

Sulphidation Resistance of Nickel-Aluminide Coatings on Austinitic Stainless Steel AISI 321

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ABSTRACT

Nickel – aluminide coatings were performed on austinitic stainless steel base alloy (321AISI) by packcementation method. Nickel was used as electrodeposition coating before aluminization. Hot corrosion (Sulphidation) behavior of the coatings after exposure in molten salt (Na_2SO_4) at (884 °C) were studied under cyclic condition. The Al-rich intermetallic compound was very effective in reducing the corrosion rate in molten salt, while (Ni) or Ni-rich and Fe-rich intermetallic compounds were less resistances. Uncoated stainless steel reveals very poor resistance to Sulphidation in molten salt environment with sever spallation of the protective oxide scale.

321AISI

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(321AISI)

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.(884 °C)

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INTRODUCTION

The application of aluminide coatings on metals and alloys has beneficial influence on the high temperature performance of boilers and gas turbine operating at elevated temperatures. Nickel aluminide coating are known to possess high temperature mechanical strength, as well as, the possibility of improving oxidation and hot corrosion resistance by forming protective external alumina scale (Ying and Pint, 2003). Many

alloys sometimes experience accelerated oxidation when their surfaces are covered with a thin film of fused salt in an oxidising gas atmosphere (hot corrosion).

In hot corrosion, metals and alloys are subjected to degradation at much higher rates than in gaseous oxidation, with a porous non-protective oxide scale formed at their surface and sulfides in the substrate (Buta and prakash, 2003).

Many attempts had been made to improve the protective capability of the aluminide coatings. This capability is conferred by the ability of (Ni Al) layer to provide aluminum to maintain an (Al_2O_3) based scale at the surface. It is believed that the incorporation of the rear earth element (RE) such as, (Pt, Ir and Pd) and to some extent (Rh) can increase the stability of undoped (β -NiAl) (Leyens et al., 2000).

The double-step Boro- Aluminide coatings had showed some increase in corrosion resistance of low-alloy steel to steam oxidation (Maragoudakis et al., 2003) and also, did Yattria (Houngninou et al., 2003).

The beneficial effects of a cerium-oxide coating on isothermal and cyclic oxidation of austenitic steels were reported (seal et al., 2000). The beneficial effect of the rare - elements and their oxides, either in form of oxide- dispersion and alloy addition or by superficial coating of there oxides to both chromia or alumina forming alloys have exhibited improved scale adherence to alloys substrate.

Postulated mechanisms on scale adherence corresponds to, vacancy condensation and modification of the lateral growth of oxide were reported (Rhys and Grabke, 1988).

Many investigator directed their attentions towards the intermetallic compounds (TiAl), as these compounds, expected to be condidates for a new alternative structural material usable in high temperature applications (Yoshihara et al, 1991).

During the service at high temperature, loss of (Al) from the aluminide coating by interdiffusion with the substrate element becomes a major concern. (Al) content will fall below the minimum level required to a void spinal formation, however, the effect of inward diffusion of (Al) in the substrate, can also alter the solubility of refractory elements used for strengthening of the substrate, resulting in precipitation of embrittling phases (Wright, 2003).

In this research an attempt had been made to obtain Nickel-Aluminde coatings on austinitic stainless steel (321AISI), by predeposition of Nickel before aluminisng by pack Cementation technique. Cyclic tests of hot corrosion, in a molten salt environments (Na_2SO_4) at (884°C) were performed for both, as-coated condition and post-coating heat treated specimens. The uncoated alloy was introduced for comparison.

EXPERIMENT TECHNIQUE

1-Coating Performance:

The nominal composition of the austenitic stainless steel (321AISI) is presented in Table (1):

Table 1 :

Composition of St. St. 321 AISI								
Type	C%	Mn%	Si%	Ni%	Cr%	S%	Ti%	Fe%
wt.	0.0544	1.477	0.604	8.962	18.636	0.0015	0.21	Balance

The steel samples were cut to form approximately (1x2x0.1 cm). The specimens were grinded to (1200 mesh), then polished before coating. The coating powders were a fine aluminum of (200 mesh), Ammonium chloride and alumina were mixed thoroughly with a composition of (25 wt %, 5 wt % and 70 wt %) respectively. A layer of nickel was Electrodeposited on the sample surface before aluminizing in avacuum furnace, the aluminizing treatment was performed by Cementation technique using a semi closed crucible at (1000°C) for (4 hr) duration, a full detail of this technique is found in (levin et al., 1998). The post coating heat treatment (Re diffusion) conducted inavacuuume furnace for (2hr) at (1000°C).

2-Hot corrosion:

Cyclic corrosion of the coated specimen were conducted using alumina crucible contains a suitable amount of sodium sulfate salt. Each sample was subjected to cycle interval of (24h), at (884°C) (melting point). After each cycle, the sample was cooled to room temperature, un-coated samples were also subjected for comparison. The weight change measurements with time were taken at the end of each cycle, using an electronic balance of sensitivity (0.0001g). The corroded sample then mounted for cross-sectioned microscopic test, others were prepared for (X-Ray Diffraction)(XRD) analysis.

RESULTS AND DISCUSSION

1-Simple Aluminide Diffusion Coatings:

The microstructure of (Al) diffusion coating is shown in Fig. (1).

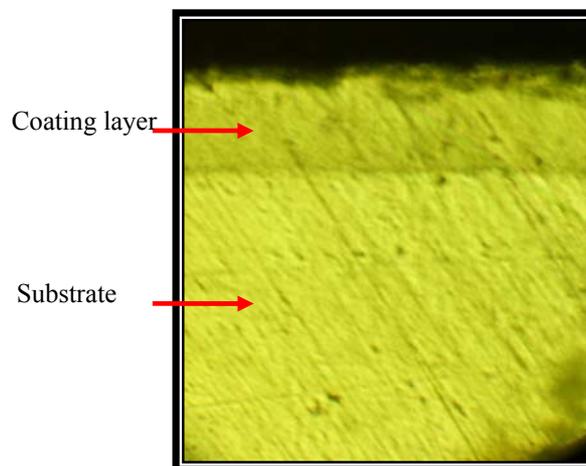


Fig 1:Microscopic structure of (Al) coating at (1000°C) for (4hr).

Coatings of one layer (60-65 μ m) with multiphase appearance were produced. Analysis of the coating surface using (XRD) reveals the formations of inter metallic compound (Fe_2Al_5), other phases of chromium aluminide also proved to be present. Because of the high activity of the pack used, this coating layer was formed by inward diffusion of (Al). into the substrate. And because of the limited solubility of the Cr (5%), the chromium can be precipitated as chromium aluminide. See Table (2).

Table 2 : XRD of aluminized specimen at (1000°C) for (4hr).

Phase Type	Relative Intensity
Fe ₂ Al ₅	VS
FeAl	W
Cr ₂ Al	VS
Al ₅ Cr	S

S = Strong
W=Weak

VS = Very Strong

However, after the heat treatment (re diffusion), the coating was consisted of two equ-thick layers (30µm), an outer layer of (FeAl) and inner layer of iron –rich aluminide (Fe₃Al) may be formed Fig. (2):

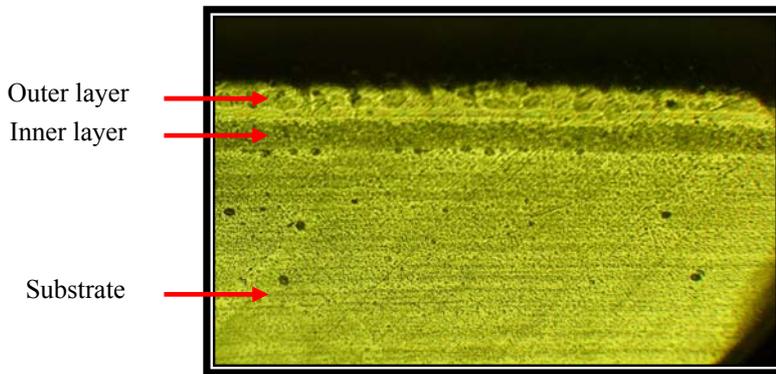


Fig. 2 : Microscopic structure of (Al) coating after the heat treatment at (1000°C) for (2hr).

During the heat treatment, it appears that the loss of (Al), from the coating surface Deeper in the substrate, resulted in a phase transformation of the outer layer, meanwhile the counter-diffusion of Fe from the substrate may contribute in the iron-rich aluminide formation as the inner layer. XRD, however, confirms these results, See Table (3).

Table 3 : XRD of aluminized specimen after the heat treatment at (1000°C) for(2hr).

Phase Type	Relative Intensity
FeAl	S
Fe ₃ Al	W
Cr ₃ Al ₂	W
Cr ₂ Al	W

The microstructure of the coatings after cyclic corrosion in a molten salt (Na_2SO_4) at (884°C) for both, as coated condition and after re-diffusion are shown in Fig. (3-3a,b).

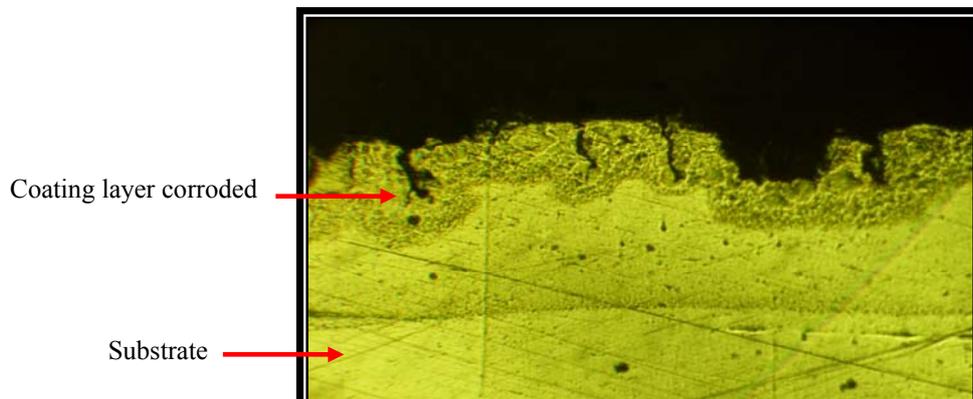


Fig. 3a : Microscopic structure of aluminized specimen exposed to cyclic oxidation in a molten salt of (Na_2SO_4) at (884°C) for (192hr)

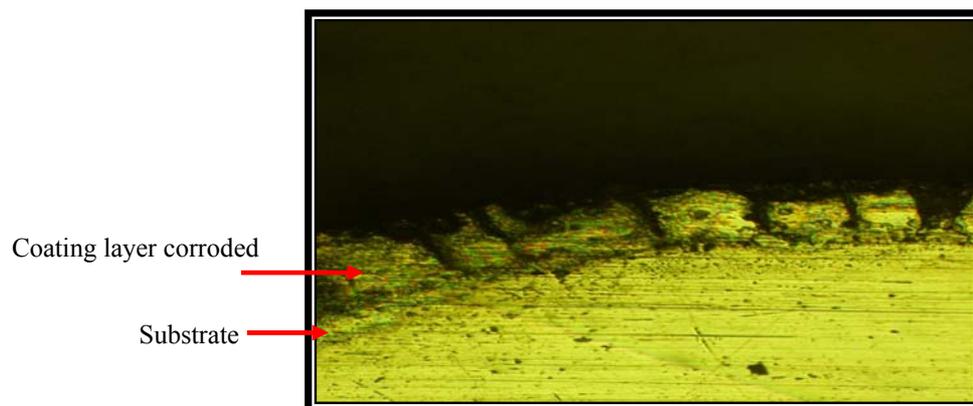


Fig. 3b : Microscopic structure of the heat treatment aluminized specimen exposed to cyclic oxidation in a molten salt of (Na_2SO_4) at (884°C) for (192hr).

The weight change per unit area versus time of exposure for the heat-treated specimen shows a higher weight loss than as coated conditions, as shown in Fig. (4), this may interpret the observation of cracks and local spallation of the protective oxide scale.

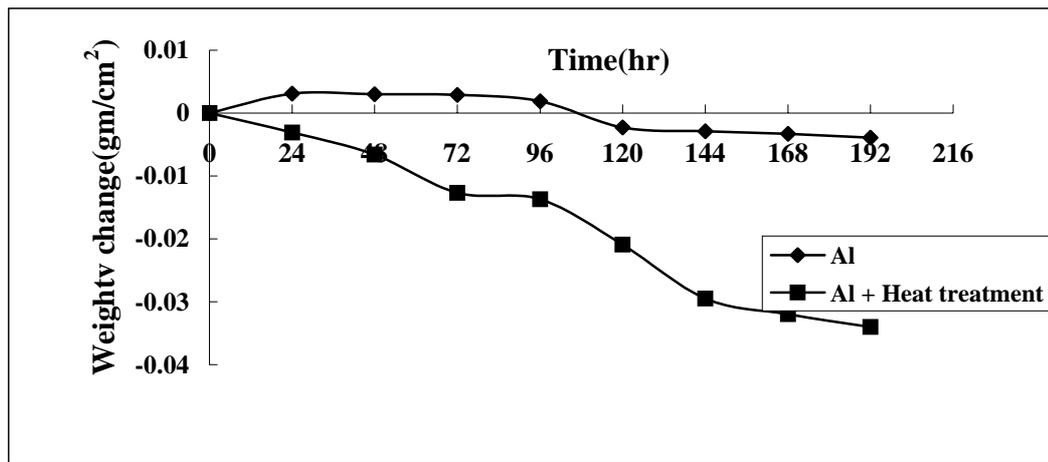


Fig. 4 :Weight gain vs. time curves for coated (Al, Al + Heat treatment) exposed to cyclic oxidation in amolten salt of (Na_2SO_4) at (884°C) for (192hr).

XRD, Table (4), proved the presence of spinal type (FeCr_2O_4) scale and probably (NiAl_2O_4) for the as-coated specimen, (Ni_2O_3) and iron sulfide (FeS_2) (FeS) was also present, but there is a weak indication for the presence of ($\alpha\text{-Al}_2\text{O}_3$) scale.

Table 4 :XRD of aluminized specimen exposed to cyclic oxidation in amolten salt of (Na_2SO_4) at (884°C) for (192hr).

Phase Type	Relative Intensity
$\alpha\text{-Al}_2\text{O}_3$	W
Fe_2O_3	W
FeS_2	S
FeS	S
Ni_2O_3	S
FeCr_2O_4	VS
NiAl_2O_4	S

For the heat-treated specimen, however, shows no protective scale, but spinel type (NiCr_2O_4) and (FeCr_2O_4) were detected, as well as, (FeS) and (FeS_2), see Table (5). It seems that the deleterious effect of porous spinels and low melting point of iron sulfides. Allows the out word Diffusion of cations from the coating to contribute in a faster oxidation rate and there fore a thicker ($\alpha\text{-Al}_2\text{O}_3$) can be formed which easy to spall. However, during the cooling from high temperature oxidation, thermal stresses may also produced and easier scale spallation can occurred.

Table 5 :XRD of the heat treatment of aluminized specimen exposed to cyclic oxidation in amolten salt of (Na_2SO_4) at (884°C) for (192hr).

Phase Type	Relative Intensity
$\alpha\text{-Al}_2\text{O}_3$	VW
Cr_2S_3	VW
NiO	W
FeS	S
FeS_2	S
NiCr_2O_4	VS
FeCr_2O_4	S

VW=Very weak

2- Nickel- Aluminide coatings:

Characterization of the nickel-aluminide coatings on stainless steel (321AISI) is Shown Fig. (5).

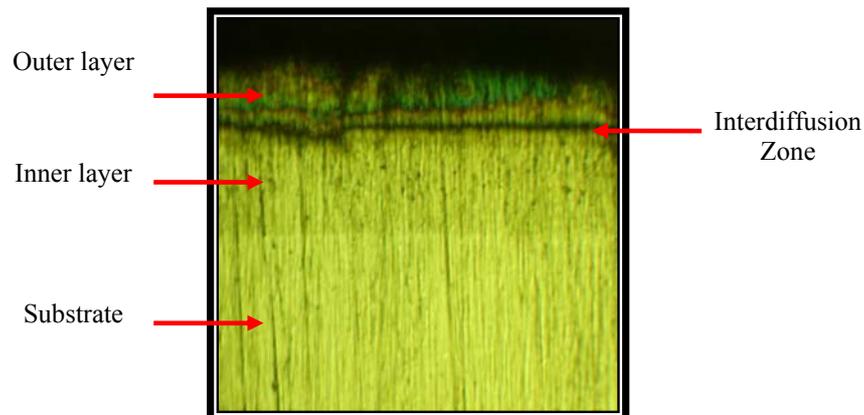


Fig 5 : Microscopic structure of (Ni-Al) coatings at (1000°C) for (4hr).

The coating produced was consisted of a thin outer layer ($15\text{-}20\mu\text{m}$) and thick inner layer ($70\text{-}75\mu\text{m}$), these layers are separated by an Interdiffusion zone ($5\mu\text{m}$). The outer most layer of the coating has, at least, two phase appearance based on (Ni_2Al_3) matrix, others, iron aluminide and chromium aluminide may also present as secondary phases, see Table (6):

Table 6 : XRD of (Ni - Al) coatings specimen at (1000°C) for (4hr).

Phase Type	Relative Intensity
Ni ₂ Al ₃	VS
FeAl ₃	S
FeNi	VW
FeAl	VW
Cr ₃ Al ₂	S
CrAl ₅	W

After re-diffusion treatment of this model of coatings, a phase transformation has been occurred, while the coating morphology is not much different from the as-coated one, except in thickness, The total thickness is measured to be about (30-40 μ m), an interdiffusion zone of thickness was also present (7 μ m), see Fig (6):

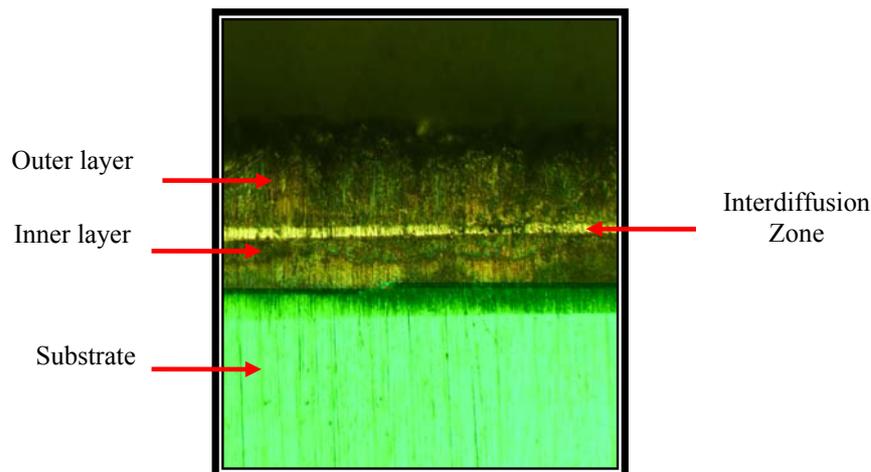


Fig. 6 : Microscopic structure of (Ni - Al) coatings after the heat treatment at (1000°C) for (2hr).

Indeed the outer layer of the coating was degraded to stoichiometric (NiAl) via the inter diffusion between the coating and substrate elements as we see in Table (7), the X-Ray result Confirms this transformation and indicating to the formation of (FeAl) phase which may represents the inner layer of the coating.

Table 7 : XRD of the heat treatment (Ni - Al) coatings specimen at (1000°C) for (2hr).

Phase Type	Relative Intensity
NiAl	VS
Ni ₃ Al	W
FeAl	VS
FeNi	S
CrAl ₅	W
Cr ₂ Al	W
Fe ₃ Al	W

The microscopic test of the coating system after the exposure time in a molten salt, Fig. (7a, b). Reveals a very localized cracks along the outer layer and these cracks could be considered an easy access to sulfides to reach the interface between outer / inner layer of the coating and may cause sulphidation of some coating elements. A close look of the coating system, we can recognize the presence of adhesive oxide scale and no coating collapse were observed. After re-diffusion treatment, the coating shows a higher density of sulfides compound formation specially at the upper region of the outer layer and even more cracks were occurred along this layer, and occasionally some oxide spallation were noticed.

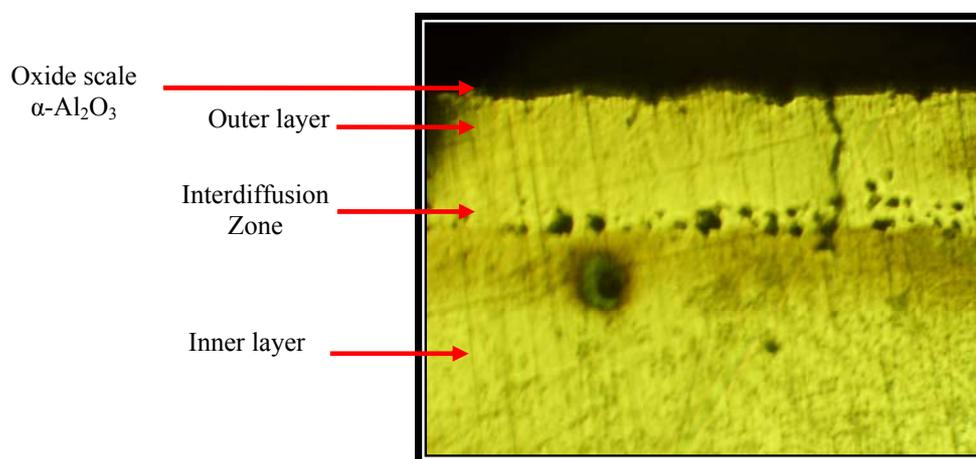


Fig 7a : Microscopic structure of (Ni - Al) coatings exposed to cyclic oxidation in a molten salt of (Na₂SO₄) at (884°C) for (192hr)

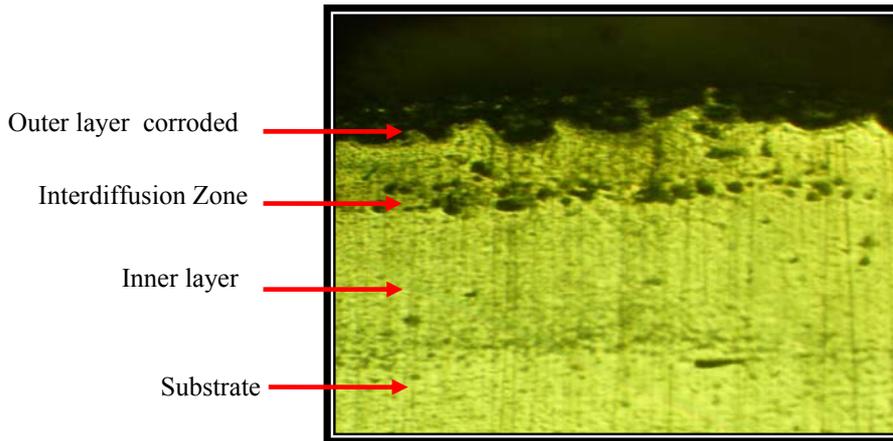


Fig 7b : Microscopic structure of the heat treatment (Ni -Al) coatings exposed to cyclic oxidation in amolten salt of (Na₂SO₄) at (884°C) for(192hr)

The weight change per unit area, Fig. (8), showed a lower rate of oxidation for the heat treated coating, compared to the as-coated condition, after the first interval (24hr) of the exposure time, a significant mass loss was detected corresponding to scale spallation, healing and re-healing processes were continue along the exposure time in contrast to the as-coated specimen, where such spallation was not recorded.

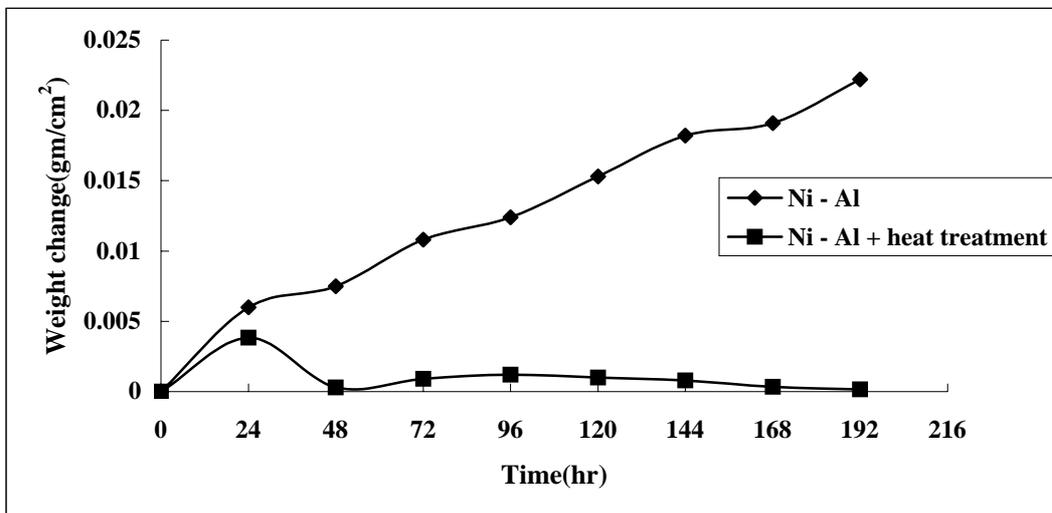


Fig 8 :Weight gain vs. time curves for coated (Ni -Al, Ni -Al + Heat treatment) exposed to cyclic oxidation in amolten salt of (Na₂SO₄) at (884°C) for (192hr).

XRD-analysis for both the as-coated and re-diffused specimen Table (8,a, b) Proved the Presence Of protective oxide scale (α - Al₂O₃), others oxides of Nickel and spinel oxide may also present but not for the as-coated specimen.

Table 8a : XRD of (Ni - Al) coatings specimen exposed to cyclic oxidation in amolten salt of (Na₂SO₄) at (884°C) for(192hr).

Phase Type	Relative Intensity
α -Al ₂ O ₃	VS
Ni ₂ O ₃	S
NiO	VS
FeS	W
FeS ₂	W
NiAl ₂ O ₄	VW
Ni ₃ Al	W

Table 8b :XRD of the heat treatment (Ni- Al) coatings specimen exposed to cyclic oxidation in amolten salt of (Na₂SO₄) at (884°C) for(192hr).

Phase Type	Relative Intensity
α -Al ₂ O ₃	VS
Ni ₂ O ₃	VS
Ni ₃ S ₂	S
FeS ₂	S
Fe ₃ Al	W
NiAl ₂ O ₄	S
FeCr ₂ O ₄	S

However, Nickel and iron sulfides were detected for the heat-treated specimen but not for the as-coated one. The formation of elements sulfides and spinel type oxide, could be lead eventually to premature scaling and spallation of the protective oxide, but this is not observed, at least up to the end of the exposure time. This result actually agreed with investigation reported by (Svenson, 2003), who also observed that the high degree of scale spallation had been occurred for the low (Al-NiAl), the case which we obtained after the re-diffusion treatment.

For advanced coating performance conducted by (Leyens et al, 2000), it seems Hf-doped (NiAl) exhibited slow oxide scale growth rate and excellent spallation resistance obtained in flowing oxygen test, however, the addition of (Cr) appears an essential element to provide resistance to corrosion in molten salts, which is already

present in the alloy coated in this investigation, While the Al availability considered an essential element for the long-term resistance (pint et al., 2000).

3-Nickel coating:

Nicked coatings on stainless steel were conducted by Electrodeposition technique of thickness ($13\mu\text{m}$). The coated specimens were then subjected to heat treatment in avacuum for (2hr), at ($1000\text{ }^\circ\text{C}$). A diffusion layer obtained was consisted of (Fe Ni) solid solution, See Fig (9 a, b)

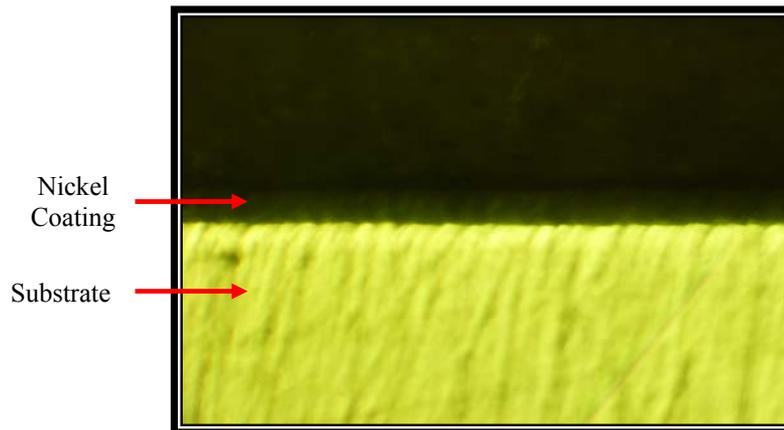


Fig 9,a :Microscopic structure of Nickel coating.

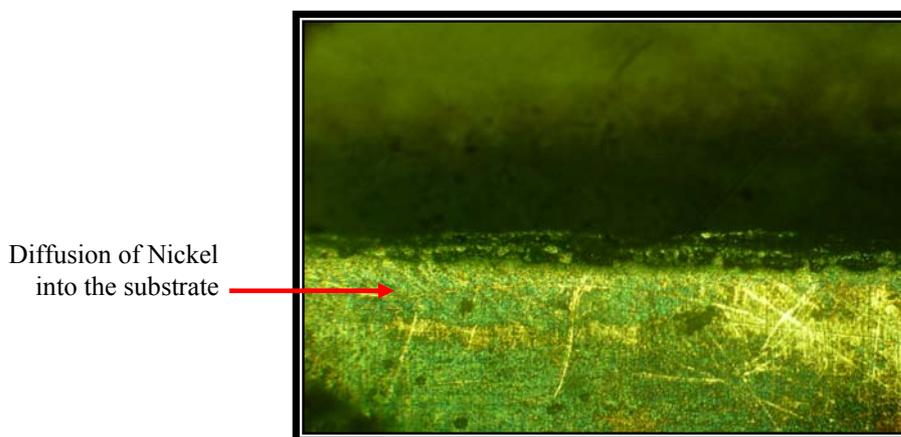


Fig 9,b :Microscopic structure of the heat treatment Nickel coating at (1000°C) for (2hr).

Cyclic corrosion test in a molten salt, showing that the coatings were highly attacked and severely collapse at the end of exposure time, Fig. (10).

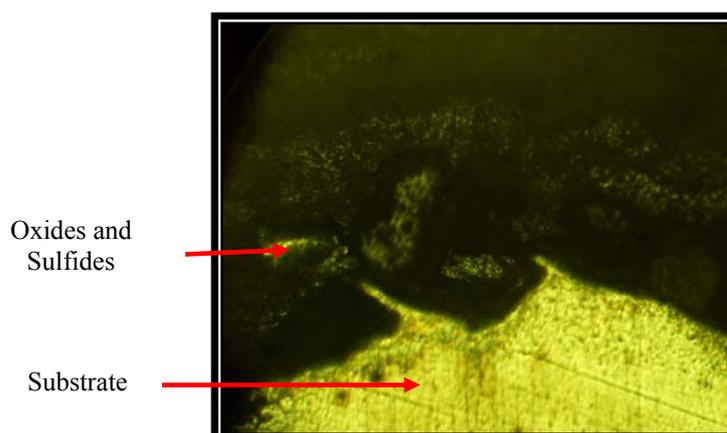


Fig. 10 :Microscopic structure of Nickel coating specimen exposed to cyclic oxidation in molten salt of (Na_2SO_4) at (884°C) for (192hr).

The weight loss occurred began even before the end of the first cycle, this could indicate the fast spallation of oxides which is formed during the early stage of oxidation. However, some improvement in corrosion resistance has been attained compared with the Un-coated specimen, See Fig. (11).

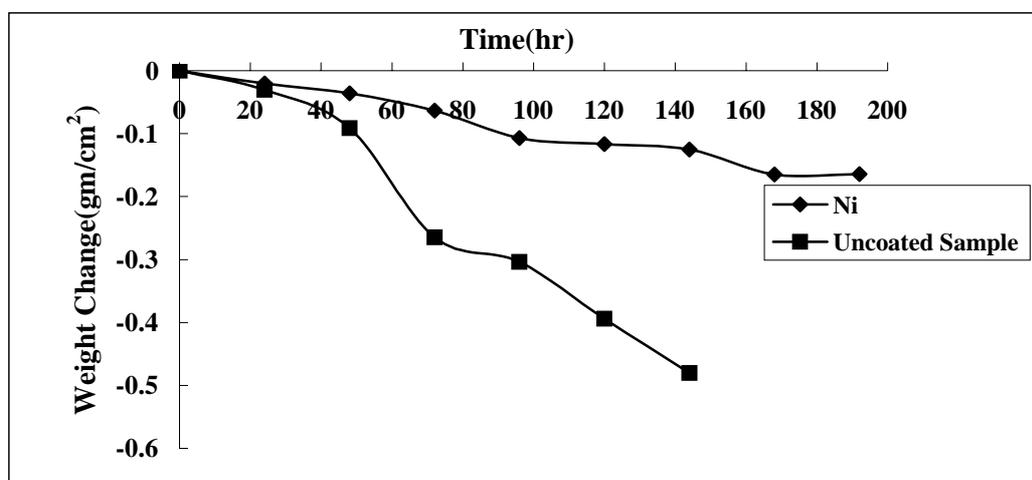


Fig. 11 :Weight gain vs. time curves for (Ni coating and Un-coated sample) exposed to cyclic oxidation in molten salt of (Na_2SO_4) at (884°C) for (192hr).

XRD, results proved the formation of Nickel oxides and some element sulfides such as (Ni_3S_2), (Fe_7S_8) as well as spinel type (FeCr_2O_4), as shown in Table (4-9).

Table 9: XRD of Nickel coating exposed to cyclic oxidation in molten salt of (Na_2SO_4) at (884°C) for (192hr).

Phase Type	Relative Intensity
Ni_3S_2	VS
NiS_2	VW
Ni_2O_3	VS
NiO	S
Fe_7S_8	VS
FeS	W
FeCr_2O_4	S

It seems the improvement in corrosion resistance obtained could be interpreted on the basis of nickel oxide formation as subscale beneath the protective chromia, which may form and spall during the oxidation processes. The formation of Nickel oxides as a subscale might slow down the outward diffusion of (Fe) which contributes to the formation of (Fe_2O_3) as subscale, the formation of (Fe_2O_3) oxide as subscale, could lead to a higher rate of oxidation and therefore a thicker oxide layer produced which may spall off faster.

CONCLUSION

From the available results for the coating of (321 AISI) stainless steel, it appears that the pre-coating of stainless steel with (Ni) before aluminizing can improve the hot corrosion resistance in the presence of molten salts (Na_2SO_4). Simple aluminide and to a lesser extent, (Ni) can improve hot corrosion resistance when compared to uncoated alloy. Notably the electrodeposition of (Ni) to stainless steel before aluminizing resulted in a coating production of nickel-aluminide intermetallic compounds in the state of iron-aluminide intermetallic compounds. The nickel-aluminide coating, however, proved to form a nickel-oxide as subscale underneath the protective alumina scale, and reduces the probability of iron-oxide formation and iron-sulfide compound, which is characterized by a low melting point and can accelerate the spallation of the protective alumina scale. Further knowledge of the alloy and coating composition is required, an extensive investigation of the oxides and their morphology, using more advanced techniques may also be needed.

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