of H$_2$SO$_4$. (CP 101 Elmetron pH-meter). After preparation of sulfamate bath, 200 g/l of commercially pure aluminum powder (99.5%) was added to the electrolyte. Based on quantitative image analysis, the mean particle diameter was 1 µm. The suspension was sonically treated for 10 minutes prior to deposition processes to avoid excessive agglomeration of the aluminum powder in the bath.
The coatings were deposited on a RA330 austenitic stainless steel piece substrate with dimension of 50x10x6 mm placed parallel to the vessel wall (Pyrex® glass cell, Radiometer No. 1734). The cell volume was 2 litters. Deposition was carried out in the vessel containing 1.5 L of the electrolyte. R-round nickels were served as a counter electrode. Before plating, the substrate was prepared by mechanical polishing on abrasive paper (Struers, P 800, SiC) and using diamond pastes (Struers, DP grain size: 9 µm), and chemical etching in HCl solution (v/v 1:1) for 5 min. The electrodeposition process was carried out at 50 °C and applied current density of 3 A/dm² under conditions described in Table 1. The pH of the solution was 3.8 and the stirring rate was 150 rpm. After co-deposition process, two as-deposited samples were nickel plated at surface to be prepared for post heat-treatment and then all three samples were rinsed with water, acetone and then dried for further characterization. Figure 2 demonstrate the schematic diagram of the experimental setup.

Typical annealing condition was 4 hours at 900 °C. After annealing, the samples were air cooled. The samples were sectioned and the coatings were metallographically prepared. Coating-substrate assemblies were analyzed in the as plated and heat-treated condition. Samples were mounted in cold-setting epoxy and prepared using standard metallographic techniques. Grinding was conducted with successively finer silicon carbide papers from 120 to 600 grit. Polishing steps
included 6 and 1 µm diamond pastes, 0.3 mm alumina suspension, and 0.05 mm colloidal silica. To achieve a suitable polish for photomicroscopy and image analysis, a final polish was performed with a vibratory polisher for 5 hours with 0.05 mm colloidal silica. The coating microstructure and particle distribution were found to be the same in the planar and cross-sectional orientations. The thickness of layers was estimated by the microscopic method. The influence of the metal powders amount in the bath and the deposition current density on the coatings chemical composition was investigated and reported in the chapter 6.1. The surface morphology and microscopic cross-section investigation of the coatings were carried out using a scanning microscope (JOEL 7000F) provided with a digital system of the image recording. Quantitative chemical analysis of the coatings was determined by means of energy dispersive X-ray method (EDS). Microstructural investigations of the coatings were conducted by XRD method using PANalytical Empyrean x-ray diffractometer (X’Pert model) with Cu Kα-radiation (1.54178 Å) monochromatized by a graphite monochromator. The diffraction patterns were registered using “step-scanning” in the angular range from 30° to 100°. Registered XRD patterns were the basis of qualitative and phase analysis. Qualitative phase analysis was carried out based on ICDD card standards (2000). Electron backscatter diffraction method (Oxford), EBSD, was used for phase analysis and microstructure examination of the deposited and heat-treated samples.
6.2.4. Results

X-ray diffraction (XRD) patterns of the as-deposited Ni and Ni-Al composite coating are shown in Figure 3. The as-deposited composite coating exhibits two phases of Al particles and Ni matrix with face-centered cubic crystal structure. The patterns show typical peaks corresponding to (111), (200), (220), (311), and (222) crystallographic planes of nickel. As it was demonstrated in figure 3, three planes Ni (111), Ni (200), and Ni (220) have the main intensity in pure nickel coating and this result confirms that these three planes compose the most surface area of coatings. Contrary to intensity of Ni (200) peak which increases by addition of 200 g/l Al particle load, the intensities of Ni (111) and Ni (220) peaks decreased with additional Al content. The preferred orientation of the pure nickel is (111), however, it was suppressed for Ni-Al composite coating with 200 g/l Al load and the Ni–Al coating preferred orientation shifts to (200). The results of XRD confirms that addition of Al particles to the deposited coating leads to the texture evolution from (111) plane to predominant (200) plane which changes the preferred orientation of the coating (Figure 3b).
SEM micrographs of co-deposited Ni-Al composite coating (as-deposited sample) are shown in figure 4. The average thickness of the electrodeposited coating, which was predicted by Faraday’s law, is 160 µm. A uniform distribution of aluminum particles exists throughout the composite coating and there are no cracks, voids, or other defects in the microstructure.

Figure 5 demonstrate EDS map analysis of the as-deposited Ni-Al coating at the surface (5a) and cross-section of the coating (5b). The concentration of Al in the composite was measured using XRD and EDS as 16.4 wt.%. Coincide with SEM micrographs, the distribution of the Al particles is uniform and random throughout the coating.

XRD pattern of Ni-Al composite with 200 g/l Al load after 4-hours heat treatment at 900 °C is shown in figure 6 which provides the phase information of the late composite. Five phases, NiO, Ni2AlO4, γ-Ni, γ’-Ni3Al, and β-NiAl, are developed after heat treating the coating at 900 °C for 4 hours.
Figure 4 SEM surface micrograph of Ni-Al coatings with 2200 g/l Al load at (a, b) surface, (c, d) cross-section. Figure 7a and b show the SEM top-view of the heat-treated composite coating for 200 g/l Al load at 900 °C for 4 hours. According to EDS map analysis (figure 8) and XRD pattern of heat-treated composite (figure 5), Well-faceted NiO with average grain size of 1 µm covered the entire surface. Cross-sectional SEM micrograph of the coating indicates that nickel electroplated layer is oxidized and formed NiO layer. The thickness of the top NiO layer is not uniform and there are some protruded NiO. Underneath NiO layer, Alumina layer (dark layer) was formed. EDS map analysis and XRD patterns of the heat-treated sample suggests the existence of a thin region of spinel NiAl₂O₄ between Al₂O₃ and NiO oxide layers (gray areas between the Ni electroplated and dark layer) which is the product of the reaction between NiO and Al₂O₃.
Figure 5 EDS cross-section map analysis of Ni-Al coating with 200g/l Al (a) top-view (b) cross-sectional view.
Based on EDS measurements, aluminum atoms migrate throughout the composite coating due to heat-treatment of the sample. Unlike uniform distribution of aluminum in as-deposited sample, the distribution of aluminum in heat-treated coating is not uniform throughout the coating. It can be seen that despite presence of $\gamma$-Ni at the substrate/coating interface, which is the result of diffusion of aluminum in wood’s strike nickel layer, the concentration of aluminum is maximum at the vicinity of the nickel strike layer/composite coating and it decreases by distancing from the interface. The region at the top of the composite coating and below the NiO and surface oxide layers has relatively low aluminum concentration in compare to other locations in the coating. This region mostly consists of solid solution of aluminum in nickel ($\gamma$-Ni).
Figure 7 (a,c) surface and (b,d) cross sectional morphology of the oxide scales formed on heat treated Ni-Al composite with 200 g/l Al load for 4 hours.

EBSD map analysis of the heat-treated sample merged with band contrast and EDS measurements at two different locations: (a) at the close distance to substrate/coating interface and (b) middle of coating. These two locations have been presented in figure 9 and figure 10, respectively. These maps indicate γ’-Ni$_3$Al and β-NiAl are the major phases in these areas of the heat-treated composites which is in agreement with XRD patterns and EDS map analysis results.
According to EBSD and EDS map analysis, at close distance to substrate/coating interface, the phase fraction of $\beta$-NiAl is low but and there is a layer of face-centered cubic $\gamma$-nickel (gray phase) solid solution with Fe and Al solute substitute atoms at the interface. Next to the nickel layer, there is a matrix of $\gamma'$-Ni$_3$Al (green phase). At average distance of 12 µm from the interface, $\beta$-NiAl phase appears and forms around the porosities. By distancing from the interface, phase fraction of $\beta$-NiAl (yellow-orange phase) increases which agrees with the EDS measurement. The reason for
existing nickel layer can be explained by the fact that before Co-deposition of the Ni-Al composite, a thin layer of nickel was plated at the active surface of the substrate to enhances the adhesion of composite to the substrate.

Figure 9 EBSD cross-sectional analysis of heat-treated Ni-Al composite with 200 g/l Al load for 4 h.

Figure 10 shows the EBSD phase analysis merged with EDS measurements of the sample at the 40 µm distance from the interface. Although the β-NiAl phase (orange phase) formed at the vicinity of the porosities, the fraction of this phase is larger in compare to the location with closer distance from the surface. The number density of the twins in γ’-Ni₃Al matrix are also larger than one at the vicinity of the interface. By using EBSD measurements, the average grain size of the coating was measured as 350 nm.
6.2.5. Discussion

The phase transformation of heat-treated Ni-Al composite is well studied [4, 12, 16-20]. It has been reported that at temperatures above 600 °C, the diffusion will control the process and the final phase structure is controlled by Al content in Ni-Al composite [19]. Thus, at higher temperature, there is a high probability to predict the final phases by knowing Al wt.% using phase diagram. By Exposure of as-plated Ni-Al coatings to high temperature and the delay in formation of continuous alumina layer leads to formation of the inward protruded NiO containing minor Al-rich oxides (NiAl$_2$O$_4$, dark regions on figure 7) at the surface. However, the outward NiO has different composition and does not contain Al (bright areas on figure 7). The Ni-Al composite coating showed improved oxidation resistance in compared to pure nickel which is due to the formation of the slow growing, protective layer of Al-rich oxide on the composite surface.

When as-plated Ni-Al coatings are exposed to high temperature, diffusion occurs between the Al particles and the Ni matrix. The final phases present in a heat-treated, 16.4 wt.% Al coating depend
on temperature and the Ni-Al phase diagram. 16.4 wt.% Al coating annealed at 900 °C lies in the two-phase γ' + β field of the Ni-Al phase diagram (Figure 11).

![Figure 11 The binary Ni–Al equilibrium phase diagram](image)

However, aluminum concentration of the heat-treated sample is not uniform throughout the composite coating causing formation of different regions with different phases. In addition, small pores are found throughout the coating microstructure. Microstructure of heat-treated Ni-Al composite coatings contains significant amount of Kirkendal porosities which is consistent with SEM cross sectional micrographs of the coatings (figure 6 (c,d)). The number density of the porosities depends on Al content of composite and post-heat treatment time and temperature. The local volume shrinkage during the transformation of Ni (ρ=8.9 g/cm³) to γ'-Ni₃Al (ρ=7.5 g/cm³) and β-NiAl (ρ=5.9 g/cm³) is the main reason of the porosity formation after post-heat treatment of the Ni-Al composites. During post-heat treatment at 900 °C, Al particles melt and evaporate (Tₘ=660 °C). On the other hand, inward diffusion of Al into Ni matrix is faster in compared to outward diffusion of Ni into Al-rich regions which results in formation of Kirkendall pores.
For recognition of $\gamma$-Ni and $\gamma'$-NiAl, EBSD phase analysis results alone were not conclusive since both phases have same face-centered cubic crystal structure and very similar lattice parameters. Therefore, merging EBSD phase analysis with EDS measurements provides the opportunity to distinguish these phases.

The grain size measurements for the Ni matrix, using XRD characterization on the basis of the Scherrer method indicates that the average grain size for Ni–16.4 wt.% Al was 220 nm. It must be noted that the Scherrer method of grain size determination might not give an accurate determination of grain size in some cases since other effects such as stacking faults and macrostrains can also cause broadening of the diffracted beam. For this reason, the grain size of both Ni–Al composite coatings was examined by EBSD. The EBSD band contrast reveals that the average grain size is 350 nm.

6.2.6. Conclusion

The purpose of this study was understanding the effect of post-heat treatment on the co-deposited composite. Some conclusions could be drawn as followed:

- The surface of the coating after post-heat treatment contains different oxides: NiO, Al$_2$O$_3$, and NiO (minor Al-rich oxides), and NiAl$_2$O$_4$.
- Post heat-treatment of Ni-Al composite with 16.4 wt.% Al at 900 °C for 4 hours leads to formation of three major phases: $\gamma$-Ni, $\gamma'$-Ni$_3$Al, and $\beta$-NiAl.
- Formation of porosities are inevitable due to diffusion-controlled process at high temperature (higher than 600 °C), low melting point of aluminum, and the local volume shrinkage during the transformation of Ni to $\gamma'$-Ni$_3$Al and $\beta$-NiAl. The vol% of Porosities depend on Al content in composite.
• Despite uniform distribution of aluminum throughout the as-deposited composite coating, the distribution of the aluminum in heat-treatment is ununiform and by distancing from the substrate/coating interface the aluminum concentration drops.

• Due to a promotion in the formation of a protective alumina layer, Ni-Al composite coating can improve the life service of RA330 austenitic stainless-steel substrate at high temperature applications such as carburization.

• Higher aluminum content of the composite coating leads to formation of nickel aluminides with higher aluminum contents which act as aluminum reservoir for formation of alumina at the surface.

6.2.7 Reference

Chapter 7: Conclusion

The performance of RA330 in an industrial carburizing furnace were investigated. RA330 specimens were exposed in both the as fabricated and packed aluminized condition for times up to twenty months. Failure analyses were conducted on exposed alloys. Austenitic RA330 stainless steel was cyclically carburized at 900 °C carburizing furnace for 12 months. The average thickness of the diffusion zone was measured 810 µm and it consists of five layers: (1) graphite, (2) \( \text{Cr}_2\text{O}_3+\text{FeCr}_2\text{O}_4 \), (3) \( \text{Cr}_2\text{O}_3+\text{austenite} \), (4) \( \text{Cr}_7\text{C}_3+\text{austenite} \), (5) \( \text{Cr}_{23}\text{C}_6+\text{austenite} \). Despite formation of two-layer oxide scale at outer surface, consisting of :(a) a continuous but unprotective oxide layer of FeCr\(_2\)O\(_4\) (chromite), and (b) an uncontentious layer of Cr\(_2\)O\(_3\), the integrity of the alloy could not maintain for a long time and carburization and oxidation occurs in the exposed alloys. Due to consumption of chromium content by either formation of carbides in the alloy or chromium oxide scales the concentration of chromium drops and it would not be enough for formation and maintain the continuous protective Cr\(_2\)O\(_3\) for long time. Furthermore, due to disintegration of the chromium oxide protective layer, carbon diffuses into alloy forming chromium carbides. The main reason for failure is due to the excessive carburization that leads to formation of Cr\(_7\)C\(_3\) and Cr\(_{23}\)C\(_6\) carbides in the grain boundaries, and subsequent cracking because of embrittlement of carbides. In this case, the key to suppressing metal dusting is to stop the dissociation of the carbon source or subsequent carbon diffusion into the susceptible materials. It was found that continuous \( \alpha\)-Al\(_2\)O\(_3\) layer on the surface of aluminized RA330 alloy was maintained after 24 months exposure in gas carburization furnace. This alumina resulted is a reduced oxidation rate and decreased carbon absorption.
Due to a promotion in the formation of a protective alumina layer, Ni-Al composite coating can improve the life service of RA330 austenitic stainless-steel substrate at high temperature applications such as carburization. Aluminizing the RA330 stainless steel caused formation of multi-layer reaction zone which varies by carburization time. The reaction zone has 4 layers consists of: 1) thin alumina layer at the outer surface, 2) $\alpha_2$ phase (in as-aluminized and 6-month exposed samples) or $\alpha_1 + \alpha_2$ (in 24 months exposed sample), 3) $\alpha_2$ phase and carbides, and 4) sigma phase and $\alpha_2$ phase. Addition of alloying elements like chromium in the samples used for this study (> 25 wt.% Ni in the coating) accelerates the decomposition of the $\alpha_2$ phase to $\alpha_2$ (Ordered BCC_B2) and $\alpha_1$ (disordered BCC_A2) phases at the second layer of the reaction zone. This phase decomposition may weaken mechanical properties of the coating at the high temperatures by formation of $\alpha_1$ phase in spinodal-like microstructure. Also, they may be a quicker diffusion pass than ordered $\alpha_2$. By increasing the time of exposure, the number density of the cracks, their width, and their lengths increases. The migration of aluminum from ordered $\alpha_2$ phase to crack surface and formation of protective alumina layer causes increase in Al-sublattice vacancies and subsequently, they would increase diffusion and acceleration in $\alpha_2$ decomposition.

Ordered $\alpha_2$ layer with BCC_B2 is important for maintaining effective protection for aluminized alloys or alloys that contain high aluminum content. Aluminizing coating extended the life of alloys in gas carburizing atmosphere. The service lifetime of alloys in furnace and fixtures increased by at least two years because of $\alpha_2$ phase kept continues $\text{Al}_2\text{O}_3$ on the surface of alloys that eliminated the inward diffusion of carbon.

Beside pack aluminizing method, two different surface treatments of RA330 have been investigated in this project: (1) Aluminum hot-dipping, and (2) co-deposition of Ni-Al composite coating by electrophoresis. Aluminum hot-dipping of austenitic stainless steel developed a five
layers of reaction zone: (1) a thin alumina layer at the surface of the sample, (2) (Fe,Ni,Cr)Al₉ precipitates in aluminum matrix which contains the majority of the diffusion layer, (3) a multiphase layer with aluminum, (Fe,Ni,Cr)Al₉ precipitates, island-shape phase of Al₄₅Cr₇, and CrAl₅ phase formed at immediate boundary of Al₄₅Cr₇ islands and aluminum, (4) a porous layer of (Fe,Cr,Ni)₄Al₁₃ with monoclinic crystal structure next layer 5, and (5) a continuous layer of tongue-shaper Fe₂Al₅. Post heat-treatment of as-aluminized sample completely transforms microstructure of the aluminized sample. All Fe-Al and Cr-Al intermetallic phases has been dissolved in reaction zone after heat-treatment and causes formation of a multilayer reaction zone. The reaction zone has 5 layers consists of consists of five different layers: (1) a thin layer of alumina at the outer surface of the sample, (2) chromium carbide precipitations in matrix of ordered α₂-(Fe,Ni)Al with BCC_B2 crystal structure, (3) a thin dual phase layer of ordered α₂-(Ni,Fe)Al (BCC_B2#2) and disordered α₁-(Fe) (BCC_A2) which are the product of α₂-(Fe,Ni)Al phase breakdown, (4) a layer consists of carbide precipitates in matrix of saturated α₂ phase, and (5) a layer at the immediate interface of stainless steel/coating consists of sigma phase and α₂ rich in nickel and aluminum. The phase decomposition may weaken the high temperature mechanical properties of the coating by formation of α₁ phase in spinodal-like microstructure. Although, the phase breakdown of α₂-(Fe,Ni)Al will reduce the performance of the aluminide coatings, however, even coating with phase separation improve the life service of the RA330 stainless steel at 900 °C. Moreover, increasing nickel or reducing chromium contents of the coating, delays the phase breakdown of α₂-(Fe,Ni)Al which exceptionally enhances the properties of the coating.
The maximum Al content of 16.4 wt.% Al in Ni-Al composite coating on RA330 stainless steel was obtained using electrophoresis. Post heat-treatment of Ni-Al composite at 900 °C for 4 hours leads to formation of three major phases: γ-Ni, γ′-Ni₃Al, and β-NiAl.

Formation of porosities are inevitable due to diffusion-controlled process at high temperature (higher than 600 °C), low melting point of aluminum, and the local volume shrinkage during the transformation of Ni to γ′-Ni₃Al and β-NiAl. The vol% of Porosities depend on Al content in composite. Higher aluminum content of the composite coating leads to formation of nickel aluminides with higher aluminum contents which act as aluminum reservoir for formation of alumina at the surface.
Chapter 8: Future works

- Investigation the performance of the hot-dipped aluminized RA330 under carburizing environment
- Investigation the performance of the electrophoresed Ni-Al composite coated RA330 under carburizing environment
- Continue characterization of Ni-Al hot-dipped RA330 before and after post heat-treatment
  - A metallographic characterization using optical microscope, SEM with EDS, and EBSD has been conducted on Ni-Al hot-dipped RA330 before and after post heat-treatment, however, the results need to be analyzed.
- Continue characterization of hot-dipped nickel plated RA330 before and after post heat-treatment
  - A metallographic characterization using optical microscope, SEM with EDS, and EBSD was conducted on hot-dipped nickel plated RA330 before and after post heat-treatment, however, the results need to be analyzed.
- Conduct modeling investigation of diffusion process of alloys during the carburizing
- Conducting bending tests on samples to characterize the ductility of alloys and coated alloys.
- Financial Evaluation of different methods
- Providing industrial recipes
- Investigating why the Ni bulk diffusion into molten Al is different from diffusion of electroplated Ni