Hot Corrosion Behavior of Thermal Spray Coating

by

Karabo Masipa

15218

Dissertation submitted in partial fulfillment of the requirements for the Bachelor of Engineering (Hons) (Mechanical Engineering)

JANUARY 2015

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CERTIFICATION OF APPROVAL

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Approved by,

Dr Subhash Kamal (Supervisor)

Universiti Teknologi PETRONAS TRONOH, PERAK

January 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein has not been undertaken or done by unspecified sources or persons.

KARABO MASIPA

ABSTRACT

Austenitic stainless steel AISI 304 and Boiler steels (such as P11, P22, P12) find their largest application in the manufacturing industry. These are preferred because of their superior mechanical strength, surface stability, creep and fatigue resistance. However, they are highly susceptible to hot corrosion. Therefore, surface engineering imparts hot corrosion resistance properties in high temperature corrosive environments. In the present study, Cr_3C_2 -25NiCr coating was deposited on the substrate 304SS by High Velocity Oxygen Fuel (HVOF) technique in order to investigate the behavior of the Cr_3C_2 -NiCr thermal spray coating. The bare specimens were boilier steel alloys P11, P12 and P22. Hot corrosion test was conducted on bare and coated specimens in 40%K₂SO₄ -40%Na₂SO₄ -10%NaCl -10%KCl environment at 900 °C for 10 cycles. Corrosion kinetics was monitored using weight gain measurements. Characterization of corrosion products was carried out by scanning electron microscope with energy-dispersive x-ray spectroscopy (SEM/EDS) technique. The observed corrosion resistance of the Cr_3C_2 -NiCr coating can be attributed to the formation of protective oxide scale Cr_2O_3 . The corrosion mechanism of the coating is discussed.

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TABLE OF CONTENTS

TITLE PAGE		i
CERTIFICATION	OF AI	PPROVALü
CERTIFICATION	OF OI	RIGINALITYüii
ABSTRACT		iv
ACKNOWLEDGEN	MENT	V
LIST OF FIGURES		viii
LIST OF TABLES .		ix
ABBREVIATIONS	•••••	Х
CHAPTER 1:	INTE	RODUCTION 1
	1.1	Background of Study1
	1.2	Problem Statement
	1.3	Objectives
	1.4	Scope of the Project4
CHAPTER 2:	LITE	ERATURE REVIEW
CHAPTER 3:	MET	'HODOLOGY
	3.1	Substrate Materials
	3.2	Sample Preparation
	3.3	Corrosion Test11
	3.4	Characterization Techniques11
CHAPTER 4:	RES	ULTS AND DISCUSSION12
	4.1	Visual Observation
	4.2	Weight Change Measurements13
	4.3	Morphology and Composition of Scales

	4.4	Discussion	17
CHAPTER 4:	CON	NCLUSION AND RECOMMENDATION	19
REFERENCES			
APPENDICES			

LIST OF FIGURES

Figure 1: Basic Principle of Thermal Spraying [6]2
Figure 2: Coating deposition and the oxidation process [12]3
Figure 3: FESEM micrograph of coating powders (a) Cr_3C_2 -25NiCr, (b) Cr3C2-25(NiCr)+0.4%CeO ₂ , (c) Cr3C2-25(NiCr)+0.4%CeO ₂ with EDS [17]7
Figure 4: Macrophotos of (a) Superni 600, (b) Superni 718, and (c) Superco 605 after cyclic hot corrosion in Na2SO4-25%NaCl at 900° C for 100 cycles [14]8
Figure 5: Macrographs of specimens after cycle 1; a) P11, b) P12, c) P22 and d) Cr_3C_2 -NiCr coated specimen
Figure 6: Macrographs of specimens at cycle 10; a) P11, b) P12, c) P22 and d) Cr ₃ C ₂ -NiCr coated specimen
Figure 7: Weight change curves for bare and Cr_3C_2 -NiCr coated specimens14
Figure 8: SEM micrograph of hot corroded bare P11 surface15
Figure 9: SEM micrograph of hot corroded bare P12 surface15
Figure 10: SEM micrograph of hot corroded bare P22 surface15
Figure 11: SEM micrograph of hot corroded Cr_3C_2 -NiCr coated surface16
Figure 12: SEM micrographs of bare P11 hot corroded surface
Figure 13: SEM micrographs of bare P12 hot corroded surface
Figure 14: SEM micrographs of bare P22 hot corroded surface
Figure 15: SEM micrographs of bare P22 hot corroded surface23

LIST OF TABLES

Table 1: Chemical Composition of the Materials	10
Table 2: Elements found in the hot corroded Cr ₃ C ₂ -NiCr coated surface	16
Table 3: Project Milestone for FYP I	24
Table 4: Project Milestone for FYP II	24

ABBREVIATIONS

- AISI American Iron and Steel Institute
- Cr₃C₂-NiCr Chromium carbide-Nickel chrome
- HVOF High Velocity Oxygen Fuel
- SEM Scanning Electron Microscope
- XRD X-ray diffraction
- Na₂SO₄-Sodium sulfate
- NaCl-Sodium chloride
- $V_2O_5-Vanadium$ pentoxide
- SO3-Sulfur trioxide
- LVOF Low Velocity Oxygen Fuel
- AIP Arc ion plating

CHAPTER 1

1. INTRODUCTION

1.1. Background of Study

Engineering systems operating at high temperatures of above 650° C involve contact metallic materials with combustion product gases. This leads to the detrimental phenomenon of hot corrosion. Hot corrosion is the most aggressive form of degradation of components operating in high temperatures such as gas turbines, furnaces, boilers and diesel engines. It is an accelerated corrosion, resulting from the presence of salt contaminants such as Na₂SO₄, NaCl and V₂O₅ that combine to form molten deposits [1]; consequently causing the dissolution of protective surface oxides at the metal surface, contributing to the weakening of the material as the surface is rapidly consumed.

Hot corrosion can be characterized into two types, i.e. Type I, also known as high temperature hot corrosion, is characterized by temperature range $800-950^{\circ}C$ [1,6]; and Type II, also known as low temperature hot corrosion, occurring at temperatures below $800^{\circ}C$ [3]. Type I corrosion is caused by molten salt deposition on the material surface, while Type II hot corrosion mechanism involves acidic fluxing of protective oxides by sulfur trioxides (SO₃) dissolved in molten sulfates [6].

Compounds such as sodium, vanadium, potassium and sulfur are common impurities that are present in many high temperature environments. They react together to form low melting molten salts that get deposited on the material surface as a thin film and induce hot corrosion [4, 5].

Components used in aggressive environments require materials capable of withstanding increasing operating temperatures, chemical degradation and with good mechanical properties. However, it is not possible for a single material to have different properties to meet today's industrial demand [4]. Therefore, the use of protective coatings on the material surface could enhance the material properties to

withstand the aggressive environments. Protective coating techniques such as thermal spraying and laser cladding have become more popular [4].

Thermal spray coating offers an effective and economic way to counteract the hot corrosion problem since it alters the surface without affecting any other properties of the components [4, 6]. Thermal spray coatings are produced by rapidly heating the feedstock material in a hot gaseous medium and simultaneously projecting it at a high velocity onto a prepared surface where it builds up to produce the desired coating [4]. There are various thermal spraying techniques that can be used to apply coating, such as plasma, detonation gun, high velocity oxygen fuel (LVOF) and arc ion plating (AIP).



Figure 1: Basic Principle of Thermal Spraying [6]



Figure 2: Coating deposition and the oxidation process [12]

1.2. Problem Statement

Austenitic stainless steel AISI 304 and Boiler steels (such as P11, P22, P12) find their largest application in the manufacturing industry; these are preferred because of their superior mechanical strength, surface stability, creep and fatigue resistance. Materials used for high temperature strength are highly susceptible to hot corrosion and the surface engineering plays a key role in effectively combating the hot corrosion and oxidation problems. The contaminants such as sodium, sulfur and vanadium cause the metals to undergo a rapid degradation. Consequently, the metals weaken and their life span is shortened, leading to the catastrophic failure of the components. This phenomenon occurs as a result of contaminants reacting with one another, forming molten salts that get deposited as a thin film on the metal surface. This is called hot corrosion and is a common occurrence in high temperature operating systems.

1.3. Objectives

The aim of this study is to investigate the behavior of bare and Cr_3C_2 -NiCr coated alloys under molten salts environment (40%K₂SO₄ -40%Na₂SO₄ -10%NaCl - 10%KCl) at of 900 °C for 50 hours (10 cycles).

1.4. Scope of Study

Hot corrosion is a serious problem, recent studies show that the high temperature strength materials are highly susceptible to hot corrosion and surface engineering plays a key role in effectively alleviating hot corrosion. Therefore, the combination of two materials, i.e. base and coating must be considered as an integral system to avoid hot corrosion.

Owing to the aforementioned facts, there is a significant scope in understanding the reaction kinetics and the nature of the surface scales formed during hot corrosion. The hot corrosion behavior of bare and coated alloys has not been studied extensively and is not well understood. Therefore, further studies are needed on hot corrosion behavior particularly those used for high temperature applications.

CHAPTER 2

2. LITERATURE REVIEW

The following section is a brief review of the earlier studies relevant to the present study. The literature contains a comprehensive review of the different protective coatings in molten salts. Researchers have conducted experiments to simulate real cases of hot corrosion conditions as in gas turbines, incinerators and jet engines environment to study the hot corrosion behavior.

Wu et al. [8] investigated the hot corrosion behavior of the Cr –modified aluminide coating exposed to molten salt with Ni-based superalloy DSM11 as the substrate. Hot corrosion behaviors of the DSM11 alloy, the aluminized coating and Al-Cr coating specimens were exposed to Na_2SO_4/K_2SO_4 (3:1) and $Na_2SO_4/NaCl$ (3:1) mixtures, at 900 °C. The exposure was done at regular intervals of 20 hours. The results showed that Cr-modified aluminide (Al-Cr) coating and aluminized coating both exhibited excellent corrosion resistance in the mixture salt of Na_2SO_4/K_2SO_4 . Moreover, the Cr-modified aluminide coating showed good resistance in the mixture of $Na_2SO_4/NaCl$ due to the beneficial effect of Cr in the coating; while the aluminized coating was seriously damaged and lost its protective effect after corrosion.

Sidhu et al. [9] comparatively evaluated the hot corrosion behavior of the Cr_3C_2 -NiCr and Ni-20Cr coatings sprayed by HVOF on Ni-based superalloy in a molten salt environment of Na₂SO₄-60% V₂O₅ at 900°C. The study compared coated and uncoated specimens of Superni 600. The uncoated specimen showed less resistance to hot corrosion in the molten salts due to spalling behavior of the scale. The cumulative weight gain of the uncoated specimen was more than the coated specimen. The hot corrosion resistance of the Cr_3C_2 -NiCr coating may be due to the formation of protective phases like NiO, Cr_2O_3 and NiCr₂O₄. A rich in chromium dense oxide scale formed on the coated specimen.

In the study that investigated the behavior of the NiCrAIY coatings deposited on the Superni76 under cyclic conditions at 900 °C in $Na_2SO_4 + 60\% V_2O_5$ salt, Rana et al. [10] showed that Cr_2O_3 formed and dissolved in the corrosive salts, and spallation of

the scale was observed. There was also the formation of Al_2O_3 sublayer at the coating/scale interface which provided a corrosion resistance layer. The results further showed that during the initial cycles the salt reacted with coatings and formed a corrosive compound $Ni_3V_2O_8$ and Y reacted with vanadium to form YVO_4 . However, from cycle 100 to 200 cycles, a minimum rate of the corrosion was observed.

Lin et al. [11] conducted a study investigating high-temperature oxidation and hot corrosion behaviors of Cr₂AlC at 800-1300 °C in air. The tests were carried out in the exposure of Na₂SO₄. The thermogravimetric-differential scanning calorimetric test revealed that oxidation began at 800 °C, which is 400 °C higher than that of other ternary transition metal aluminium carbides such as Ti₂AlC and Zr₃Al₃C₅. Moreover, CrAlC displayed excellent oxidation resistance, with parabolic rate constants of 1.08×10^{12} and 2.96×10^9 kg³m⁴s⁻¹ at 800 and 1300 °C, respectively. Cr₂Al₂ exhibited good hot corrosion resistance against Na₂SO₄ salt. The basic dissolution of Cr₂O₂ lowered the basicity of the molten salt, thus stabilizing the Al₂O₃ scale.

In another study conducted by Mudgal et al. [17], Cr_3C_2 -25NiCr and Cr3C2-25(NiCr)+0.4%CeO₂ coatings were deposited on nickel-based superalloy Superni 600. The study investigated the corrosion behavior of bare and coated alloys in molten salt environment (Na₂SO₄-25%NaCl) at 900°C under cyclic conditions. Results demonstrated that bare Superni 600 corroded in the molten salt environment, with a porous scale which was accompanied by weight loss due to minor internal oxidation. Whereas the Cr₃C₂-25NiCr and Cr3C2-25(NiCr)+0.4%CeO₂ coatings developed a dense scale and an overall weight gain. Cr₂O₂ and Na₂CrO₄ were found to be the common phases in the corrosion products of bare and coated specimens.



Figure 3: FESEM micrograph of coating powders (a) Cr₃C₂-25NiCr, (b) Cr3C2-25(NiCr)+0.4%CeO₂, (c) Cr3C2-25(NiCr)+0.4%CeO₂ with EDS [17]

Kamal et al. [13] deposited the coating powder NiCrAIY + 0.4 wt.% CeO₂ on the substrates superni 75, superni 718 and superfer 800H using a detonation gun. The specimens were subject to corrosive attack in the salt mixture of Na₂SO₄-60% V₂O₅ for 100 cycles under cyclic conditions. Each cycle consisted of 1 hour heating at 900° C. The results showed that there was 60 and 15% saving in overall weight gain for NiCrAIY + 0.4 wt.% CeO₂ coated superfer 800H and superni 75 in comparison to the bare superfer 800H and superni 75. Furthermore, a dense oxide formed on the coated superalloys and hot corrosion resistance of coating could have been due to the formation of protective phases like NiO, Cr₂O₃, Al₂O₃, NiCr₂O₄ and NiAl₂O₄. Formation of small amounts of oxides of iron and silicon showed diffusion from the substrate to the top surface of coating.

Mudgal et al. [14] conducted a study investigating the behavior of bare superalloys, Superni 718, Superni 600 and Superco 605, in the presence of Na_2SO_4 -25%NaCl.

The hot corrosion test was conducted at 900° C for 100 cycles. The Ni-based alloy 718 and alloy 600 showed a very marginal weight gain at the end of the test. However, in the case of alloy 718, NiO was seen as the major component of the scale and there is a formation of thin Cr_2O_3 layer between the scale and the substrate. This layer was capable of stopping diffusion of cation and anion species, therefore, stopping further reaction. Whereas in the case of alloy 600, the scale was thin and was mainly of Cr_2O_3 , and the reacting species has penetrated through the metal layer and has reacted with the substrate. In the case of Co-based alloy, Superco 605, there was enormous weight gain accompanied with intense spalling due to the non-protective nature of the scale. The main constituents of the scale are oxides of cobalt, chromium and tungsten. The final scale consisted of only cobalt and nickel. It was concluded that Ni-based alloys are more suitable to withstand aggressive corrosive environment than Co-based alloys.



Alloys in their respective alumina boats

Surface of alloys after 100 cycles



To increase the corrosion resistance of boiler components, Oksa et al. [16] applied three Ni-based coatings with high amounts of chromium were thermally sprayed on short boiler tube sections. The coatings were commercial powders, Alloy 59 (NiCr16Mo), Inconel 625 (NiCr9Mo) and NiCrAIY (NiCr10Al). The coatings were applied on a carbon steel tube (St35.8 DN 17175-79). The coatings were tested in the boiler for two years. The carbon steel tube St35.8 corroded strongly during the two year exposure in the biomass boiler. The corrosion rate was measured to be

2.3mm/year. However, the coatings had endured the boiler exposure well, the Nibased coatings offered excellent corrosion and erosion protection to the substrate material. The extreme severe corrosion of the carbon steel was caused by chlorine induced corrosion together with the effect of potassium, copper, zinc and lead in the deposits.

To investigate hot corrosion behavior of Superfer 800H, Kamal et al. [16] exposed the superalloy substrate to two different molten salt environments $Na_2SO_4+60\%V_2O_5$ and $Na_2SO_4+5\%V_2O_5+5\%NaCl$ respectively. The test was conducted for 50 cycles at 900° C. the results showed that there was crack initiation after 10 cycles in the presence of NaCl salt. Through the cracks, molten salts attack the substrate and cause hot corrosion. The formation of protective oxide scales NiO, Cr_2O_3 and NiCr₂O₄ provided resistance to hot corrosion. During the initial cycles, the results exhibited a high nickel concentration at metal interface region and as the number of cycles increase the nickel concentration increase in scale which consists of NiO and Cr_2O_3 . Crack propagation is due to the formation of Cr_2O_3 , because the region of crack propagation showed large quantities of chromium and oxygen.

CHAPTER 3

3. METHODOLOGY

3.1. Substrate Materials

The bare alloys, boiler steel P11, P12, P22, have been procured from Kalpataru Metals & Alloys, India, in the form of rolled rectangular sheets, AISI 304SS, and substrate material of AISI 304SS. The nominal chemical composition of the materials is shown in Table 1.

Alloy		Chemical Composition (wt.%)														
imoy	Fe	C	Si	Mn	S	P	Cr	Ni	Mo	Cu	Al	Ti				
P11	96.60	0.13	0.71	0.50	0.013	0.023	1.30	0.09	0.47	0.13	0.023	0.007				
P12	97.36	0.06	0.323	0.53	0.01	0.033	1.002	0.05	0.468	0.09	0.017	0.005				
P22	94.97	0.15	0.500	0.60	0.025	0.025	2.60	-	1.13	-	-	-				
304SS	66.345	0.08	1.00	2.00	0.030	0.045	20.00	10.5	-	-	-	-				

Table 1: Chemical Composition of the Materials

3.2. Sample Preparation

- Bare alloy specimens, P11, P12 and P22, were cut into rectangular pieces of dimensions 10mm×10mm×5mm; while the coated substrate specimen was cut to the dimensions of 30mm×30mm×5mm.
- The specimens were grinded and polished using 120, 180, 240, 320 and 400 emery paper followed by alumina polishing of 0.05 µm. They were then cleaned using acetone.
- They were preheated to 300 °C for 2 hours before applying the salt solution.
- Salt solution was prepared using distilled water and 8g $Na_2SO_4 + 2g$ $NaCl + 8g K_2SO_4 + 2g KCl$. A layer of salt (3-5 mg/cm²) was applied uniformly on the preheated specimens using a camel hair brush. The specimens were dried at the temperature of 250 °C for 3 hours for good adherence of the salt on the surface.

• After drying the specimens were weighed to ensure the quantity of salt application was correct. They were kept in the boats and weight was recorded as initial measurement.

3.3. Corrosion Test

The specimens were kept in the furnace for 10 cycles under cyclic conditions. Each cycle consisted of 5 hours of heating at 900 °C followed by 20 minutes cooling at room temperature. The weights of the specimens along with the boats were recorded after each cycle; therefore spalled material fallen in the boat is included in the weight measurements. Weight change measurements are performed to know the corrosion kinetics.

3.4. Characterization Techniques

Microstructural characterization of the specimens and corrosion products was carried out by scanning electron microscope with energy-dispersive x-ray spectroscopy (SEM/EDS) in order to understand the corrosion mechanisms.

CHAPTER 4

4. RESULTS AND DISCUSSION

4.1.Results

4.1.1. Visual Observations

Surface macrographs for bare and Cr_3C_2 -NiCr coated specimens after the hot corrosion studies at 900 °C for 10 cycles in Na₂SO₄ + NaCl + K₂SO₄ + KCl environment are shown in Figure 5 and Figure 6. The bare alloys showed an adherent compact corrosion scale on the surface. The oxide scale lasted up to 10 cycles, that is, no spallation was observed. The colour of the scale on the bare alloys was brownish with a mixture of grey and black phases on the surface. Cracks were also observed on the scale.

The Cr_3C_2 -NiCr coated alloy showed an intense yellow hue, particularly on the area where the salt was more concentrated. A greenish colour developed at the end of cycle 3. Mudgal et al. [18] and Rana et al. [10] reported the formation of similar oxide when Cr_3C_2 -NiCr coating is exposed to high temperatures and aggressive environment. The corrosion scale then turned greyish black with the progression of the study. Light spallation began at the end of cycle 4 (20 hours). No further spallation occurred till cycle 8, where there was great spalled material. Cracking was confined to the top edge of the specimen.



Figure 5: Macrographs of specimens after cycle 1; a) P11, b) P12, c) P22 and d) Cr_3C_2 -NiCr coated specimen



Figure 6: Macrographs of specimens at cycle 10; a) P11, b) P12, c) P22 and d) Cr₃C₂-NiCr coated specimen

4.1.2. Weight Change Measurements

Weight change (mg) vs time plot for the bare and coated specimens in $Na_2SO_4 + NaCl + K_2SO_4 + KCl$ environment at 900 °C for 10 cycles is shown in Figure 7. Hot corroded bare specimens showed higher weight gains.





Figure 7: Weight change curves for bare and Cr₃C₂-NiCr coated specimens

4.1.3. Morphology and Composition of Scales

The samples were subject to SEM-EDS analysis to characterize the surface morphology of the hot corroded specimens and the results are shown in Figure 8 to Figure 11. The microstructure of the hot corroded surface of bare P11 is shown in Figure 8. The oxide scale exhibited a dense structure with small and large globules which are irregularly distributed in the scale, with the presence of iron and oxygen as the major elements. While the microstructures of the hot corroded surfaces of bare P12 and P22, as shown in Figure 9 and Figure 10, exhibited iron and oxygen as the major elements and manganese as a minor element. The EDS analysis on the hot corroded surface for the presence of the elements iron, oxygen, potassium, sodium, chromium, manganese and sulfur.



Figure 8: SEM micrograph of hot corroded bare P11 surface



Figure 9: SEM micrograph of hot corroded bare P12 surface



Figure 10: SEM micrograph of hot corroded bare P22 surface



Figure 11: SEM micrograph of hot corroded Cr₃C₂-NiCr coated surface

The following are the elements found on the overall hot corroded Cr_3C_2 -NiCr coated surface.

Element Symbol	Element Name	Wt. %	Error %
Fe	Iron	65.3	0.9
0	Oxygen	20.4	1.3
К	Potassium	2.4	1.2
Cr	Chromium	2.9	1.8
Mn	Manganese	3.5	1.7
S	Sulfur	1.4	1.5
Na	Sodium	4.1	1.3

Table 2: Elements found in the hot corroded Cr_3C_2 -NiCr coated surface

4.2.Discussion

Figure 7 shows the corrosion kinetic curves of the bare and Cr_3C_2 -NiCr coated specimens. The mass change consists of a mass gain and mass loss. The mass gain is attributed to the formation of the scales, and the mass loss is caused by scale spallation and dissolution. The bare alloys demonstrated a rapid weight gain due to an accelerated formation of an oxide layer. Subsequent increase in weight was gradual as the dense oxide scale formed on the bare specimens, efficiently protecting the underlying layer from further corrosion attack. Mudgal et al. [18] reported that once the oxide formed at splat boundaries, the scale becomes dense and the diffusion of oxidizing species to the underlying sub-region gets slow which makes the weight gain and oxidation rate steady.

The Cr_3C_2 -NiCr coated specimen exhibited a loss in weight during the initial cycles of the hot corrosion study. According to Mudgal et al. [17] this decrease in weight may be due to reaction between the oxide formed on the coating surface and its chlorides in the presence of oxygen as shown in Eq 1.

$$2NaCl + Cr_2O_3 + 0.5O_2 \rightarrow Na_2Cr_2O_4 + Cl_2$$
 (Eq 1)

SEM/EDS analysis was conducted to understand the mechanism of hot corrosion on the bare and coated specimens. High amounts of Fe and O were detected on the bare hot corroded specimen surfaces which implied that Fe_2O_3 formed a solid solution. The formation of the corrosion layer is described in Eq 2. The dense solid oxide layer slowed down the hot corrosion process.

$$4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$$
(Eq 2)

While the Cr_3C_2 -NiCr coated specimen surface indicated significant amounts of Cr thus implying the formation of Cr_2O_3 . The analysis also showed the amount of Na to be higher than that of Cr, which implied that at the coating surface the dissolution of Cr_2O_3 took place as seen in Eq 3 [11]; therefore causing the spallation of the top surface of the coating.

$$Cr_2O_3 + 2Na_2O + 1.5O_2 \rightarrow 2Na_2CrO_4$$
 (Eq 3)

With the protective feature of the Cr_3C_2 -NiCr coating deteriorated during the dissolution, oxygen and sulfur could easily penetrate into the coatings and trigger the formation of internal oxides and chromium sulfides [8]. These would consequently speed up the corrosion process.

The intense spallation of the top surface of the coating may also be attributed not only to the salt attack but a combination of voids and oxygen.

CHAPTER 5

5. CONCLUSION AND RECOMMENDATION

- Bare alloy and coated specimens were oxidized at 900 °C in the presence of Na₂SO₄ + NaCl +K₂SO₄ + KCl for the exposure period of 10 cycles in order to learn the behavior of the thermal spray coating in comparison to the bare alloy.
- 2. The surface morphology showed the bare alloy to be prone to hot corrosion, whereas the Cr_3C_2 -NiCr coating morphology showed the substrate was still intact.
- 3. The observed corrosion resistance of the Cr_3C_2 -NiCr coating can be attributed to the formation of protective oxide scale Cr_2O_3 . The dissolution of the Cr_2O_3 scale by the molten salts and the presence of voids led to the intense spallation of the top surface of the coating. The top surface did not show any corrosion products, thus the coating prevented the penetration of hot corrosion to the substrate material.

Recommendation

The Cr_3C_2 -NiCr coating may have consisted of voids and porosity originating from the spraying process, through which the coating was mainly attacked. The porosity of the coating plays an important role as far as corrosion resistance is concerned. As a result, a denser coating would provide a better corrosion resistance, which then degrades less due to its more closely packed structure.

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21

APPENDIX 1



Figure 12: SEM micrographs of bare P11 hot corroded surface



Figure 13: SEM micrographs of bare P12 hot corroded surface



Figure 14: SEM micrographs of bare P22 hot corroded surface



Figure 15: SEM micrographs of bare P22 hot corroded surface

APPENDIX 2

Table 3: Project Milestone for FYP I

Item/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Project Title Selection														
Preliminary Research and Scope Determination														
Literature Review														
Extended Proposal Submission						*								
Resource Gathering														
Proposal Defence Presentation									*					
Submission of FYP I Draft Interim Report													*	
Submission of FYP I Interim Report														*

Table 4: Project Milestone for FYP II

Item/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Hot corrosion test experiments														
Submission of Progress Report							\star							
SEM/EDS Analysis										*				
Pre-Sedex										×				
Submission of Draft Final Report											*			
Submission of Dissertation (soft bound)												*		
Submission of Technical Paper												*		
Viva														*