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SELECTION AND EVALUATION TESTING OF PROTECTIVE COATINGS FOR BIOFUEL-POWERED OGT 2500 GAS TURBINE HOT SECTION

by

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A thesis submitted to the Faculty of Graduate
Studies and Research in partial fulfillment
of the requirements for the degree of

Master of Applied Science

The Ottawa-Carleton Institute for Mechanical and Aerospace Engineering
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DEDICATION

I dedicate this work to my mother Huixin Shao.

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ABSTRACT

Biofuel power generation is receiving significant international attention as a technology from a renewable resource. The use of biofuel requires an examination of the effect of the fuel on engine materials. The effects of the high alkali and low sulfur contents of the fuel on its corrosive properties need to be examined. To determine the extent and the type of corrosion, typical coating systems such as diffusion coatings (DC), overlay coatings (OC), and Thermal Barrier Coatings (TBC) were exposed to biofuel combustion products in flame tunnel and furnace environments under conditions designed to promote high-temperature corrosion. The current study is a preliminary examination of the hot corrosion resistance of ten different coatings to biofuel combustion products at three service temperatures typical of an operating gas turbine.

Results show that: Type I hot corrosion prevailed when the temperature was the range of 800°C to 850°C. Sulfidation reactions took place in some coatings despite the low levels of sulfur. For most coatings in the test, the oxidation depended on the exposure temperature. When temperature was high (>850°C), the oxide layer consisted of a mixture of Al_2O_3 , Cr_2O_3 and $\text{Ni}(\text{Al,Cr})_2\text{O}_4$ scale. At low temperature (< 770°C), the oxide layer seems to be primarily Al_2O_3 scale. At a temperature range of 800-850°C, mixed porous oxides were predominant due to hot corrosion. TBC I and TBC II spalled off within 250 hours of furnace exposure. Their bond coatings, however, exhibited excellent resistance to oxidation. DC I revealed excellent resistance to oxidation and hot corrosion, but it suffered pitting corrosion at 850°C. OCI and TBC III also showed excellent resistance to oxidation at 850°C. DC III and DC IV provided oxidation resistance at 770°C. DC II, DC V and DC VI were subjected to severe hot corrosion and sulfidation at

800°C, and DC IV suffered hot corrosion at 800°C and hot corrosion with sulfudation at 850°C.

Based on results of the flame tunnel test and furnace test, following coatings are recommended for hot section components of OGT2500 gas turbine:

Combustor liner: TBC III, OC I, and the bond coating of TBC I;

Stage 1 and stage 2 nozzles: DC I;

Stage 1 blade: DC I, DC IV, and DC III.

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NOMENCLATURE

ASTM	American Society for Testing and Materials
ASPS	Argon-Shrouded Plasma Spraying
Biofuel	A dark brown, free flowing liquid comprised of highly oxygenated compounds and converted from pyrolyzed biomass
Biomass	Materials containing lignin, cellulose or hemi-cellulose that can be pyrolyzed into fuel, such as wood and forest residues, animal manure and waste, grains, crops and aquatic plants
BIGCC	Biomass Integrated-Gasification-Combined-Cycle
BIPCC	Biomass Integrated-Pyrolysis-Combined-Cycle
CANMET	Canada Center for Mineral and Energy Technology
Char	The remains of solid biomass that has been incompletely combusted, such as charcoal if wood is incompletely burned
CETC	CANMET Energy Technology Center
CVD	Chemical Vapor Deposition
EB-PVD	Electron Beam Physical Vapor Deposition
EDM	Electron Discharge Machine
EDS	Energy Dispersive X-ray Spectrometry
Emission	Waste substances released into the air or water
EPMA	Electron Probe Micro-Analysis
FT	Flame Tunnel Test
FHT	Furnace Hot-Corrosion Test
Hot Corrosion	An accelerated corrosion of metal surfaces that results from the

combined effect of oxidation and reactions with sulfur compounds and other contaminants, such as chlorides, to form a molten salt on a metal surface that fluxes, destroys, or disrupts the normal protective oxide

HTHC	High-temperature Hot Corrosion
HVOF	High-Velocity Oxy-Fuel Thermal Spray
IGCC	Integrated Gasification Combined Cycle
IPCC	Integrated Pyrolysis Combined Cycle
LPPS	Low Pressure Plasma Spraying
LTHC	Low-Temperature Hot Corrosion
MCrAlY	CoCrAlY, NiCrAlY, or CoNiCrAlY coating
MTL	Material Technology Laboratory (part of CANMET)
OGT2500	The OGT2500 package is designed by Orenda Aerospace Corporation to suit the requirements of utilities, industrial power generation, oil and gas applications, including paper mills, hospitals, petrol-chemical facilities and other cogeneration applications. Orenda has modified the same dependable OGT2500 design to fire using biofuel.
OEM	Original Equipment Manufacturer
PECVD	Plasma-Enhanced Chemical Vapor Deposition
PVD	Physical Vapor Deposition
SCXI	Signal Conditioning Extensions for Instrumentation
SEM	Scanning Electronic Microscope
TBC	Thermal Barrier Coating
TGO	Thermally Grown Oxide

VPS	Vacuum Plasma Spraying processes
YSZ	Yttria partially Stabilized Zirconia ceramic coating

CHAPTER 1

1 Introduction

Biomass power generation is receiving significant international attention as a technology from a renewable resource. The movement toward the use of biomass as fuel comes from both environmental concerns and the cost-effective use of waste. A major international effort is underway to reduce the emission of global warming gases of which CO₂ produced from fossil fuel is a significant contributor. Biomass-produced energy is an effective means to help reduce this greenhouse gas since the CO₂ released during combustion is captured during the biomass growth, resulting in no net CO₂ contribution to the atmosphere. In addition to environmental aspects, this technology provides a cost-effective means for power generation in industries and communities where significant biomass is available. This can result in converting a waste disposal problem into a valuable resource for the production of electricity. Under these circumstances, Orenda Aerospace Corporation is developing the OGT 2500 gas turbine engine using biofuel (refer to Figure 1).

Because biomass is a CO₂ neutral fuel, it will have a positive environmental impact. As a renewable energy technology, this displaces fossil fuel power generation and the corresponding CO₂ emissions. For example it is estimated that a single 2.5 MWe OGT2500 engine can displace about 17,000 tons of CO₂ emissions per year [1]. CO₂ has been identified as a critical emission resulting in climate change, which can be mitigated through the commercialization of this technology. Biofuel is intended to be a more environmentally friendly source of energy than current fuel utilities.

1.1 Background

Over the last nine years, Orenda has been developing technologies to operate gas turbines on biofuel. To date, more than 13,000 liters of biofuel have been combusted in engine tests and 8,000 liters in rig testing [1]. Although continuous operation was achieved, results indicate that the elevated levels of ash found in biofuel are highly reactive and require special coatings to protect the hot gas path components from hot corrosion. This is necessary to ensure reliable and durable operation of the engine

Hot corrosion occurs in an environment where reactive metals exist in a hot gas. This is the case for any combustion system where an ash-bearing fuel is utilized. This includes heavy fuels such as crude oil, No. 6 fuel oil and solid fuels such as coal, biomass or municipal solid waste. During the combustion process, reactive elements, such as Na, K, and Ca, combine with oxygen or sulfur and form low melting point eutectics. It is the formation of this liquid phase, which is key to the severity of the attack; these liquid droplets adhere to the components and attack the surface. In standard gas turbine fuels, specifications have been developed to limit the concentration of these critical elements to single ppm levels. However, in biofuel, these elements (such as Na, K, and Ca) are 5-200 times higher [2]. Another key factor is the significantly lower level of sulfur in biomass relative to fossil fuels. This element is one of the major factors of hot corrosion in typical distillate fuels. Therefore, current coatings are designed with sulfur in mind but not for this high ash level. A different mechanism may be taking place and it is necessary to examine and develop alternate coating systems for this unique application.

1.2 Objectives

The objective of this thesis is to identify and quantify the effectiveness of various coatings to protect the gas turbine hot section components from corrosion when combusting biofuel. This will be achieved by:

- (1) Identification of various coating compositions suitable for operating in the biofuel environment,
- (2) Application of coatings to the range of hot section materials utilized in the engine,
- (3) Exposure of coated test samples to biofuel combustion environment simulating the hostile engine environment,
- (4) Perpetuation of the reaction for long term duration in a furnace environment, and compounds formed during combustion,
- (5) Destructive examination of exposed specimens to identify optimum coatings.

The major results to be derived from this work are:

Identification of optimum coatings for each coating/environment condition.

CHAPTER 2

2 Literature Review

2.1 Power Generation Using Biomass

A wide range of processes and routes are available for power generation from biomass. Usually there are four routes for power generation around 5MW range [3].

(1) Biomass combustion-Rankine cycle: the direct combustion of biomass to generate steam and run a turbine.

(2) Biomass gasification-gas engine: a thermal conversion technology where a solid fuel is converted into a combustible gas used by an engine or gas turbine.

(3) Biomass Integrated-Gasification-Combined-Cycle (BIGCC): a process which uses a combined cycle format with a gas turbine driven by the combusted gas produced from solid or liquid carbonaceous feedstock, while the exhaust gases are heat exchanged with water or steam to generate superheated steam to drive a steam turbine.

(4) Biomass Integrated-Pyrolysis-Combined-Cycle (BIPCC): a process which converts biomass to liquid fuel, gases, and char; liquid fuels are used to drive a gas turbine.

Pyrolyzed biomass converted to a liquid product can be referred to as: biofuel, bio-crude, pyrolysis oil, and liquid wood. The term biofuel is used in this thesis.

2.1.1 Pyrolysis Process

Biofuel is a combustible liquid produced from biomass through a process called pyrolysis. The complex structures of the biomass feedstocks (lignin, cellulose and hemicellulose) are broken into useful fuel or chemical “building blocks” by intense thermal action achieved by very rapid heating and a short (fraction of a second) process time

(refer to Figure 2) [4]. This chemical process involves the division of the large molecules and their reformation. In the biomass community, it is better known as “fast pyrolysis”. Rapid cooling then preserves the initial decomposition products. This prevents the valuable components from degrading into non-reactive or low value residues. Maximum liquid yields are obtained at high heating rates, at reaction temperatures around 500°C and with short vapor residence times to minimize secondary reactions [4]. Most biomass forms give maximum liquid yields of up to 80%(wt%) on a dry feedstock basis at reactor temperatures of 500-520°C with vapor residence time not more than one second [4]. Very short residence time can result in incomplete depolymerization of the lignin macromolecule resulting in a less homogeneous liquid product. Alternatively, longer residence time can cause secondary cracking of the primary products, reducing yield and adversely affecting the properties of the biofuel. The process parameters are therefore adjusted to provide the best balance of heating rate, maximum temperature, residence time and cooling rate to ensure acceptable fuel properties are attained.

2.1.2 Properties of Biofuel

Biofuels have unique characteristics that distinguish them from petroleum-based (hydrocarbon) products. As a clean fuel, biofuel has a number of advantages over petroleum-based fossil fuels including:

- No SO_x Emissions—Biofuel does not produce any heavily regulated SO_x (sulfur dioxide) emissions.
- CO₂ Neutral—Because biofuel is manufactured from organic matter; it is considered greenhouse gas neutral and can generate CO₂ (carbon dioxide) credits.

- Low NO_x—Biofuel fuels have lower NO_x (nitrogen oxide) emissions than diesel fuel when combusted.
- Renewable and Locally Produced—Biofuel is produced from forest and agricultural waste such as sawdust, bark, or sugar cane bagasse.

The biofuel has also been characterized for: calorific value, flash point, temperature dependence of viscosity and density, surface tension, moisture, ash content and trace element content and pH value. The results are provided in detail in Table 1 and Table 2 [1]. Compared with diesel, properties of biofuel have

- Lower heating value
- Poor ignition
- High viscosity
- High moisture content
- Lower pH value
- High ash and alkali contents.

A gas turbine using biofuel must be modified because of the difference in fuels [5]. Among these properties, ash and alkali contents have significant influences on the hot corrosion of coatings or alloy surface during gas turbine operation. The ash is from minerals in the soil drawn up by plants and trees during their growth. During the pyrolysis process, these minerals are primarily found within the char particles which, if not separated out of the vapor phase, carry through to the liquid phase (biofuel) during condensation. Therefore, fuel quality is often determined by the ability of pyrolysis process to prevent the entrapment of char in the vapor phase. Any ash that is in the

biofuel will carry through to the engine. The effect is that the ash will deposit on the components downstream of the fuel inject point. This can lead to a build-up of deposited materials, which form low melting point eutectics that result in hot corrosion.

2.2 Coating Degradation Mechanisms

Coatings, which are designed for high-temperature applications, are subject to a wide spectrum of degradation mechanisms. The degradation mechanisms are complex combinations of surface morphology, microstructure, alloy composition, oxygen partial pressure, service atmosphere, and so on. In general, most coatings fail due to oxidation and hot corrosion.

2.2.1 Oxidation of Metal

Oxidation of a metal can be broken into a five-step sequence:

- (1) Adsorption of oxygen onto the metal surface from the gaseous environment;
- (2) The formation of island of oxide; the formation of a continuous surface film;
- (3) The continued availability of oxygen in the atmosphere and the transport of ionic species through the oxide film make the growth of the film stable. This step is an important step in providing long-term oxidation resistance at elevated temperature.
- (4) With the scale growth a variety of local defects can be formed such as porosity and micro cracks at the oxide/substrate interface.
- (5) Extensive cracking of the oxide scale can occur due to volumetric stress. This occurs readily when the oxide has a specific volume that differs greatly from that of the substrate metal.

There are three principal rate equations, which describe oxidation of metal and alloys [6]:

- (1) At lower temperature ($<500^{\circ}\text{C}$), many metals such as aluminum, exhibit oxide growth behavior, which is described by the logarithmic-type rate equation. This describes very thin oxides, which form rapidly and then grow slowly with time.
- (2) At elevated temperature ($>500^{\circ}\text{C}$), the growth of the oxide scale is usually limited by thermally activated transport processes, or diffusion. The growth rate in such scales is then activated proportional to the oxide thickness and parabolic-type rate equations are observed.
- (3) When the oxide scale undergoes extensive cracking or spalling linear-type rate equations develop.

The formation of a dense, continuous, and adherent oxide film which allows slow diffusion that represents the best means for protection of high-temperature alloys or coatings. For diffusion-limited growth across a continuous oxide film, the growth rate of the oxide layer is proportional to the flux of ionic species through the oxide film. This flux is proportional to the diffusion coefficient and the oxygen gradient.

For the protection of components at elevated temperature the oxides SiO_2 , Al_2O_3 , and Cr_2O_3 are almost exclusively used. Al_2O_3 scales are the primary means of protection for nickel-based superalloys or coatings in gas turbine engines. Silicide-based coatings are used to protect some refractory metal alloys, which are unable to form protective Al_2O_3 scales, by selective oxidation. Cr_2O_3 scales are utilized in many heat-resistant alloys where sulfidation is a major concern.

In complex alloys such as nickel-based superalloys the desired protective oxide scale is usually formed by selective oxidation [7]. Selective oxidation is the process by which one alloying element is exclusively oxidized from the bulk alloy substrate to form a pure, protective oxide for the alloy. In this process the alloying element whose oxide is the lowest free energy of formation will have the strongest driving force to form an oxide.

2.2.2 Hot-Corrosion Degradation Mechanism

(1) Introduction to Hot Corrosion

Hot corrosion of metallic alloys is a form of degradation that has been important for at least the last 50 years. It occurs whenever salt or ash deposits accumulate on the surface of the coatings and alter the environment-alloy reaction that would have occurred had the deposit not been present. The severity of hot corrosion in combustion processes can vary substantially and is significantly affected by the type of fuel used and its purity as well as the quality of the air required to support the combustion. The nature of the hot-corrosion attack almost always involves more severe degradation of the alloy compared to that occurring in the same gas environment in the absence of the deposit. Since hot corrosion is an important form of degradation, considerable research and development has been performed to advance the theory of hot corrosion and to develop alloys and coatings with improved resistance to this form of degradation. A number of comprehensive reviews on hot corrosion have been prepared [6, 8]. Significant advances have been achieved. In this part the hot-corrosion mechanisms of alloy and coating will be considered.

It was recognized in the early 1960s that surface wastage of superalloy airfoils by hot corrosion was probably caused by deposition of sodium sulfate (Na_2SO_4), which was formed by the reaction of sodium chloride and sulfur oxide byproducts of combustion of

sulfur-bearing fuels. Because the microstructure representative of the process contained sulfides, for many years the process was called 'sulfidation'. Sulfidation is the degradation of an alloy by sulfur attack from a gaseous sulfur species such as SO_2 , SO_3 , and H_2S . In such an environment, the diffusion of sulfur into the coating or substrate can significantly shorten the period of time over which an alloy can form a protective oxide via selective oxidation [6], and then a continuous oxide scale cannot be formed. For this reason much early work centered on the effects of sulfur but it proved difficult to develop a coherent description of the process on this basis alone. It was not until about 1969 that N.S. Borstein, M.A. DeCrescente [9, 10] and J. A. Goebel; F. S. Pettit [11, 12] reported the logical mechanisms which recognized the acid-base properties of molten Na_2SO_4 . Molten Na_2SO_4 containing dissolved sulfur trioxide (SO_3), from sulfur in fuels, is acidic, whereas molten Na_2SO_4 which is deficient in SO_3 or high in oxide ion concentration is basic. Dissolution of protective oxides on the acidic side is termed 'acidic fluxing' and on the basic side 'basic fluxing'. The phenomenon is now universally known as high-temperature or Type I hot corrosion.

In late 1970s, the accelerated corrosion of CoCrAlY in a marine gas turbine running at low power and low airfoil metal temperatures was discovered. The phenomenon is now universally known as low-temperature or Type II hot corrosion. It is widely recognized by now that chromium and silicon are particularly beneficial in coatings for protection against Type II corrosion.

All hot-corrosion processes can be separated into an initiation and propagation stage. During the initiation stage the corrosion rate is comparatively low as breakdown of the surface oxide occurs. However, once this has happened and repair of the oxide is no

longer possible, then the propagation phase results in the rapid consumption of the alloy. It becomes apparent, therefore, that for a particular component one would like to extend the initiation stage as long as possible and remove the component from service before the propagation stage occurs. However, once coating penetration occurs, the propagation stage often results in catastrophic corrosion rates.

Rapp and Zhang [13] and others measured the solubility in Na_2SO_4 of oxides important to surface protection as functions of acidity, that is, activity of SO_3 in the molten medium. While not absolutely complete, workable hot corrosion mechanisms based on these phenomena are now available to guide coating and superalloy development. These include the recognition of so called 'good elements' (chromium, platinum, silicon) and 'bad elements' (molybdenum, tungsten, vanadium) to use or avoid in development of hot corrosion resistant superalloys and coatings. Some of these fit the acid-base theory for example MoO_3 , WO_3 and V_2O_5 are acidic in molten Na_2SO_4 , and SiO_2 is relatively insoluble in acidic media.

A number of fluxing mechanisms have been proposed to account for the different corrosion morphologies that are observed.

(2) Hot Corrosion Mechanism

The degradation of coatings as a result of hot corrosion can be explained based on basic fluxing and acidic fluxing [14].

Basic fluxing. An essential feature of basic fluxing is that oxide ions are produced in the deposit due to the removal of oxygen or sulfur from the deposit via reactions with alloys or metals. Furthermore, the oxide scale (MO) that normally would form a protective barrier on the surfaces of alloys can react with these oxide ions via reactions

such as

and their protective properties are destroyed. Such basic fluxing has a number of distinct features. Sulfides are usually found in the substrate as a result of sulfur removal from the deposit to produce oxide ions. Furthermore, the amount of attack depends on the production of oxide ions by the melt. Hence, a supply of deposit is necessary for the attack to continue. In other words, this form of basic fluxing hot corrosion is often not self-sustaining and it is usually restricted to high temperature (above 800°C) since the processes that produce oxide ions proceed slowly at lower temperature.

Acidic fluxing. Acidic fluxing is the development of a non-protective oxide scale via reactions whereby oxide ions are donated to the molten deposit by oxide that would have developed as a protective barrier had the deposit not been present, namely,

Acidic conditions can be developed in molten deposits on alloys by two different processes. In particular, an oxide of an element present in the alloy can cause the molten deposits to be acidic and a component can be present in the gas, which causes the deposit to be acidic. These two processes result in alloy-induced acidic fluxing and gas phase acidic fluxing, respectively.

Alloy-Induced Acidic Fluxing. In alloy-induced acidic fluxing elements such as molybdenum, tungsten, or vanadium cause melts to become acidic as oxides of these elements are incorporated into the melt. Typical reactions would be

where the Al_2O_3 dissolves into the melt at regions where MoO_3 activity is high and could precipitate out wherever the activity of MoO_3 is low. The most significant feature of alloy-induced acidic fluxing is that it is self-sustaining and only one application of the liquid deposit can cause total destruction of the alloy. It is frequently observed in structural alloys since the solid-solution strengtheners are the elements whose oxides can make the melts acidic. Alloy-induced acidic fluxing is usually observed at higher temperatures due to the substantial amount of oxidation required to provide a sufficient amount of refractory metal oxides to make the melts acidic.

Basic fluxing and alloy-induced acidic fluxing are usually observed at high temperature. They are often referred to as type I hot corrosion.

Gas Phase Acidic Fluxing. In the case of gas phase acidic fluxing, the acidic component is supplied to the liquid deposit by the gas. Two examples of acidic components in gases are SO_3 and V_2O_5 vapor. As these species are incorporated into the liquid deposit, the important reactions are

Gas phase acidic fluxing has some very distinctive features. First, it is observed most often, at least in regard to SO_3 -induced attack, at temperatures between about 650-800°C and hence is often called “low-temperature” or type II hot corrosion. This low – temperature restriction results from the need to form sulfates such as CoSO_4 , NiSO_4 , and $\text{Al}_2(\text{SO}_4)_3$ which require higher SO_3 pressures as the temperature is increased. The SO_3 pressures, however, in many combustion environments frequently decrease as

temperature is increased. Second, gas-phase-induced hot corrosion exhibits certain microstructural characteristics that depend on the alloy composition and the environment causing the attack. No alloy-depleted zone is evident in advance of the corrosion front. The hot corrosion is due to the formation of non-protective Al_2O_3 and Cr_2O_3 scales on the alloy as a result of the rapid removal of cobalt and nickel from the alloys surface via the deposit.

According to fluxing mechanisms, the general classifications of hot corrosion can be as follows:

(1) High-Temperature (type I, 800-950°C) Hot Corrosion (HTHC): high temperature reaction between a coating, a molten deposit of alkaline salts, and sulfur-containing combustion gas. It includes basic fluxing, acidic fluxing, and alloy-induced acidic fluxing.

(2) Low-Temperature (type II, 650-800°C) Hot Corrosion (LTHC): low temperature reaction between a coating, a solid deposit of alkaline salts, and sulfur-containing combustion gas. This corrosion produces low-point-eutectic phases of nickel and cobalt, which become molten at 650-800°C (refer to Figure 3) [15].

Rapp [16] defined hot corrosion based on oxide solubilities in pure fused Na_2SO_4 and proposed a “negative solubility gradient” as a general criterion for continuing hot corrosion attack.

$$\left[\frac{d(\text{oxide} - \text{solubility})}{dx} \right]_{x=0} \leq 0$$

Figure 4 shows a schematic drawing of this “fluxing” mechanism. Three specific examples which satisfy the negative solubility gradient condition are illustrated in Figure 5. In case A, continuing basic fluxing and precipitation is favored because a dominant

basic solute has a higher solubility at the oxide/salt interface than at the salt/gas interface. In case C, a dominant acidic solute has a higher solubility at the oxide/salt interface than at the salt/gas interface. In case B, a negative solubility gradient is realized whenever the local conditions and the corresponding solubilities straddle a minimum. In each case, the protective oxide is favored to dissolve at the oxide/salt interface and reprecipitate as non-protective particles within the salt film. In contrast, if the specific conditions should dictate that a “ positive solubility gradient” exists, then the salt film should saturate to the solute concentration established at the oxide/salt interface and the reaction should stop.

Electrochemical Model. Since hot corrosion is the accelerated oxidation of a material at elevated temperature induced by a thin film of fused salt deposit which is an ionic conductor, the corrosion mechanism is certainly electrochemical in nature. A number of papers have discussed the chemistry and electrochemistry of hot corrosion [e.g., 17, 18, 19,20].

Based on the mixed potential theory, the corrosion reaction is expressed by the combination of two electrochemical reactions, i.e., oxidation of the metal, which can take place at an anodic site to form metal ions

and the reduction of oxidizing species at the cathode site leading to the reduced species

These two electrochemical reactions can be measured by the current density and are a characteristic of electrode potential. The rate of any anodic reaction increases with increasing potential while that of any cathode reaction increases with decreasing potential. In the absence of any external current (no polarization), the sum of all anodic

and cathode current is zero. This condition is called “free corrosion” which occurs at the free corrosion potential where the current of the anodic metal dissolution reaction is equal to the current of the cathode reduction reaction.

The electrochemical reaction mechanisms in different environments under hot corrosion are different. In a sodium chloride containing environment, hot corrosion occurs by the oxidation of nickel, cobalt, chromium and aluminum at the anodic site and forms Ni^{2+} , Co^{3+} , Cr^{3+} and Al^{3+} ions while at the cathode, SO_4^{2-} is reduced to SO_3^{2-} , S or S^{2-} . The metal ions are unstable at elevated temperature and therefore react with the sulfur ions to form metal sulfides. The metal sulfides can easily undergo oxidation at high temperatures and form metal oxides by releasing free sulfur ($\text{MS} + 1/2\text{O}_2 = \text{MO} + \text{S}$). As a result, sulfur concentration increases at the surface of the coating and enhances sulfur diffusion into the coating. Practical observation of sulfides inside the coating is a clear indication of an electrochemical reaction taking place during the hot corrosion process.

In a vanadium containing environment, the reaction at the anodic site is similar to that of sodium chloride containing environment, but at the cathode site, O_2 is reduced to O^{2-} . The metal ions react with the oxide ions to form metal oxides. At high temperature, metal oxides dissociate and form metal ions and oxygen ions. As a result, oxygen concentrations increase at the surface of the coating and enhance oxygen diffusion into the coating and thus form oxides inside the coating. The dominating reaction in a vanadium containing environment is oxide formation while sulfide formation dominates in sodium chloride containing environment.

Therefore, it can be concluded that hot corrosion of NiCoCrAlY coatings in both the environments studied is electrochemical in nature and the relevant electrochemical

reactions are shown as follows:

Since hot corrosion is an electrochemical mechanism, then the electrochemical techniques should be quite helpful, not only in evaluating coatings for hot corrosion resistance but also for understanding the hot corrosion mechanism of coatings and for developing hot corrosion resistant coatings for the superalloys. As the anodic polarization curve provides information on the stability of an oxide film in a given environment, it has been extensively applied to evaluate the corrosion resistance of metals and alloys [21]. In addition, the impedance spectroscopy technique has been tried to detect the propagation of a catastrophic corrosion process [22].

Research for corrosion in a biofuel combustion environment started in the early 1990s [1, 23]. Most efforts focused on effects of alkaline elements on corrosion [24, 25, 26], because they are primary factors in corrosion and cannot be washed out of biofuel due to the water-based nature of the fuel. Sodium sulfate, compared with potassium sulfate, was found to be key driver of the NiCoCrAlY coating corrosion process [25]. Type I hot corrosion is obviously prevailing despite the low levels of sulfur in biofuel [27]. It is possible that with the high alkali content a substitute for the sulfidation reaction is taking place.

Some failure analyses for gas turbine components indicate that the typical

microstructure for hot corrosion are porous scales and ‘spikes’ [28, 29, 30].

2.3 Protective Coatings for Gas Turbine

2.3.1 Introduction to Superalloy Coatings

Structural components used in high-temperature applications are often protected by surface coatings. The reasons for the application of these coatings are:

- (1) To maintain component shape
- (2) To ensure operation of the component through its designed lifetime.

In essence, the role of the coating is to serve as a barrier separating the component from the corrosive environment. Indeed, it follows that a very important design parameter of a coating is that it should have minimum interaction with both the environment and the component.

An example of where protective coatings are of a certain necessity is on hot section components of turbine engines. These components are required to retain their strength and structural integrity for thousands of hours of operation under conditions of very high stresses at elevated temperatures. In addition, the components of gas turbine engines used in applications such as aircraft propulsion, marine propulsion, and electric power generation, are often exposed to gaseous environments, which can be aggressively corrosive. Consequently, coating systems for use in gas turbine environments typically must meet a number of requirements. Table 3 lists the coating property requirements for turbine blade and nozzle application [31].

The need for high-temperature coatings has evolved from a continual increase in the operating temperature of gas turbines over the past 50 years. For example, the turbine inlet temperature of the first Whittle engine, built in 1941, was about 700°C [32],

whereas the inlet temperature of a modern industrial gas turbine may be as high as 1300°C and the life requirement for the highly loaded high-temperature components is 25 000-50 000 hours [33]. At these higher temperatures, coatings become a necessity for prolonged component life. This is because the corrosion resistance of the component is often decreased as a result of improving its high-temperature mechanical properties. This relationship highlights an unfortunate reality for alloy designers: certain elements used to improve an alloy's mechanical properties at high temperature often have adverse effects on the alloy's corrosion resistance. The opposite is also true.

In the case of nickel-based superalloys used for gas turbine blades, optimization of their high-temperature mechanical properties has involved reducing their chromium content and increasing the amount of aluminum and titanium to precipitate the ordered phase γ' , $\text{Ni}_3(\text{Al,Ti})$. The resulting alloy compositions are such that the chromium content, as well as the aluminum content is often too low to provide adequate corrosion resistance through the formation of an external scale of their slow-growing oxides, Cr_2O_3 and Al_2O_3 . To compensate for this limited corrosion resistance, coatings enriched with aluminum, and perhaps chromium, are applied to the alloys. The types of coatings currently used on hot section components of turbine engines fall into three basic groups:

- (1) Diffusion coatings
- (2) Overlay coatings
- (3) Thermal barrier coatings.

A number of comprehensive reviews on coatings for high temperature have been prepared [e.g., 34, 35].

2.3.2 Diffusion Coatings

Diffusion coatings involve the enrichment of a surface with the desired metals by diffusion processes. The method of application of a diffusion coating is typically by:

(1) Chemical Vapor Deposition (CVD): the reaction occurs in a generator placed remotely from the deposition zone; the reactive species are then transported by gas flow into the retort and diffuse into substrate.

(2) Pack cementation: the components are immersed in a powder mixture in a semi-sealed retort which is placed inside a furnace and heated at high temperature under a protective atmosphere.

(3) Slurry technique: the process is comprised of the allying a mass-controlled layer of the slurry onto the substrate by dipping and subsequent heating in a furnace. The slurry consists of pure Al, Si, Mg, and resin. Usually Si-modified coatings are applied by a slurry technique.

For all these processes, coatings are formed at elevated temperature via diffusion transport of one or more elements from the gas phase to the substrate surface, where the element(s) are deposited and consequently interact with the substrate to form a coating. Among the three processes, CVD gives the best control over composition and growth rate of the coatings. It is the cleanest and only one capable of coating long internal passages [36].

A qualitative description of diffusion mechanisms for the formation of aluminide coatings on nickel-based superalloys enabled classification of the coatings as either inward diffusion types, based on the singular motion of aluminum in Ni_2Al_3 and high

aluminum NiAl, or outward diffusion types, based on the higher rate of diffusion of nickel in low aluminum NiAl. This simple classification has found broad use in the coating community. A comparison between inward (RT22) and outward (MDC-150L) grown coatings indicated that the outward grown coating provide a better resistance to oxide spallation [e.g., 37, 38].

The processes for diffusion coatings can be modified to improve the corrosion resistance of coatings. Different routes have been proposed to modify aluminide coatings by pretreatment prior to the aluminizing process and by co-deposition.

A typical pretreatment consists of chromizing before aluminizing to obtain a chromium-enriched aluminide coatings. Research on hot corrosion behavior of chromium-modified aluminide coating helped find that the best coating contained chromium, which was in the outer layer of inward diffusion aluminide coatings. Chromized and chrome-aluminized coatings also offer protection under type II corrosion conditions. Industrially available Cr-modified aluminide coatings include PWA70/73 and MDC-315.

Platinum modification is another type of coating pretreatment. Most often platinum is electrodeposited as an 8-10 μm thick layer prior to aluminizing. After aluminizing, platinum is concentrated in the external region of the coating which is generally constituted of a mixture of PtAl_2 and $\beta\text{-NiAl}$ enriched in platinum [39]. The addition of platinum improves the resistance of simple $\beta\text{-NiAl}$, particularly against type I hot corrosion. Recent work by D. He et al. [40] indicates that platinum may be replaced by chemically similar and less expensive palladium.

LDC-2E, RT22, MDC-150 and MDC-150L are typical platinum-modified aluminide coating. MDC-150L (CVD) is an outward grown coating, compared with inward LDC-2E, RT22 (pack cementation), and MDC-150 (CVD) coatings. In the as-coated condition, inward Pt-modified coatings have a two-phases (Ni, Pt)Al plus PtAl_2 outer layer on top of a (Ni, Pt)Al layer and finally a thin diffusion zone. In contrast, the MDC-150L coating has a single-phase (Ni, Pt)Al additive layer, and about one-third of the thickness is the diffusion zone. A well-developed diffusion is characteristic of a growth process dominated by the outward transport of nickel. After the post-aluminizing heat treatment, inward coatings exhibit significant changes in structure, composition and thickness, while the MDC-150L is relatively unaffected, and MDC-150L provides a better resistance to oxidation and oxide spallation than inward Pt-modified coatings.

Of the other diffusion coatings, the silicon-containing diffusion aluminides, for example Sermaloy J and Sermaloy 1515 [41], perform well under either type I or type II hot corrosion conditions. Thus, silicon containing and chromium-rich diffusion coatings offer improved corrosion resistance at lower temperatures that are often encountered within utility turbine environments.

Another coating modification is co-deposition which is a single-step cementation treatment in which two or more elements are deposited into aluminide coatings. Rapp and co-worker [42] explored the thermodynamic details of processes for co-deposition of elements such as chromium, silicon, yttrium, hafnium, etc., with aluminum. B. M. Warnes [43] applied a CVD low activity co-deposition apparatus to modify aluminide coatings with Hf, Zr, and Si. Co-deposition coatings exhibit good degradation resistance either as bond coatings for TBC or as the only turbine airfoil coating used. Co-deposition

does not seem to be a widespread technique in industrial practice although it was envisaged a long time ago and lots of research has been done recently.

With the discovery that diffusion aluminide coatings can serve as bond coats for thermal barrier coatings, the goal is now to provide ‘perfect resistance’ to spalling of alumina. This will allow the use of ‘prime reliant’ thermal barrier coatings with the capability of decreasing blade airfoil cooling air flow to gain still higher turbine efficiency. Understanding of the effects of platinum and various forms of active metals and their oxides will lead to further improvements in the use of diffusion aluminide systems as thermal barrier bond coats.

Aluminide coatings that have been specified for engine service are shown in Table 4. Among the coatings, Sermaloy 1515 is regarded as the best LTHC-resistant coating.

2.3.3 Overlay Coatings

In the late 1960s, the first overlay coating program was carried out by Pratt and Whitney to develop coatings with compositions nominally independent of substrates, and with the capability of tailoring them to the wide range of requirements of gas turbine applications. A model composition FeCrAlY, with 10-15% aluminum, was applied as a coating to nickel-based superalloys by electron beam physical vapor deposition (EB-PVD). Although the coating was not practically useful at high temperature because nickel in the substrate alloys reacted with aluminum in the coating to form a layer of NiAl between the coating and the alloy, it was a start towards development of a new type coating: MCrAlX overlay coating.

Overlay coatings are typically of the composition MCrAlX (where M= Ni, Co, Fe or combination of these, and X= Y, Hf, Zr). They are deposited on the surface of a substrate

typically by physical vapor deposition (PVD) or some spraying techniques. The major methods of coating application include:

Electron Beam Physical Deposition (EB-PVD),

Argon-Shrouded Plasma Spraying (ASPS),

Vacuum Plasma Spraying (VPS),

Low Pressure Plasma Spraying (LPPS),

High-Velocity-Oxy-Fuel thermal spray (HVOF).

In these procedures, application of coating is carried out at temperatures and /or for times where interaction between the deposited elements and the substrate is negligible. Consequently, the composition of the coating applied by these techniques can be controlled and tailored precisely for optimum corrosion resistance under a particular environment.

The earliest production method was EB-PVD, but because of the high capital cost in setting up a commercial EB-PVD plant, spray methods have found wide acceptance, particularly the argon-shrouded and vacuum spray process. More recently, High-Velocity- Oxy-Fuel (HVOF) has been used to deposit overlay coating system. However, coatings produced by EB-PVD processes are still considered the commercial standard against which other process routes are compared.

Components for EB-PVD coatings are generally preheated in vacuum to 800-1100°C, and rotated within the evaporant cloud during the deposition process. High temperatures result in increasing surface diffusivity, ensuring a dense coating and permitting some interdiffusion between the coating and the substrate for good adhesion. Therefore, coatings from EB-PVD are the densest and cleanest overlay coatings.

Plasma spraying has the advantage of being able to deposit metals, ceramics, or a combination, generating homogeneous coatings with microstructure consisting of fine, equiaxed grains. High deposit rates are possible with little significant change in composition occurring from the powder feedstock through to the coating. The most important limitations of this process are that the coating processes are limited to line of sight, requiring complex robotic manipulation for complete coverage, and the more reactive elements may oxidize during the spraying process. Carrying out the plasma-spraying process in a closed chamber at reduced pressure, known as a low-pressure plasma spraying or vacuum spraying, permits close control of the gaseous environment. This removes the possibility of unwanted gas-metal reaction and also permits high particles velocities, providing improved adhesion and higher densities.

Most currently used MCrAlY coatings are manufactured by EB-PVD, ASPS, VPS and LPPS processes. These techniques provide dense and oxide-free coatings. However, due to the vacuum procedures, these production methods are cost intensive and time consuming. In recent years, a new thermal spraying process called High-Velocity Oxy-Fuel thermal spray (HVOF) [44, 45, 46, 47] was developed to produce a dense MCrAlY coating with low oxygen content. In the HVOF spraying process, fuel is burnt with oxygen at a high pressure and generates a high-velocity exhaust jet; and the particles reach the surface of the component with the exhaust jet. The main advantages of this process are a shorter residence time in flame (lower powder temperature), and a higher kinetic energy of the particle impacting. This produces a dense coating. The third generation of HVOF systems nowadays offers processing of materials that are sensitive to oxidation even in atmospheric conditions, due to the achievements of higher particle

kinetic energy of the particles and lower melting temperature which enables particles flattening in a plastic state. The deposition of the MCrAlY coatings has to be carried out at low temperature to avoid the oxidation of the spray particles, but high enough to melt the powder and to assure certain homogeneity level in the coating. The microstructure and properties of HVOF sprayed coatings are strongly determined by the powder particle size [e.g., 48, 49], the spray gun-substrate distance, the substrate temperature, the composition of the fuel gas, the content of free oxygen in the combustion gas and the geometric parameters of the spray gun. By proper selection of the processing parameters, HVOF-sprayed coatings with a quality comparable to that of the VPS coating could be produced [e.g., 50, 51].

The oxidation behavior of MCrAlY coatings depends on various factors: alloy composition, temperature, oxygen partial pressure, exposure time, and thermal cycling. A typical oxidation sequence for MCrAlY coatings starts from the formation of a Al_2O_3 (alumina) and Cr_2O_3 (chromia) scale. The extended oxidation that forms a protective $\text{Ni}(\text{Al,Cr})_2\text{O}_4$ or NiO spinel scale which grows rapidly until a continuous stable oxide layer has formed [e.g., 52, 53]. The diffusion of oxygen and metal species is very slow in chromia and even slower in alumina, and this layer ensures the oxidation-resistance of coatings. The presence of chromium in these alloys reduces the Al level necessary to form a protective alumina scales. Alumina scales formed on MCrAl alloys are not adherent in thermal cycling condition. To improve the adherence of the alumina scales, active elements such as Y are incorporated in these alloys in small amounts (less than 1wt%).

Overlay coatings of classic design, with 18-22% Cr and 8-12% Al, generally perform better at higher temperatures where oxidation is the dominant failure mode (above 900°C), reflecting the good adherence of the thin alumina scales, which is promoted by the presence of active elements such as yttrium. Generally under these high-temperature oxidizing conditions NiCrAlYs and NiCoCrAlYs out-perform the cobalt-based systems.

However, at low temperatures where type II hot corrosion predominates, 650-800°C, corrosion rates for the NiCrAlY and NiCoCrAlY overlay coatings can be relatively high. CoCrAlYs generally out-perform NiCrAlY-based systems, with the high chromium containing (25-40%), CoCrAlYs showing best performance [e.g., 43, 54] whereas 15-20% Cr are usually recommended for type I hot corrosion [55]. This is illustrated schematically in Figure 6.

Methods have been investigated to improve the traditional MCrAlY coatings by use of a platinum underlayer and overlayers. Surface modification by CVD, PVD or slurry cementation techniques [56] have also been considered with varying degrees of success. For example, the GT29 coating is formed by a gas phase diffusion treatment of a plasma sprayed MCrAlY coating. Silicon modifications to the surface of CoCrAlY coatings [57] have also been proposed and improved the resistance to low temperature hot corrosion.

Surface modification results in the improvement of performance. For example, a pulsed electron beam treatment MCrAlY coating exhibits superior corrosion resistance at 950 °C compared to its plasma sprayed counterpart [58].

Some duplex coating (aluminide/MCrAlX) [59] and multi-layer coating systems called functionally gradient coating systems have also been developed. The typical coating is SMARTCOAT [60]. The SMARTCOAT's design consists of a MCrAlY base, enriched

first in chromium, then aluminum to provide a chemically graded structure. At elevated temperature, above 900°C, the coating oxidizes to form a protective alumina scale. However, at lower temperatures this alumina scale does not reform rapidly enough to confer protection under type II hot corrosion. The coating is therefore designed with an intermediate chromium-rich interlayer, which permits the rapid formation of chromia healing areas of type II corrosion damage. The process for SMARTCOAT is as follows:

The combination of plasma spraying plus diffusion aluminizing results in a layered microstructure. This chemically graded coating is rich in aluminium at the coating surface, with chromium rich compositions displaced inwards towards the center of the coating. Laboratory and burner rig tests have been carried out on a series of development smart overlay coatings. These have shown that the development of an intermediate chromium-rich phase provides protection under low temperature hot corrosion conditions, while the aluminum-rich surface layer provides resistance to high-temperature oxidation and type I hot corrosion. It is said that the single application of SMARTCOAT permits operation over a broad range of industrial and marine turbine conditions.

Typical commercial overlay coatings are shown in table 4.

Generally, the processes for overlay coatings, except for EB-PVD, offer a significant advantage of flexibility in term of composition and thickness compared with diffusion coatings because the vapor pressures of the coating elements are not a concern. Any materials that can be produced as a powder of appropriate size fraction can be sprayed by plasma spray or HVOF processes. A major disadvantage of overlay processes to diffusion processes is that they are line-of-sight processes. With the complex shapes common in turbine nozzles and blades designs, this limitation causes problems with coating thickness control; and the internal passages cannot be coated by overlay processes. A hybrid coating consisting of the overlay coating on the external surface and a vapor aluminide coating on the internal surface can be used to provide complete protection. The aluminide coatings are most often limited by oxidation and hot corrosion behavior, while the overlay coatings are more susceptible to thermal fatigue cracking in highly cyclic applications. Considerations of component shapes and service environments will be taken into account when coating processes are selected.

2.3.4 Thermal Barrier Coatings

The earliest programs that were involved in thermal barrier coatings were initiated in the late 1970s to solve topcoat spalling problems with the goal of using insulating properties to lower temperature and cyclic thermal stresses of turbine airfoils. Early work used EB-PVD CoNiCrAlY as bond coats and topcoats of zirconia partially stabilized with 8% yttria by plasma spray. A breakthrough came in the early 1980s when it was demonstrated that columnar, low modulus zirconia structures applied by EB-PVD had thermal cyclic lives of the order of a factor of 10 over the best plasma-sprayed coatings.

Thermal barrier coatings are often duplex in structure, i.e., comprised of an inner MCrAlX bond layer between an outer ceramic layer and the substrate. The function of the ceramic layer is to reduce the heat transfer to the metallic substrate. For many years, yttria partially stabilized zirconia (YSZ) has been a prime choice, because it reveals a thermal conductivity which is more than an order of magnitude below that of the Ni-based superalloy. Furthermore, as a ceramic, it also shows a relatively high coefficient of thermal expansion, which comes close to that of the metal substrate and allows upon thermal cycling to accommodate for certain straining without spalling immediately. The purpose of the inner bond layer is primarily to accommodate the large differences in thermal expansion between the ceramic and the substrate, and to protect the substrate from oxidation or hot corrosion. During processing and in service, a thermally grown oxide (TGO) layer forms as a result of bond coat oxidation which often plays the most important role for the adherence of the TBC. Methods for bond coating application are either those for diffusion coatings or for overlay coatings; methods for the ceramic layer are typically EB-PVD or plasma spraying. The large beneficial effects possible in gas turbine efficiency by the use of TBC lowering of blade surface temperature (e.g., up to 170°C), have sparked a resurgence in research on all aspects of scale adherence and failure mechanisms involved in the loss of ceramic layers.

For most TBCs, the degradation is the spallation of the YSZ coating at or near the TGO during thermal cycling. Efforts have been made to determine the types of TGO and spallation mechanisms [e.g., 61, 62, 63, 64]. The types of TGO depend on the temperature [65]. In the temperature range of 700-850°C, γ -Al₂O₃ is growing at a relatively high rate; the growth of θ -Al₂O₃ is in the temperature range of 850-1050°C,

followed by transformation to α -Al₂O₃. When the exposure temperature is still high, α -Al₂O₃ is quickly formed. With the transformation of θ -Al₂O₃ to α -Al₂O₃, oxidation becomes stable [66]. Instability of the TGO/bond coating interface leads to localized cracking at the YSZ/TGO interface and within YSZ. Significant void formation at the TGO/bond coat interface and formation of a Ni/Co rich oxides at the TGO/bond coat interface due to rapid internal oxidation of the Al-depleted MCrAlY bond coat are strong contributors to spallation failure of the TBC. Final spallation of the TBC results from a 'link-up' of damage at the TGO/bond coat interface with the rumpling-induced micro-cracking at the YSZ/TGO interface.

Knowledge that active elements in nickel-based superalloys and platinum modifications which cause improved scale adherence in diffusion aluminide coatings and in overlay coatings must have surely led to the use of these coatings as bond coats. Some modifications to the bond coating and some gradient TBCs were developed to provide a high adhesion of the coating to the substrate. Pre-treatments applied to overlay coatings can be used to modify the bond coating, such as pulsed electron beam treatment [67] and Pt-modified aluminide coatings [68]. The treated samples appeared to have a strongly enhanced oxidation resistance without spinel formation in the α -Al₂O₃ oxide scale. The bond coatings that are pre-treated in vacuum and an Ar-H gas-mixture prior to deposition of an EB-PVD-TBC have been proven to improve the lifetime of the TBC system [69]. Most gradient TBCs include a second bond coating or transition layer [e.g., 70, 71, 72]. The second bond coat with a high content of aluminium has been proven to increase adhesion between the TBC and the MCrAlY bond coat, which is formed either by EB-PVD or by PECVD (Plasma-Enhanced Chemical Vapor Deposition) [73].

Some research has been performed on possible effects of hot corrosion on the ceramics used as thermal barrier. In conditions most likely to be encountered in industrial turbine, destabilization of the preferred crystal structures occur by leaching out of stabilizer, such as Y_2O_3 , by molten acidic sodium sulfate ($Na_2SO_4-SO_3$). This does seem less likely to occur in industrial engines fired with clean natural gas at the higher temperatures required for improved efficiency. Several barrier coatings on top of TBC have been evaluated in molten Na_2SO_4 [74]. Mullite ($3Al_2O_3 \cdot 2SiO_2$) and BAS ($BaO \cdot Al_2O_3 \cdot 2SiO_2$) barrier coatings showed the best promise as potential hot corrosion barrier. TBCs with mullite and BAS barrier showed life similar to that of standard YSZ TBC under thermal cycling in air. Sealing treatments for YSZ TBC are supposed to improve hot corrosion resistance [75]. Other ceramics, such as $YTaO_4$ stabilized zirconia, Ta_2O_5 stabilized zirconia [76], and Lanthanum hexaaluminate [77] have been examined. They have been proven to be promising competitor to YSZ.

It is anticipated that the extensive research now in motion will yield incremental improvements in scale adherence toward the goal of ‘perfection’ required to attain prime reliant status necessary to take advantage of saved cooling air.

2.4 Test Methods

Laboratory tests for high-temperature materials can be divided into two general types. The first type places emphasis on simulating the conditions of the service application of interest. An example of this type of approach in the gas turbine industry is the use of burner rigs. The second type stresses the definition of the test conditions. In this latter test, conditions representative of the application are considered. Laboratory tube furnace tests and electrochemical cell tests are utilized in the second approach. A number of

previous papers have discussed the testing methods [20, 78].

2.4.1 Burner Rig Test

Generally, the apparatus consists of a burner for gas or liquid fuels, attendant air and fuel supplies, a combustion chamber and a specimen fixture on which the specimens may be rotated or stationary. Specimen shapes are often cylindrical or flat. A contaminant, such as seawater, may be injected into the combustion chamber or it may be mixed with the fuel. The object is to have the contaminant cause a deposit to accumulate upon the specimen. The extent of hot corrosion may be assessed by several different kinds of measurements, but the two most frequently used are weight loss after descaling and penetration depth of the reaction products. Detailed metallographic analysis is also mandatory to thoroughly characterize the specific features common to the type of hot corrosion being induced. For design purposes a correlation of burner rig data with performance in service must be established. Burner rig conditions are usually much more severe than service exposure, and extrapolations must be performed with care since different degradation mechanisms may be operative. The burner rig tests are adequate for ranking alloys, but their value for predicting lives in specific applications is limited to special cases.

It should also be universally accepted that burner rig tests involving deposition of Na_2SO_4 , which do not control partial pressure of SO_3 in the gas phase, are essentially useless for evaluation of corrosion resistance of superalloys and coatings. This is particularly true in the Type II temperature range: 650-800°C.

2.4.2 Oxidation Test

The oxidation test includes two tests: a static oxidation test and a cyclic oxidation test.

Static oxidation test: coated specimens are exposed isothermally in static air. Testing is stopped at set intervals for specimen review. Visual observation, weight loss measurements, and destructive evaluations are used to characterize coating performance. Test temperatures are usually above 980°C.

Cyclic oxidation test: this test is basically the same as the static oxidation testing, but with an increased emphasis on thermal cycling between the exposed temperature and a low temperature. Typically, specimens are withdrawn from the furnace at set intervals. Forced air can be added to increase the severity of the thermal shock on the test specimens.

2.4.3 Laboratory Tube Furnace Tests

There are a variety of tube furnace tests that have been used to study hot corrosion. The simplest is to coat the specimen with the desired deposits and then to expose it to a controlled gas mixture at a specific temperature. Deposits are applied by spraying warm test coupons with solutions containing the compound of interest. Continuous weight change versus time measurements can be recorded to attempt to define the hot-corrosion kinetics. Depending on the test conditions, vaporization of the deposit may occur, which complicates the interpretation of such data, and detailed metallographic analyses of the exposed specimens are usually necessary. In some such tests the specimens are removed periodically from the hot zone of the furnace in an attempt to induce cracking and spalling of the oxide scales. For resistant alloys the deposits must be removed to permit to observations and then a fresh deposit is applied for subsequent testing. At times it may be appropriate to immerse the specimens in crucibles containing the deposit.

2.4.4 Electrochemical Cell Tests

Since the hot corrosion of alloys usually involves liquid deposits and is regarded as an electrochemical mechanism, a number of investigations have attempted to study this process by using electrochemical techniques [20, 79, 80]. In such tests the specimens are usually exposed to the environments similar to that of a crucible test. The experimental arrangement usually involves an electrochemical cell composed of a fuse salt as the electrolyte, a reference electrode, a working electrode, and sometimes auxiliary electrodes.

Similar tests can be referred to as static hot corrosion tests if the specimens are only immersed in fused salt without an electrode. The purpose of the test may be either to investigate the properties of the salt mixture or to determine the corrosion resistance of the specimens. The advantage of this method is that it takes less time to get results than other methods. The problem is that the specimens generally must be exposed to thick melts, but situations in an actual gas turbine are a little different. There is not much fused salt in a gas turbine, so the rate of hot corrosion is not as high as that in the electrochemical cell method.

2.5 Coatings and Test Method Selection

Based on the knowledge shown in this chapter, coatings for components of a gas turbine which uses biofuel usually fail due to oxidation and type I hot corrosion. The selections of coatings for the test are based on behaviors of coatings in various conditions. Si-modified coatings are resistant to both high-temperature and low-temperature hot corrosion. They are also very resistant to oxidation. In Si-modified coatings, layers of silicon-rich phases are distributed throughout the coating layer.

Chromium silicide phases are particularly resistant to acidic hot corrosion, and also act as physical barriers to sulfate corrosion in service. So a Si-modified coating is an ideal candidate for testing. A platinum-modified aluminide coatings was selected, since it performs exceptionally well under high-temperature oxidation conditions and in type I hot corrosion environments. Cr-modified aluminide coatings were selected is that they offer protection under type II corrosion conditions. Generally, under high-temperature oxidizing conditions NiCrAlYs, NiCoCrAlYs or CoNiCrAlYs out-perform the cobalt-based systems. However, CoCrAlYs generally ,with the high chromium, are good for hot corrosion. So a CoNiCrAlY coating applied by HVOF was selected for the combustor liner. A CoCrAlY diffusion coating was selected for the nozzle. Although there is no evidence to demonstrate that thermal barrier coatings have a good resistance to oxidation and hot corrosion, the beneficial effects of lowering temperature up to 170°C were considered and two of them were selected. Liner from the OEM was cut for evaluating in this test.

Laboratory tube furnace method called furnace hot-corrosion test (FHT), was selected to carry out in this experiment. Before FHT, coated specimens were deposited with ash in a flame tunnel test (FT).

CHAPTER 3

3 Experimental Materials and Methods

3.1 Materials for Hot Corrosion Test

All coatings which were used for evaluation are shown in Table 5. Substrate materials and coatings representing gas turbine components are shown in Table 6. Coatings are proprietary to a third party and permission to identify them by name has not been received. Some specimens were cut so that they can be separated for analysis without machining after testing (refer to Figure 7). Three specimens were needed for each coating at its service temperature; one was for SEM and EDS analysis; the second one was for weighing; the third was for back-up. There were three different types of coatings to be chosen: diffusion coatings, overlay coatings, and TBC coatings. Bare alloy (uncoated) specimens were also tested as a baseline.

3.1.1 Diffusion Coatings

DC I is a Si-modified coating which is composed of CrSi_2 in a NiAl matrix (refer to Figure 8a). DC II (refer to Figure 8b) is similar to DC I and applied by thermal diffusion method from slurry.

DC III is a low Al activity CVD coating (refer to Figure 8c).

DC IV and DC V are all chromium-rich aluminide pack coatings (refer to Figure 8d and 8e).

DC VI is a CoCrAlY coating (refer to Figure 9f) applied by a thermal diffusion method from gaseous phase.

3.1.2 Overlay Coatings

OC I is an HVOF thermal-sprayed CoNiCrAlY coating as illustrated in Figure 9.

3.1.3 Thermal Barrier Coatings

TBC I is a thermal barrier coating (TBC) system, which consists of yttria partially stabilized zirconia (YSZ), thermally grown oxide (TGO; primarily Al_2O_3) and NiCoCrAlY bond coating (refer to Figure 10a).

TBC II is a CoCrAl+ZrO₂ coating applied by method of electronic-beam evaporation and condensation in vacuum (EB-PVD), which is shown in Figure 10b.

TBC III is a barrier coating similar to BAS ($\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) which were cut from a combustion liner from the OEM. The coating for the liner consists of 50%SiO₂, 18%Al₂O₃, 6.6%B₂O₃, 6.6%CaO, 6.6%Cr₂O₃, 3.3%TiO₂, 1.7%MgO and 8.3%Ba (refer to Figure 10 c).

3.1.4 Biofuel for Flame Tunnel/Kiln Test

The biofuel for the flame tunnel test was manufactured by DynaMotive. It is also characterized for: calorific value, temperature dependence of viscosity and density, moisture, ash content and trace element content. The results are provided in detail in Table 7.

3.2 Fixture Design

This fixture was designed to support three sets of coated specimens that are used to evaluate the hot-corrosion resistance of the material in flame tunnel. Since the range of temperatures in the flame tunnel is 600-900°C, materials for the components are either hastelloy or stainless steel. Specimens for set C are a flat rectangle sheet; Specimens for set B and F are rod bars with a concentric hole for cooling air. An assembly view of the fixture is provided (refer to Figure 11)

The fixture includes the following main parts (refer to Table 8):

Tube: holds the specimens and provides a channel for cooling air.

Support: supports and sustains the tube.

Band and retaining ring: holds and fastens the flat specimens.

Outer band I and inner band I: holds and fastens the rod specimens and provides a chamber for cooling air.

Air-blocking ring: prevents cooling air from blowing towards the specimens directly.

Four ceramic fiber spacers: seal the chamber.

Outer band II and inner band II: holds and fastens rod specimens without holes

Moving rod: moves specimens along the tube.

The exploded view of the fixture is shown in Figure 12. Two thermocouples were fastened onto the two specimens for each group of specimens (refer to Figure 12c).

3.3 Flame Tunnel/Kiln Test

3.3.1 Flame Tunnel/Kiln Facility Description

The test was performed by the CANMET Energy Technology Center (CETC), which is located in Ottawa, Ontario. The rotary kiln at CETC incorporates key design features and environmental safeguards: afterburner, cyclone, baghouse and wet scrubber. The equipment is a standard feature in continuously operating commercial plants. CETC's rotary kiln is 4.27 m long with an inside diameter of 0.41 m and an outside diameter of 0.66 m (refer to Figure 13a) The material of the inside lining is a high-temperature, erosion-resistant refractory that can withstand temperatures up to 1200°C. The kiln is fitted with lifting bars also made from refractory material to expedite continuous movement of the feed through the kiln and to achieve good contact between gas and

solids. If required, the speed or rotation is adjustable within the range of 3 to 6 rpm. Feeding material in the form of solid matter or sludge can be processed at rates of 20-200kg/h. Change in the rotating speed and the slope of the kiln, or both can vary the residence time of the feeds.

The kiln can be fired with gas or fuel oil, or a combination of both and has two burners, one at either end of the reactor. The burners may be operated manually or automatically. Their input is 1 MW thermal. Draft in the kiln is controlled by a variable speed ID-fan. The exhaust gas flows counter-current to the feed. The gaseous environment in the kiln can either be oxidizing or reducing; the choice depends on the requirement of the research.

The emission control units for the CETC rotary kiln include afterburner, multiclone, baghouse and two-stage wet scrubber. The afterburner unit, with its own two burners and a separate air and fuel control system, is used to achieve complete combustion of volatile and organic matter in the flue gas. The flue gas passes from the afterburner to the multiclone and the baghouse where particulates are captured. Sulfur dioxide (SO₂) is captured by the two-stage wet scrubber through the addition of limestone. Entrained particulates in the flue gas stream can be withdrawn to determine loading, particle size, and chemical compositions, etc.

The facility is monitored continuously for temperature, pressure and flue-gas composition by a dedicated set of instrumentation and computers. The process is monitored using Lab View based software by a high-performance, multi-channel signal conditioning SCXI (Signal Conditioning Extensions for Instrumentation) and data acquisition system.

3.3.2 Flame Tunnel Test Using Biofuel

The flame tunnel was used to combust the biofuel and make the ash deposited on the surface of specimens which would be tested further in the furnace. Test conditions were matched to that seen during operation of the biofuel engine. The specimens were located specifically at points within hot gas flow to provide the same hot gas and metal surface temperatures as would be seen in the engine to ensure the reproduction of a representative environment. To monitor the temperature distribution during the test, thermocouples were inserted into the test chamber. It was important that full combustion had been achieved to ensure that only ash was deposited on the specimens and not liquid biofuel. As well, a regulated air supply was provided to inject coupon cooling air to the stage 1 blade and nozzle specimens. The diagram of flame tunnel test is shown in Figure 14.

It was necessary to heat the biofuel to attain a suitable viscosity for combustion. Therefore, a heating system was included as part of the biofuel delivery system. However, it was critical that no parts of the fuel system in contact with the biofuel exceeded 90°C because of the high rate of polymerization of the biofuel above that temperature. This is true in the fuel nozzle as well; therefore, efforts were made to minimize the exposure temperature and time at that temperature for the biofuel throughout the entire fuel system.

Due to the poor ignition characteristics of biofuel, it was necessary to ignite the kiln on a standard fuel and then commence biofuel injection. Therefore natural gas was used as a secondary fuel source/ system.

In addition to the hot gas exposure and ash deposition, it was necessary to measure the combustion emissions and moisture to estimate the quality of combustion and provide

data required to simulate the appropriate environment in the furnace hot-corrosion test to be followed after the flame tunnel test.

The ash being exhausted was collected for later use in the furnace portion of the corrosion test and for characterization.

3.3.3 Test Procedure

This section outlines the critical steps in conducting this test. There were a few stages for the test.

(1) Test preparation

- Each specimen was marked before coating.
- Each specimen was photographed when received from the coating process.
- Each specimen was machined by EDM as required.
- Each specimen was weighed before installation into the fixture.

(2) Pre-test

- The specimens without coatings were installed into the fixtures.
- The fixture was installed into the combustion chamber.
- The specimens' positions in the fixtures and combustion chamber were mapped out.
- Photographic documentation was taken to show the pre-test conditions of all the test specimens as mounted in the fixture.
- Following the established ignition and transition procedure for biofuel, the test rig was brought up to the equivalent of full power operation of the biofuel engine operation on biofuel.
- Exposure was recorded as well as the temperatures seen by the specimens

during the test.

- The amount of biofuel was controlled to around 10kg/hour in order to keep the temperatures listed in Table 6.
- Ash removal and recovery from the exhausted gas were carried out.
- The pre-test was carried out for three days, and then the specimens and the fixture were checked.
- Following shut down and cooling of the rig, the specimens were photographed.

(3) Formal test

- All specimens were divided into two groups; the first one included the flat specimens and one rod specimens; the second group contained the remaining rod specimens.
- Each group of specimens was tested for 50 following the same procedure that was used for the pre-test.
- The test results were recorded as listed in Table 9 and Table 10.

3.3.4 Comments for Flame Tunnel Test

(1) Biofuel

At the beginning of testing, the nozzle was blocked after two or three hours. The reason may have been biofuel degradation due to 8 years storage or polymerization due to heating. After changing to a new batch biofuel, the nozzle did not block.

(2) Combustion

It is important that full combustion be achieved to ensure that only ash is deposited on the specimens instead of liquid biofuel. Based on the emissions the combustion was

completed because the content of CO was very low(refer Table 10).

(3) Biofuel Consumption

During the test, the biofuel consumption rate was kept to around 10kg/hour to hold the temperature steady. Some increase was still observed. (refer to Figure16 and 17).

(4) Temperature

The temperature of the specimens was required to be kept at the temperature listed in Table 6. However, the temperatures changed with time (refer to Figure 16) The main purpose of the flame tunnel test was to deposit the ash on surface. The variations of temperatures were considered acceptable because the time in the flame tunnel (50 hours) was much shorter than that in the furnace (1000 hours).

(5) Fixture performance

The fixture worked well as its design purpose. During the test the temperature of the specimens that were cooled by air seldom reached service temperatures. Therefore, the air-cooling system was used only occasionally.

3.4 Furnace Test

3.4.1 Furnace Test Description

Subsequent to the flame tunnel exposure, the specimens were exposed to their respective components' service temperatures for a number of residence hours in three atmosphere-controlled furnaces (refer to Table 11). These furnaces are located at CANMET-MTL. The atmosphere of the furnaces was adjusted to match that of the biofuel combustion hot gas environment in order to simulate the type and the rate of corrosion expected in service during biofuel operation (refer to Table 12).

There were three separate groups of samples for testing. Testing of the samples consisted of placing sets of three samples within ceramic boats and covering the exposed surfaces with ash obtained from the combustion of biofuel. The boats were placed within ceramic tube furnaces and exposed to specific elevated temperatures. A specimen map was developed which indicated the location of each specimen in the furnace. The testing was to be stopped every 250 hours (1 cycle) to allow sample sections to be removed and analyzed.

3.4.2 Test Procedure and Facility

(1) Boats

There were two different sizes of samples for exposure within the furnace. As such, two different sizes of boats were used to contain the samples and the ash. Each boat was capable of holding a set of three samples. The position and identification of each sample within a boat was painted on the wide edge of each boat. As well, each boat was given a letter to identify it (this letter was written on the opposite side of the other identification). The paint used to mark the boats was a ceramic marking paint with the ability to penetrate the ceramic material and survive at elevated temperatures. Excess unoccupied space in the boats was eliminated through the use of ceramic spacers. This use of the ceramic spacers allowed for the conservation of the ash, as it was limited in quantity. The details are illustrated in Figure 18.

(2) Furnaces

There were three separate furnaces used to test the samples provided. Each furnace used for heating the samples consisted of a ceramic tube furnace using a mullite tube with an approximate length of 122 centimetres, and an approximate diameter of 7 centimeters.

As each furnace had a hot zone limited in length to approximately 30 centimeters, the boats needed to be stacked on top of one another to allow all the samples to occupy the hot zone. Stacking of the boats was again facilitated through the use of ceramic spacers in order to maintain a steady surface. Each stacked set of boats was inserted into the furnace so that the entire set of samples occupied one end of the furnace as a single block of boats (refer to Figure 19). The entire block was slowly pushed into the center of the furnace with the use of a stainless steel rod. Once the samples were centered within the furnace, 10 centimeters of refractory were placed at each end of the furnace hot zone to minimize heat loss. The ends of the ceramic furnace tubes were sealed and checked to ensure that there were no leaks. The exhaust end of the ceramic tube end was installed with a thermocouple port so that the internal temperature could be monitored (refer to Figure 19d).

Each furnace was purged with nitrogen for 90 minutes to minimize the amount of oxygen in the system. After 90 minutes, the furnaces were energized to bring them up to the desired temperature. The furnaces were allowed 24 hours to reach the specified set point and to ensure that the temperature was stable. After 24 hours, the nitrogen was switched off, and the desired gas mixture was flowed through the system.

(3) Gas Composition and Mixing

This gas was ordered premixed (without the water) from Praxair, a local gas manufacturer. However, due to safety concerns by the manufacturer, the gas was shipped in two separate bottles, with the NO_x being shipped separately. Therefore, the concentrations were altered such that upon mixing, the correct composition would be achieved. There was a request to supplement the final mixture with extra CO_2 – this

resulted in the use of three separate bottles of gas. The flow of the premixed gases was controlled through the use of a gas mass flow controller that ensured a constant steady flow of the gases with minimal fluctuations. The flow rate of the gases was verified through the use of a 10 cc soap bubble flowmeter. The gases were directed to a mixing manifold, and the final gas composition was redirected to each of the three furnaces with the flow being controlled by more traditional rotameters. Each furnace had a heated water bath attached to the inlet port. The gas mixture was bubbled through the water bath before entering the furnace in order to introduce water vapor to the system. The controlling of the temperature of the water bath allowed the amount of water vapor 'picked up' by the gas to be controlled. Experimental evidence from prior experimentation demonstrated that a water bath temperature of 72°C would provide a water content of 14% vol.

(4) Furnace Temperature Monitoring

The temperature of the furnace was measured by placing a long type K thermocouple from the exhaust end cap to the center of the furnace. The temperature was monitored at the center of the furnace and also at one end of the group of samples. This was done to ensure that the set point was reached and that the hot zone was adequate.

(5) Specimens and Sample Removal

Upon completion of one cycle of testing, the gas flow and furnaces were shut off and allowed to cool for 24 hours. The samples were removed from the furnace by inserting a hooked steel rod beneath the sample boats and pulling them to one end of the ceramic tube. Samples from each furnace were kept separate and the desired samples were examined independently from the samples from the other furnaces.

The desired samples were carefully removed from the boat so that the excess ash remained in the boat but any adhered ash remained on the sample. Each sample was photographed, the desired section was removed, and the sample re-photographed along with the removed section. The majority of samples were pre-cut with grooves (refer to Figure 20) allowing for easy sample separation with minimal impact on the external surface of the sample. However, some samples could not be pre-cut due to the non-conductivity of TBC coatings. This required that the desired section be cut from the main section with the use of a slow speed diamond cut off wheel. The slow speed provided a clean cut of the desired section while minimizing the amount of ash lost through vibration, handling, etc.

Upon retrieving all the desired samples, the remaining sections of the specimens were replaced into their respective boats, covered in ash, and re-inserted into the furnace.

(6) Mounting and Polishing

The sections removed for (SEM) examination, and microprobe analysis needed to be mounted prior to examination. The samples were mounted in low viscosity epoxy under negative pressure. This forced the mounting material to penetrate all crevices and empty spaces on the sample ensuring that the sample maintained its “tested” condition. The epoxy of the mounted samples was allowed to cure before grinding and polishing. Prior to polishing, 2 mm of material was removed by grinding because the specimens were pre-cut and corrosion may attack bare sides.

(7) Cleaning

After 1000 hours exposure, specimens for weighing were cleaned ultrasonically in water or acetone for 45 to 75 minutes, refreshing the solution as necessary, followed by

10 to 20 minutes in methanol. The long cleaning time was necessitated by the adherence of the ash deposits on the surface of specimens.

(8) Optical Microscopy, SEM, EDS Analysis

For every group specimens, only one specimen which had been pre-cut was examined by optical and SEM after every 250 hours test. EDS was also used to characterize the corrosion products.

3.4.3 Comments on Furnace Test

(1) Temperature variations

The temperature variations between the center of the furnaces and the very end side of boats were 20-30° C. In order to make all specimens experienced the same conditions, the positions of boats in furnaces were changed after every 250 hours.

(2) Cracks in specimens

Cracks were found in specimens after polishing. No oxide was found in cracks by using EDS analysis, so it was assumed that cracks were created during sample preparation.

CHAPTER 4

4 Results and Discussions

4.1 Ash Change in Flame Tunnel Test and Furnace Test

After flame tunnel testing, all specimens were covered by a red ash deposit with little or no adhesion to the surface. This ash was easily flaked away from areas for inspection.

The EDS results indicate that the majority of the deposits consist of Ca, Mg, Fe, Si, S, and O (see Figure 21). Based on the analysis of the biofuel, the Fe content is much higher than other metals (refer to Table 7). This suggests that ash consists mainly of iron oxides.

The oxidation reaction for iron in the flame tunnel is expressed as follows:

The color of Fe_3O_4 is red (refer to Figure 20a). During furnace exposure, iron oxide changes from Fe_3O_4 to Fe_2O_3 as per the following reaction:

4.2 Specimen Set C

Specimens for set C were designed to simulate conditions for a combustor liner which has a service temperature of 850°C. Resident durations in the furnace were 250, 500, 750, and 1000 hours respectively.

(1) 250 hours

The TBC I coating had spalled off during 250 hours exposure (see Figure 22). Consequently, the results for TBC I coated specimens represent the behavior of NiCoCrAlY bond coating which did not appear to have suffered significant attack.

The EDS results showed that there was a mixed oxide layer on top of the coatings. The mixed oxide layer included two layers: the inner layer was the oxide layer formed during testing; the outer layer consisted of iron oxides which came from oxidation of ash (see Figure 23e)

Comparison between the thickness of the oxide layer for the various coatings indicates that DC I and OC I have the lowest oxidation rate (4-5 μ m). Pitting corrosion occurred on DC I surface and corrosion products of pits were found to be a mixture of Al₂O₃, Cr₂O₃, and SiO₂ scale. For OC I, a Ni(Al,Cr)₂O₄ spinel scale was below the oxide layer (see Figure 24b). The corner of OC I specimen, however, was severely oxidized or suffered hot corrosion.

DC IV had an even higher oxidation rate than bare alloy I. Penetrations were observed in OC I and bare alloy I.

After 250 hours' exposure, TBC III did not change significantly.

(2) 500 hours

For most coatings, there was no significant difference between 250 hours and 500 hours of testing. The pits on DC I surface penetrated further. The exception occurred to C22 (DC IV), which suffered severe hot-corrosion and the whole coating was penetrated. Sulfur diffused into the substrate to form Cr-sulfides which could be found on the whole cross section (Figure 26a).

(3) 750 hours

After 750 hours exposure, none of the coating micrographs showed much difference compared with 500 hours. DC I and OC I coatings still revealed the best oxidation

resistance. No change was observed in the thickness of either coating. Some deeper pits, however, were observed on the DC I surface.

(4) 1000 hours

After 1000 hours exposure, some deep pits on the DC I surface had penetrated through the coating layer (refer to Figure 23d). The cracks perpendicular to the coating surface had penetrated the coating and reached the substrate. TBC III did not change significantly compared with it at 750 hours exposure. The micrographs for other coatings did not show notable difference from those at 750 hours exposure.

Based on the SEM image and EDS results, it is speculated that the oxidation of the coatings usually began with the formation of a thin film of Al_2O_3 which was overgrown by colonies of Cr_2O_3 originating at the alloy grain boundary. Upon completion of this process, penetration (internal oxidation) was observed and depletion zones were formed ahead of the oxidation front by selective removal of the active elements Al and Ti. Further oxidation promoted the formation of a protective $\text{Ni}(\text{Al,Cr})_2\text{O}_4$ spinel scale below the Al_2O_3 and Cr_2O_3 layer.

DC I, an aluminide coating modified with silicon, is comprised of the nickel aluminide phase as the coating matrix and fine chromium silicides precipitates concentrated mostly in the outer zone. During the furnace exposure, a mixture of Al_2O_3 , SiO_2 and Cr_2O_3 was formed in the outer zone. SiO_2 , which is regarded as more stable than Al_2O_3 and Cr_2O_3 in some melt salts [6], acted as the major protective oxide in the outer zone. Pitting-type corrosion may have occurred where the silicon content was insufficient for selective oxidation to form SiO_2 . The formation of pits was caused by the diffusion of oxygen through the oxide scale, and the volume of oxide scale expanded during the oxidation

process. This caused cracking at the tip of the pits and the depletion layer was formed along the edge of pits. The cracks perpendicular to the coating surface had penetrated the coating and reached the substrate.

For TBC I, like most TBCs, the degradation was the spallation of the YSZ coating at or near the TGO during the furnace exposure. Its NiCoCrAlY bond coating, however, exhibited excellent oxidation resistance. The oxide layer produced on this coating was composed of a mixed oxides of Al_2O_3 , Cr_2O_3 , and $\text{Ni}(\text{Al,Cr})_2\text{O}_4$ spinel scale (refer to Figure 27 and 28). NiCoCrAlY coatings by EB-PVD are more uniform and denser on all coating surfaces than those applied by the HVOF process. Therefore, edge effects did not occur in the NiCoCrAlY bond coating.

As a typical overlay coating, OC I experienced a typical oxidation sequence from the formation of a scale of Al_2O_3 and Cr_2O_3 to an extended oxidation period that formed a protective $\text{Ni}(\text{Al,Cr})_2\text{O}_4$ spinel scale. This scale prevented overgrowth and reduced the growth rate. The HVOF process used to apply the OC I coating is a process of line-of-sight, thus the coating at the corner was not as dense and thick as the rest of the specimen surface. Therefore the coating deposited at the corner of specimens by the HVOF process is more susceptible to oxidation or hot corrosion (refer to Figure 31). As a result, the HVOF process may not be an ideal candidate for more complex components.

Type I hot corrosion and sulfidation occurred in DC IV. The discussion about hot corrosion and sulfidation will be presented in section 4.3, since most specimens of set F suffered hot corrosion, and some of them are subject to sulfidation.

TBC III is a BAS ($\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) barrier coating which is typically produced by plasma spraying. BAS, like most silicates, provides excellent resistance to oxidation and

hot corrosion due to low oxygen conductivity in BAS and the formation of high melting silicate when BAS reacts with alkaline salts. The SEM image and EDS results indicated that no oxidation or hot corrosion were observed in TBC III. After 1000 hours exposure, TBC III did not change significantly, and it is a very promising candidate for combustor liner.

The entire oxidation process for most set C coating is illustrated in Figure 32. Bare alloy I experienced the typical oxidation process that is illustrated in Figure 32, except for the formation of a protective $\text{Ni(Al,Cr)}_2\text{O}_4$ spinel scale. The oxide is a continuous Cr_2O_3 scale. The penetration (internal oxidation) was observed and depletion zones were formed ahead of the oxidation front by selective removal of the active element Al.

Corrosion for Set C specimens is mainly through oxidation. The behaviors of the coatings depended primarily on their composition and microstructure. Both the overlay coating, OC I and the bond coating of TBC I, exhibited excellent oxidation resistance due to the formation of a protective $\text{Ni(Al,Cr)}_2\text{O}_4$ spinel scale. DC I and TBC III also have excellent oxidation resistance due to SiO_2 scale, but deep pits in DC I may prevent it from application. DC IV suffered severe hot corrosion. The promising candidate coatings for combustor liner are TBC III, OC I, and the bond coating of TBC I.

4.3 Specimens Set F

Specimens for set F are designed to simulate the conditions for a stage 1 and stage 2 nozzles which have a service temperature of 800°C.

(1) 250 hours

Severe type I hot corrosion occurred on the Cr-modified coatings DC IV, DC V and DC VI. On DC IV and DC V, corrosive agents nearly penetrated the whole coating.

Corrosion on DC VI coating showed that the whole coating had been severely corroded and that the substrate had been attacked (refer to Figure 34 and 35).

Similar to the test at 850°C, the DC I coating still revealed the lowest oxidation rate (4-5 μm). The DC II coating, which is similar to DC I, saw attack by type I hot corrosion (refer to Figure 36).

Type I hot corrosion characteristics, such as mixed porous oxides, were found in all specimens except for DC I and the evidences of sulfidation was also observed in DC VI and bare alloy I as shown in Figure 37 and Figure 38.

(2) 500 hours

After 500 hours of testing, corrosion features on all coatings were similar to those observed at 250 hours. Pitting corrosion was observed in parts of the DC I surface.

(3) 750 hours

After 750 hours exposure, the pits on the surface of DC I coating were deeper than those in 500 hours exposure. DC II coating was severely corroded. For DC IV and DC VI coatings, the whole coating layers were almost penetrated.

(4) 1000 hours

After 1000 hours exposure, the corrosion features were almost the same as those at 750 hours. The whole coating of DC VI was corroded away. Sulfur diffused the substrate along the grain boundary.

Based on SEM images, EDS results, and the knowledge of hot corrosion in Chapter 2, most coatings for set F were subjected to type I hot corrosion and some of them were subject to sulfidation. An essential feature of type I hot corrosion is that oxide ions are produced in the deposit due to removal of oxygen or sulfur from the deposit via reaction

with the alloy or the metals. Furthermore, oxide scale (MO) that normally would form as protective barriers on the surfaces of alloys can react with these oxide ions and could form porous oxides, and their protective properties are destroyed. The entire process is illustrated in Figure 39.

In the Si-modified coating DC I, layers of silicon-rich phases (CrSi_2) were distributed throughout the coating layer. A continuous SiO_2 scale, which is formed during oxidation and has low solubility in melt salts, acted as a physical barrier to corrosive agents to prevent hot corrosion and the diffusion of sulfur. Silicon, unlike chromium, is unable to form sulfides and is thus resistant to sulfur diffusion. The reason that the DC II coating, which is similar to DC I, suffered type I hot corrosion may be due to insufficient silicon contents in the coating for selective oxidation to form a continuous SiO_2 scale.

Mixed porous oxides which are a distinct feature of type I hot corrosion were found in both of Cr-modified coatings DC IV and DC V. The SEM images and EDS results at different points in the corrosion products indicate that hot corrosion of both coatings was accompanied only by oxidation without sulfidation. The reason may be due to high chromium content which promoted the formation of a continuous external Cr_2O_3 scale.

Type I hot corrosion was observed in DC VI and bare alloy I and accompanied with sulfidation. Sulfidation was associated with chromium depletion due to the formation of CrS , which would de-scale the chromium-oxide, and caused scale spallation or cracking, followed by subsequent oxidation of sulfides and sulfur penetration into the alloy along the grain boundary.

The most common degradation mechanisms for the coatings of set F specimens were type I hot corrosion and sulfidation. DC I exhibited excellent hot-corrosion resistance due

to the formation of SiO_2 scale. Both Cr-modified coatings, DC IV and DC V, suffered type I hot corrosion. Type I hot corrosion also occurred in bare alloy I and DC VI with sulfidation. The promising candidate for the stage one and stage two nozzle is DC I. Based on these results, it appears that the type I hot corrosion occurs around 800-850°C in the biofuel combustion environment.

4.4 Specimens Set B

Specimens for set B are designed to simulate the conditions for a stage 1 blade which has a service temperature of 770°C.

(1) 250 hours

After 250 hours exposure, the TBC II coating had spalled off. Consequently, the results for TBC II coated specimens represent the behavior of NiCoCrAlY bond coating which did not appear to have suffered significant attack (refer to Figure 43).

All coatings revealed similar oxidation rates. The corrosion appeared to be primarily aluminum oxidation and the formation of a continuous Al_2O_3 scale.

Some corrosion pits were observed on the surface of the DC VI coating (refer to Figure 44) and penetrations (internal oxidation) were only observed in uncoated specimens (refer to Figure 45).

Corrosion on the set B specimens was much less severe and more consistent in appearance with oxidation than hot corrosion.

(2) 500 hours

Micrographs for the specimens at 500 hours indicated very similar appearance to those for 250 hours. More pits were visible on the surface of DC VI and some of them had penetrated the coating and attacked the interdiffusion zone.

(3) 750 hours

For all coatings, except the DC VI coating, micrographs did not show much difference compared between 500 hours and 750 hours. Pits on the surface of the DC VI coating had penetrated the coating to the substrate.

(4) 1000 hours

After 1000 hours exposure, the micrographs for most set B coating did not show obvious difference from those at 250 hours.

The oxidation process for the coatings in set B was simple aluminum oxidation compared with the oxidation observed for set C and hot corrosion in set F. Oxidation layers were predominantly Al_2O_3 , since low-temperatures favor the formation of Al_2O_3 scales and no penetration (internal oxidation) is observed except for bare alloy III. The oxidation process is illustrated in Figure 46.

TBC II also spalled off due to growth of the TGO between the YSZ coating and the bond coating during furnace exposure. Its CoCrAlY bond coating, however, exhibited excellent oxidation resistance.

DC VI suffered pitting at low temperature (770°C). Pitting corrosion may occur where Al and Cr contents were insufficient for selective oxidation to form protective Al_2O_3 and Cr_2O_3 scale. Based on the information from the vendor, DC VI was a CoCrAlY coating produced by thermal diffusion from a gaseous phase. Therefore, DC VI actually is a diffusion coating instead of an overlay coating, whose compositions nominally are independent of substrates and easily controlled. Some elements, such as Co and Y, are very difficult to diffuse in superalloys. That is why MCrAlYs are typically overlay coatings instead of diffusion coating. The compositions of DC VI are totally different

from those in a CoCrAlY overlay coating. Some elements, such as Co, Cr, and Y, may not be sufficient to form a continuous oxide scale. This is main reason that DC VI suffered hot corrosion at 800°C and even pitting at low temperature (770°C).

Most coatings for set B specimens exhibited excellent oxidation resistance at low temperature (770°C). DC I, DC III and DC IV coatings are the options for the stage one blade.

4.5 Weight Loss/Gain after 1000 Hours Exposure

Results for mass loss/gain are revealed in Table 13. For set C specimens, all specimens gained mass except TBC I (C 24) due to spallation. Gaining mass means absorbing oxygen during oxidation and the formation of scales adhering to the surface of the coatings. For set F, significant mass-loss happened to DC VI (F43) because of severe hot corrosion. Mass loss/gain for set B did not change significantly due to the low-temperature oxidation. Ranking of coatings cannot be done based on mass loss/gain, especially when hot corrosion occurs.

The performance of all coatings at different service temperatures is illustrated in Table 14.

DC I revealed excellent resistance to oxidation and hot corrosion, but it suffered pitting corrosion at 850°C. OCI and TBC III also showed excellent resistance to oxidation at 850°C. The OC I coating was subjected to severe oxidation at the corner region due to the limitation of HVOF process, DC III and DC IV provided oxidation resistance at 770°C.

TBC I and TBC II had spalled off after 250 hours exposure in the furnace hot-corrosion test. Their bond coatings, however, exhibited excellent oxidation resistance.

DC II, DC V and DC VI suffered severe type I hot corrosion and sulfidation at 800°C. DC VI coating suffered pitting corrosion even at low temperature (770°C). DC IV suffered hot corrosion at 800°C and hot corrosion with sulfidation at 850°C.

Comparison and ranking of the coatings at their service temperature is shown in Table 15. There are three options at 770°C DC I, DC IV, and DC III. Among three coatings, DC I is the optimum coating due to low cost. DC III will be the last choice, because Pt-modified coatings are the most expensive diffusion coating.

DC I is only choice for 800°C.

There are three options at 850°C: TBC III, OC I, and the NiCoCrAlY bond coating of TBC I. Among three coatings, TBC III is the optimum, because it had been applied in gas turbine. The NiCoCrAlY bond coating of TBC I will be the last choice, because MCrAlY coatings produced by EB-PVD are expensive.

CHAPTER 5

5 Conclusions and Recommendations

5.1 Conclusions

This study has addressed the evaluation and selection of different coatings in a biofuel combustion environment at different service temperatures. The coatings were evaluated through a flame tunnel test (FT) and furnace hot-corrosion tests (FHT). The conclusions from this study are summarized as follows:

- (1) Type I hot corrosion prevailed when the temperature range was at 800°-850°C. Sulfidation reactions took place in some coatings despite the low levels of sulfur.
- (2) At elevated temperature (>850°C), the oxide layer consisted of a mixture of Al_2O_3 , Cr_2O_3 and $\text{Ni}(\text{Al,Cr})_2\text{O}_4$ scale. At low temperature (< 770°C), the oxide layer seems to be primarily a continuous Al_2O_3 scale. In the temperature range of 800-850°C, mixed porous oxides were predominant.
- (3) TBC I and TBC II had spalled off after 250 hours exposure in the furnace hot-corrosion test. Their bond coatings, however, exhibited excellent oxidation resistance.
- (4) DC I revealed excellent resistance to oxidation and hot corrosion, but it suffered pitting corrosion at 850°C. OCI and TBC III also showed excellent resistance to oxidation at 850°C. The OC I coating was subjected to severe oxidation at the corner region due to the limitation of HVOF process, DC III and DC IV provided oxidation resistance at 770°C.

- (5) DC II, DC V and DC VI suffered severe type I hot corrosion and sulfidation at 800°C. DC IV suffered hot corrosion at 800°C and hot corrosion with sulfidation at 850°C.
- (6) Based on results of FT and FHT, the following coatings are recommended for the hot section components of the OGT2500 gas turbine:
 - Combustor liner: TBC III, OC I, and the NiCoCrAlY bond coating of TBC I,
 - Stage 1 and stage 2 nozzle: DC I;
 - Stage 1 blade: DC I, DC IV, and DC III.

5.2 Recommendations

The following recommendations should be considered as future work prior to the application of coatings to the OGT 2500 gas turbine:

- (1) Since the flame tunnel and furnace hot-corrosion tests simulate engine service conditions with the exception of gas velocity and combustion pressure, the deposition rate on the specimen surfaces is not the same as real component experience in a gas turbine. Testing using a combustor burning biofuel under conditions representative of gas turbine conditions (both pressures and temperatures) is recommended.
- (2) DC III performed well at 770°C, further tests for DC III are necessary to determine its behavior at higher temperatures.
- (3) Follow-up tests for lower temperatures are necessary to determine whether type II hot corrosion exists.

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TABLES

Table 1 Typical Biofuel Properties for the Three Fuels [1]

Analyses	Test Method	Unit	Fuel A	Fuel B	Fuel C	Diesel
Gross Calorific Value	ASTM D240	MJ/kg	17-18	18.5-19.5	17-21	45
Net Calorific Value	ASTM D240/5291	MJ/kg	15-17	15-18	15-18	42
Flash Point	ASTM D93	°C	45-50	-	63	35-60
Pour Point	ASTM D97	°C	-6	-	-21	
Specific Heat	ASTM D2766	J/Kg	-	2.55-3.75	2.31	
Kinematic Viscosity at 20°C at 40°C at 50°C at 60°C at 70°C at 80°C	ASTM D445 mod.	cSt	27-128 - 8-40 - - 3-10	(typ/max) 170/220 35/100 - 25/70 8/15 7/15	160-204 - 27-44 - - 7-11	6
Surface Tension at 20°C at 25°C at 40°C at 60°C at 80°C	D971 mod.	mN/m	- 38-40 - - 28	- 39 - - -	- 34.8@28 - - -	29
Water Content	ASTM D95 and/or D1744	wt%	21-24	18-25	22-25	0
Density at 20°C at 30°C at 40°C at 50°C at 60°C at 80°C	ASTM D4052- 91	g/ml	1.199@15 C - - - -	- - 1.1946 - 1.1765 1.1663	- 1.217 - - - 1.18-1.20	0.84
Solids Content >0.1 µm >1.0 µm >3.0 µm >5.0 µm Ash	PTFE Type Millipore Membrane Filtration ASTM D482	wt%	0.18-0.20 - 0.189 - 0.01-.02	0.595 - 0.419 - 0.04-0.09	.124-0.19 - - - 0.26-48	0.01
pH	Accumet 925 pH meter	pH	2.3-2.5	2.3-2.6	2.5-3.0	5

Table 2 Trace Element Content in Biofuel [1]

Analysis	Test Method	Units	Fuel A	Fuel B	Fuel C
Specific Analysis					
Na	AASA or	ppm	2-76	2-75	36-57
K	ICP	ppm	1-17	4-118	128-345
Ca	“	ppm	1-20	15-130	383-1300
Mg	“	ppm	2-4	4-11	30-125
V	“	ppm	<1	<1	<1-2.5
Pb	“	ppm	<1	<1	3-118
Ni	“	ppm	<1	-	5-15
Cl	“	ppm	-	<1	<1
S	ASTM D240 ASTM D4294	wt%	0.02-0.05	0.013i	0.05- 0.070

Table 3 Turbine Blade and Nozzle Coating Property Requirement [31]

Property	Requirements
Hot corrosion and oxidation resistance	<ul style="list-style-type: none">▪ Initially rapid formation of a continuous thin uniform, adherent protective oxide film.▪ Slow subsequent rate of scale growth.▪ Highly stable and adherent scale.▪ High concentration of scale forming elements▪ Acceptable hot corrosion and oxidation
Erosion resistance	<ul style="list-style-type: none">▪ Ductile and adherent oxide scale.▪ Moderate coating ductility
Coating and alloy interfacial stability	<ul style="list-style-type: none">▪ Low rates of diffusion across interface.▪ Minimum compositional changes, particularly with reference to brittle phase formation.
Coating adhesion	<ul style="list-style-type: none">▪ Similar/matched coating and substrate properties.▪ Clean substrate-coating interface
Mechanical properties	<ul style="list-style-type: none">▪ Ability to withdraw all strain-temperature cycle encountered by component during service.▪ Appropriate coating ductility▪ Minimum effects on substrate properties.
Aerodynamic properties	<ul style="list-style-type: none">▪ Best possible surface finish.▪ Acceptable thickness and uniformity on aerofoil.▪ Minimum loss of surface smoothness during service.
Coating process	<ul style="list-style-type: none">▪ Ability to coat complex shapes▪ Optimized for composition, structure, thickness, thickness distribution and uniformity.▪ Cost effectiveness.

Table 4 Aluminide and Overlay Coatings for Engine Service

Coatings	Designation	Fabrication Procedure	Composition	Service Condition
Diffusion Coatings	MDC-315 PWA70/73 HI 12	Cr-modified aluminide coating by pack cementation		HTHC
	RT22 LDC2E MDC-150	Pt-modified high activity aluminide coating by pack cementation and CVD		HTHC
	MDC-150L	Pt-modified low activity aluminide coating by CVD		HTHC
	Sermaloy 1515 Sermaloy J	Si-modified aluminide		HTHC LTHC Oxidation
	HI15	Cr-Al Codeposition		Oxidation
Overlay Coatings	ATD2B	EB-PVD	Co-23Cr-12Al-0.5Y	LTHC
	ATD5B	EB-PVD	Co-18Cr-11Al-0.3Y	HTHC
	LOC29	ASPS	Co-18Cr-8Al-0.5Y	HTHC
	LOC22	ASPS	Co-32Ni-21Cr-8Al-0.5Y	Oxidation
	LOC37	ASPS	Co-23Ni-30Cr-3Al-0.5Y	Oxidation
	ATD7	EB-PVD	Ni-23Co-18Cr-12Al-0.5Y	Oxidation
	PWA270	VPS	Ni-23Co-18Cr-12Al-0.5Y	Oxidation
	ATD10	EB-PVD	Ni-20Cr-11Al-0.3Y	Oxidation

Table 5 Characteristics of Coatings for Hot Corrosion Testing

Coating		Composition and process	Thickness (μm)	Refer to Figure
Diffusion coatings	DC I	Si-modified slurry aluminide coating	75 (3.0 mils)	Figure 8a
	DC II	Si-modified slurry aluminide coating	50 (2.0mils)	Figure 8b
	DC III	Pt-modified CVD	70 (2.8mils)	Figure 8c
	DC IV	Cr-Al pack coating	55 (2.2mils)	Figure 8d
	DC V	Cr-Al pack coating	75 (3.0mils)	Figure 8e
	DC VI	Thermal diffusion from gaseous phase	50 (2.0mils)	Figure 8f
Overlay coatings	OC I	CoNiCrAlY by HVOF	200 (8mils)	Figure 9
TBC	TBC I	TGO+Ceramic by EB-PVD	220(8mils)+ 75 (3mils)	Figure 10a
	TBC II	EB-PVD	50(2.0mils)+ 100 (4.0mils)	Figure 10b
	TBC III	TBC	50	Figure 10c

Table 6 The List of Coatings for Gas Turbine Components

Service Temperature (°C)	Specimens	Substrate alloys	Coating	Specimen Number		
850	Combustion liner (C set)	Alloy I	DC I	C5	C6	C8
			OC I	C11	C12	C16
			DC IV	C20	C21	C22
			TBC I	C24	C25	C26
			TBC III	C40	C41	C42
			Bare	C7	C9	C10
800	Stage 1 nozzle and Stage 2 nozzle (F set)	Alloy II	DC I	F4	F5	F6
			DC II	F40	F41	F42
			DC IV	F10	F11	F12
			DC V	F7	F8	F9
			DC VI	F43	F44	F45
			Bare	F27		F28
770	Stage 1 blade (B set)	Alloy III	DC I	B4	B5	B6
			DC III	B7	B8	B9
			DC IV	B10	B11	B12
			DC VI	B43	B44	B45
			TBC II	B40	B41	B42
			Bare	B24	B25	B26

Table 7 Biofuel Properties for the Flame Tunnel Test

Analyses	Test Method	Unit	Fuel A
Gross Calorific Value	ASTM D240	BTU/lb	6018
Net Calorific Value	ASTM D240/5291	MJ/kg	12032
Kinematic Viscosity at 20°C at 40°C at 50°C	ASTM D445 mod.	cSt	9.625 4.581 3.422
Water Content	E203/E1064	Mass %	34.74
Sulfur	D4294	Mass %	0.0151
Ash	D482	Mass %	0.108
Density at 20°C at 40°C at 50°C	ASTM D4052-91	g/ml	1.1473 1.1389 1.1294
Solids Content (0.45um)	D4870	Mass %	0.01
Ultimate analysis C H N O	D5291	Mass %	32.56 7.92 0.08 59.32
Metals Vanadium Iron Sodium Potassium Calcium Silicon Chromium Nickel Manganese Mercury	ICP MS	Mass % ppm	4.05 380 <1.0 2.9 <1.0 1.05 1.07 5.01 1.63 <10

Table 8 The List of Components for the Fixture

Groups for Specimens	Part Name	No of Parts	Materials	Method of Manufacturing
Common Parts	Support	1	Hastelloy	Welding
	Screw	1	Stainless steel	Machining
	Tube	1	Hastelloy	Welding
Flat Specimens (Set C)	Band	1	Hastelloy	Machining and welding
	Retaining ring	1	Hastelloy	Welding
	Bolt	3	Stainless steel	Machining
	Nut	3	Stainless steel	Machining
	Bushing	1	Hastelloy	Machining
	Screw	1	Stainless steel	Machining
	Flat Specimen	1	Hastelloy	Coated
Rod Specimens (Set F and B)	Fixed gasket	1	Hastelloy	Machining
	Spacer 1	1	Ceramics	Molding
	Nut 2	4	Stainless steel	Machining
	Outer Band I	1	Hastelloy	Machining
	Spacer 2	1	Ceramics	Molding
	Spacer 3	1	Ceramics	Molding
	Spacer 4	1	Ceramics	Molding
	Air-blocking ring	1	Hastelloy	Bending
	Bolt 2	1	Stainless steel	Machining
	Nut 3	1	Stainless steel	Machining
	Inner band I	1	Hastelloy	Machining and welding
	Bolt 3	8	Stainless steel	Machining
	Nut 4	8	Stainless steel	Machining
	Nut 5	8	Stainless steel	Machining
	Round Specimen	20	Hastelloy	Coated

Table 9 Temperatures for Flame Tunnel Test

TIME	SPECIMEN TEMP (°C)						FLAME TUNNEL TEMP (°C)								OTHERS (°C)		
	Flat		Rod 1		Rod 2		Position								Air	Biofuel 1	Biofuel 2
	Top	Bottom	Top	Bottom	Top	Bottom	1	2	3	4	5	6	7	8			
9:30	603	596	566	538	528	501	487	510	519	488	421	428	428	395	25.4	26.6	36.3
10:00	638	628	585	552	541	515	559	589	600	558	474	478	465	419	24.9	28.6	38.1
10:30	716	704	646	616	593	562	635	667	682	631	532	546	509	448	24.9	30.7	39.4
11:00	721	704	655	637	607	581	694	726	741	689	585	590	555	482	24.7	30.2	40.3
11:30	795	785	710	693	660	629	735	774	797	741	631	652	595	514	24.9	32.4	40.1
12:00	859	845	768	752	712	677	795	838	864	806	689	715	650	557	25.8	33.4	42.9
12:30	861	849	773	756	712	686	831	877	907	851	733	752	694	595	26.6	34.2	44.2
13:00	843	836	758	723	683	656	853	905	931	874	756	770	718	621	27.7	34.8	44.6
13:30	851	843	766	732	689	662	870	923	949	891	773	784	738	640	28.1	34.5	44.3
14:00	859	849	772	740	694	670	881	936	962	905	786	796	754	655	28.6	34.4	44.2
14:30	865	860	783	751	706	681	893	951	976	919	797	808	767	669	29.5	34.5	44
15:00	879	872	795	765	719	695	905	966	990	933	810	820	781	684	30.6	34.8	43.7
15:30	882	875	800	770	722	701	916	978	1002	946	821	830	794	697	31.3	35.1	43.5
16:00	888	881	806	776	729	707	919	984	1009	954	829	837	804	708	29.2	33.8	43.7
16:30	892	884	810	783	734	711	920	987	1014	960	834	842	812	717	31.3	34.7	42.9
17:00	898	891	818	792	744	723	922	990	1019	965	840	847	820	726	31.9	34.9	42.9
17:30	902	893	822	797	749	728	923	992	1021	968	842	850	823	730	32.1	35.2	42.8
18:00																	

Note: Biofuel 1 refers to biofuel temperature at gun; Biofuel 2 refers to biofuel temperature in barrel.

Date: 9-Mar-03

COMMENTS: Start to inject biofuel at 9:15 and inject air at 12:20

Table 10 Parameters for Flame Tunnel Test

Time	Weight of Biofuel (Kg)	Pressures			Kiln Draft (inches of water)	Emission				
		Pressure 1 (psi)	Pressure 2 (psi)	Pressure 3 (psi)		CO ₂ (% volume)	NO ₂ (ppm)	CO (ppm)	SO ₂ (ppm)	O ₂ (%volume)
9:30	247	15	6	30	0.2					
10:00	244	13	6	30	0.21					
10:30	238	13	6	35	0.2					
11:00	235	12	6	35	0.22					
11:30	228	12	6	35	0.21					
12:00	222	12	5	35	0.21					
12:30	216	13	5	35	0.18	5.3	60	8	15	13.7
13:00	211	10	5	35	0.18					
13:30	207	10	4	35	0.18					
14:00	203	11	3	35	0.18	5.42	60	10	20	13.5
14:30	199	10	3	35	0.17					
15:00	195	10	3	35	0.16					
15:30	191	10	2	35	0.15					
16:00	187	10	2	35	0.15					
16:30	183	10	2	35	0.15					
17:00	178.5	10	2	35	0.15					
17:30	176.5	10	2	35	0.18					

Note: Pressure 1 refers to biofuel pressure in the gun; Pressure 2 refers air pressure; Pressure 3 refers to biofuel pressure after pumping.

Table 11 Material, Temperature and Duration Specifications for Furnace Test

Specimens Group	Items	Max Surface Temperature (°C)	Residence Time (Hours)
C	Flat and Liner	850	250 500 750 1000
F	Stage 1 and Stage 2 nozzle	800	250 500 750 1000
B	Stage 1 blade	775	250 500 750 1000

Table 12 Atmosphere of the Furnace

18-18.5% O ₂	1.0-1.84% CO ₂	10-30ppmv CO	35-40ppmv NO _x	5-7ppmv SO ₂
10-15% H ₂ O	65-70% N ₂			

Table 13 Mass loss/gain for coatings after 1000 hours exposure

Coatings			Mass (g)		
			Original Mass	Cleaned after 1000 hs	Mass Change
Set C	DC I	C5	45.4243	45.5096	0.0853
	OC I	C11	50.0989	50.1625	0.0636
	DC IV	C20	45.5831	45.7184	0.1353
	TBC I	C24	51.5454	50.7196	-0.8258
	TBC III	C40	30.6744	30.7298	0.0554
	Bare	C9	45.3885	45.4766	0.0881
Set F	DC I	F4	22.2109	22.2501	0.0392
	DC V	F7	22.6254	22.6543	0.0289
	DC IV	F10	22.3510	22.3891	0.0381
	DC II	F40	21.8454	21.9074	0.0620
	DC VI	F43	22.3050	21.9125	-0.3925
	Bare	F27	23.1310	23.1648	0.0338
Set B	DC I	B4	22.1907	22.1931	0.0024
	DC III	B7	21.9762	21.9761	-0.0001
	DC IV	B10	22.2646	22.2626	-0.0021
	TBC II	B40	22.8423	22.8334	-0.0098
	DC VI	B43	22.0595	22.0688	0.0093
	Bare	B24	22.3516	22.3591	0.0075

Table 14 The performance of coatings at different service temperatures

Coatings	Coating Thick-ness (µm)	Durations	Depth of Corrosion Penetration			Surface Corrosion Characteristics
			850°C	800°C	770°C	
DC I	75	250 Hours	Pits on surface in 10µm	Occasional 20 µm	No	Continuous oxide in 3-6 µm
		500 Hours	Pits on surface in 15µm	Occasional 20 µm	No	Continuous oxide in 3-6 µm
		750 Hours	Pits on surface in 20µm	Occasional 20 µm	No	Continuous oxide in 3-6 µm
		1000 Hours	Pits penetrating coating	Occasional 20 µm	No	Continuous oxide in 6-10 µm
DC IV	55	250 Hours	All surface in 20 µm	All surface in 40 µm	No	Porous oxide above 800°C, Continuous oxide in 2-3µm at 770°C
		500 Hours	All surface in 35 µm	All coating and part substrate	No	Porous oxide above 800°C, Continuous oxide in 2-3µm at 770°C
		750 Hours	All surface in 35 µm	All coating and part substrate	No	Porous oxide above 800°C, Continuous oxide in 2-3µm at 770°C
		1000 Hours	All surface in 60 µm	All coating and part substrate	No	Porous oxide above 800°C, Continuous oxide in 2-3µm at 770°C
OC I	200	250 Hours	Occasional in 20 µm	○	○	Continuous oxide in 3-6 µm
		500 Hours	Occasional in 40 µm	○	○	Continuous oxide in 3-6 µm
		750 Hours	Occasional in 40 µm	○	○	Continuous oxide in 3-6 µm

		1000 Hours	Occasional in 40 µm	○	○	Continuous oxide in 3-6 µm
TBC I	220 (bond coating)	250 Hours	Part surface in 30 µm	○	○	Continuous oxide in 3-6 µm
		500 Hours	Part surface in 30 µm	○	○	Continuous oxide in 3-6 µm
		750 Hours	Part surface in 50 µm	○	○	Continuous oxide in 3-6 µm
		1000 Hours	Part surface in 50 µm	○	○	Continuous oxide in 8-10 µm
TBC III (OEM)	50	250 Hours	No	○	○	TBC remain unchanged
		500 Hours	No	○	○	TBC remain unchanged
		750 Hours	No	○	○	TBC remain unchanged
		1000 Hours	No	○	○	TBC remain unchanged
Alloy I (Bare)	0	250 Hours	All surface in 30 µm	○	○	Continuous oxide in 2-3µm
		500 Hours	All surface in 40 µm	○	○	Continuous oxide in 6-8 µm
		750 Hours	All surface in 40 µm	○	○	Continuous oxide in 6-8 µm
		1000 Hours	All surface in 50 µm	○	○	Continuous oxide in 8-10 µm
DC V	75	250 Hours	○	All surface in 60 µm	○	Porous oxide
		500 Hours	○	All surface in 30 µm	○	Porous oxide
		750 Hours	○	All surface in 60 µm	○	Porous oxide
		1000 Hours	○	All surface in 60 µm	○	Porous oxide
DC II	50	250 Hours	○	Part surface in 40 µm	○	Continuous oxide in 2-3µm and part surface in porous oxide

		500 Hours	o	Part surface in 40 μm	o	Continuous oxide in 2-3 μm and part surface in porous oxide
		750 Hours	o	All surface in 40 μm	o	Porous oxide
		1000 Hours	o	All surface in 40 μm	o	Porous oxide
DC VI	50	250 Hours	o	All coating was severely corroded	Pits on part surface in 10 μm	Porous oxide at 800°C, Continuous oxide in 2-3 μm at 770°C
		500 Hours	o	All coating was severely corroded	Pits on part surface in 20 μm	Porous oxide at 800°C, Continuous oxide in 2-3 μm at 770°C
		750 Hours	o	All coating was severely corroded	Pits on part surface in 25 μm	Porous oxide at 800°C, Continuous oxide in 2-3 μm at 770°C
		1000 Hours	o	All coating was severely corroded	Pits on part surface in 25 μm	Porous oxide at 800°C, Continuous oxide in 2-3 μm at 770°C
Alloy II (Bare)	0	250 Hours	o	All surface in 10 μm	o	Continuous oxide in 2-3 μm
		500 Hours	o	All surface in 15 μm	o	Continuous oxide in 6-8 μm
		750 Hours	o	All surface in 15 μm	o	Continuous oxide in 6-8 μm
		1000 Hours	o	All surface in 15 μm	o	Continuous oxide in 6-8 μm
DC III	70	250 Hours	o	o	No	Continuous oxide in 2-3 μm
		500 Hours	o	o	No	Continuous oxide in 2-3 μm
		750 Hours	o	o	No	Continuous oxide in 2-3 μm
		1000 Hours	o	o	No	Continuous oxide in 3-5 μm

TBC II	70 (bond coating)	250 Hours	o	o	No	Continuous oxide in 2-3 μm
		500 Hours	o	o	No	Continuous oxide in 2-3 μm
		750 Hours	o	o	No	Continuous oxide in 2-3 μm
		1000 Hours	o	o	No	Continuous oxide in 2-3 μm
Alloy III (Bare)	0	250 Hours	o	o	All surface in 10 μm	Continuous oxide in 2-3 μm
		500 Hours	o	o	All surface in 10 μm	Continuous oxide in 6-8 μm
		750 Hours	o	o	All surface in 10 μm	Continuous oxide in 6-8 μm
		1000 Hours	o	o	All surface in 10 μm	Continuous oxide in 6-8 μm

Note: o the coating was not tested at that temperature.

Table 15 Comparison of coatings at different service temperatures

Coatings	Service temperatures		
	850°C	800°C	770°C
DC I	--	++	++
OC I	++	o	o
TBC III	++	o	o
DC III	o	o	++
DC IV	--	--	++
TBC I	+	o	o
TBC II	o	o	+
DC V	o	o	--
DC II	o	--	o
DC VI	o	--	--

Note: ++ the coating performs very well;
+ the bond coating performs well, but TBC spalled off;
-- the coating was severely corroded;
o the coating was not tested at that temperature.

FIGURES

Figure 1 OGT 2500 gas turbine using biofuel [1].

Figure 2 Diagram of pyrolysis process [4].

Figure 3 Schematic diagram of corrosion rate versus temperature depicting the effect of the hot corrosion [15].

Figure 4 Precipitation of porous MO oxide supported by a negative solubility gradient in the fused salt film [16].

Figure 5 Three cases of sustained hot corrosion of pure metal [16].
 I: the oxide/salt interface; II: salt gas interface.

Figure 6 Relative oxidation and corrosion resistance of high-temperature system [55].

(a) Dimension of flat specimens

(b) Dimension of rod specimens

Figure 7 View of specimens.

(c) Flat specimens without groove

(d) Rod specimens without groove

Figure 7 View of specimens.

(e) Flat specimens with groove

(f) Rod specimens with groove

Figure 7 View of specimens.

(a) Micrograph of DC I

(b) Micrograph of DC II

Figure 8 Diffusion coatings.

(c) Micrograph of DC III

(d) Micrograph of DC IV

Figure 8 Diffusion coatings.

(e) Micrograph of DC V

(f) Micrograph of DC VI

Figure 8 Diffusion coatings.

Figure 9 Micrograph of OC I.

(a) Micrograph of TBC I

Figure 10 TBC coatings.

(b) Micrograph of TBC II

(c) Micrograph of TBC III by OEM

Figure 10 TBC coatings.

(a) Assembly view of the fixture for first group specimens

(b) Assembly view of the fixture second group specimens

Figure 11 Assembly view of the fixture.

(c) Assembly photo of the fixture first group specimens

(d) Assembly photo of the fixture first group specimens

Figure 11 Assembly view of the fixture.

(a) Exploded view of the set for flat specimens

(b) Exploded view of the set for specimens with holes

Figure 12 Exploded view of the fixture.

(a) Flame tunnel/kiln

(b) Feeding end of flame tunnel

Figure 13 Flame tunnel test system.

(c) Fuel system

(d) Apparatus to measure the vapor

Figure 13 Flame tunnel test system.

(f) Instruments to analysis emissions

Figure 13 Flame tunnel test syatem.

Figure 14 Schematic diagram of flame tunnel/ kiln test.

(a) Group one specimens and fixture in kiln after flame tunnel test

(b) Group two specimens after flame tunnel test

Figure 15 Specimens after flame tunnel/ kiln test.

(a) Temperature change for the first group specimens
Figure 16 Temperature changes during testing.

(b) Temperature change for the second group specimens

Figure 16 Temperature changes during the test.

Figure 17 Consumption of biofuel.

(a) Samples with ash

(b) Set C sample before test

Figure 18 Boat and specimens before test.

(a) General Set-up showing Furnace #1

(b) General Set-up showing Furnace #2

Figure 19 General Set-up showing Furnaces.

(c) General Set-up showing Furnace #3

(d) Thermocouple Port of Furnace

Figure 19 General Set-up showing Furnaces.

(e) Boats in furnace

(f) boats inside furnace

Figure 19 General Set-up showing Furnaces.

(a) Specimen C8 after 50 hours flame-tunnel exposure

(b) Specimen C8 after 250 hours exposure

Figure 20 Specimen C8 during furnace test.

(c) Specimen C8 after 500 hours exposure

(d) Specimen C8 after 750 hours exposure

Figure 20 Specimen C8 during furnace test.

(e) Specimen C8 after 1000 hours exposure

(f) Specimen C5 cleaned after 1000 hours exposure

Figure 20 Specimen C8 during furnace test.

(a) EDS results for ash on specimens B12

(b) EDS results for ash on specimens B26

Figure 21 EDS results for ash.

(a) C26 after 250 hours exposure

(b) C26 after 250 hours exposure

Figure 22 Specimens C26 (TBC I) spalled after 250 hours exposure.

(a) SEM Micrograph for specimen C 8 after 250 hours test (low magnitude)

(b) SEM Micrograph for specimen C 8 after 500 hours test (low magnitude)

Figure 23 SEM Micrograph and EDS results for specimen C 8 (DC I).

(c) SEM Micrograph for specimen C 8 after 750 hours test (low magnification)

(d) SEM Micrograph for specimen C 8 after 1000 hours test (low magnification)

Figure 23 SEM Micrograph and EDS results for specimen C 8 (DC I).

(e) SEM Micrograph for specimen C 8 after 250 hours test (high magnitude)

(f) EDS results for point C.

Figure 23 SEM Micrograph and EDS results for specimen C 8 (DC I).

(g) EDS results for point D

(h) EDS results for point E

Figure 23 SEM Micrograph and EDS results for specimen C 8 (DC I).

(a) SEM Micrograph for specimen C16 (low magnitude)

(b) SEM Micrograph for specimen C16 (high magnitude)

Figure 24 SEM Micrograph and EDS results for specimen C16 (OC I) after 250 hours test.

(c) EDS results for point D

(d) EDS results for point E

Figure 24 SEM Micrograph and EDS results for specimen C16 (OC I) after 250 hours test.

(a) SEM Micrograph for specimen C22 (low magnitude)

(b) SEM Micrograph for specimen C22 (high magnitude)

Figure 25 SEM Micrograph for specimen C22 (DC IV) after 250 hours test.

(a) SEM Micrograph for specimen C22

(b) EDS results for point E

Figure 26 SEM Micrograph for specimen C22 (DC IV) after 500 hours test.

(a) SEM Micrograph for specimen C26 after 250 hours test (low magnitude)

(b) SEM Micrograph for specimen C26 after 250 hours test (high magnitude)

Figure 27 SEM Micrograph and EDS results for specimen C26 (TBC I) after 250 hours test.

(c) EDS results for point C

(d) EDS results for point E

Figure 27 SEM Micrograph and EDS results for specimen C26 (TBC I) after 250 hours test.

(a) SEM Micrograph for specimen C22 (high magnification)

(b) EDS results for point E

Figure 28 SEM Micrograph and EDS results for specimen C26 (TBC I) after 500 hours test.

(c) EDS results for point F

(d) EDS results for point G

Figure 28 SEM Micrograph and EDS results for specimen C26 (TBC I) after 500 hours test.

(a) SEM Micrograph for specimen C42 (low magnitude)

(b) SEM Micrograph for specimen C42 (high magnitude)

Figure 29 SEM Micrograph and EDS results for specimen C42 (TBC III) after 250 hours test.

(c) EDS results for point E

(d) EDS results for point F

Figure 29 SEM Micrograph and EDS results for specimen C42 (TBC III) after 250 hours test.

(a) SEM Micrograph for specimen C10 (bare) after 250 hours test (low magnitude)

(b) SEM Micrograph for specimen C10 (bare) after 250 hours test (high magnitude)

Figure 30 SEM Micrograph for specimen C10 (bare) after 250 hours test.

(c) EDS results for point D

(d) EDS results for point F

Figure 30 SEM Micrograph for specimen C10 (bare) after 250 hours test.

(a) SEM Micrograph for corner of specimen C16

(b) SEM Micrograph for the part near corner of specimen C16

Figure 31 SEM Micrograph for corner of specimen C16 (OC I) after 250 hours test.

Figure 32 Schematic diagram to illustrate the oxidation process.

(a) SEM Micrograph for specimen F6 after 250 hours test

(b) EDS results for point I

Figure 33 SEM Micrograph for specimen F6 (DC I) after 250 hours test.

(a) SEM Micrograph for specimen F9 after 250 hours test (low magnitude)

(b) SEM Micrograph for specimen F9 after 250 hours test (high magnitude)

Figure 34 SEM Micrograph and EDS results for specimen F9 (DC V) after 250 hours test.

(c) EDS results for point D

(d) EDS results for point F

Figure 34 SEM Micrograph and EDS results for specimen F9 (DC V) after 250 hours test.

(a) Micrograph for specimen F12 after 250 hours test (low magnitude)

(b) SEM Micrograph for specimen F12 after 250 hours test (high magnitude)

Figure 35 SEM Micrograph and EDS results for specimen F12 (DC IV) after 250 hours test.

(c) EDS results for point C

(d) EDS results for point E

Figure 35 SEM Micrograph and EDS results for specimen F12 (DC IV) after 250 hours test.

(a) SEM Micrograph for specimen F42 after 250 hours test (low magnitude)

(b) SEM Micrograph for specimen F42 after 250 hours test (high magnitude)

Figure 36 SEM Micrograph and EDS results for specimen F42 (DC II) after 250 hours test.

(c) EDS results for point K

(d) EDS results for point L

Figure 36 SEM Micrograph and EDS results for specimen F42 (DC II) after 250 hours test.

(a) SEM Micrograph for specimen F45 after 250 hours test (low magnitude)

(b) SEM Micrograph for specimen F45 after 250 hours test (high magnitude)

Figure 37 SEM Micrograph and EDS results for specimen F45 (DC VI) after 250 hours test.

(c) EDS results for point B

(d) EDS results for point C

Figure 37 SEM Micrograph and EDS results for specimen F45 (DC VI) after 250 hours test.

(e) EDS results for point D

(f) EDS results for point G

Figure 37 SEM Micrograph and EDS results for specimen F45 (DC VI) after 250 hours test.

(a) SEM Micrograph for specimen F28 after 250 hours test (low magnitude)

(b) SEM Micrograph for specimen F28 after 250 hours test (high magnitude)

Figure 38 SEM Micrograph and EDS results for specimen F28 (bare) after 250 hours test.

(c) EDS results for point B

(d) EDS results for point C

Figure 38 SEM Micrograph and EDS results for specimen F28 (bare) after 250 hours test.

(f) EDS result for point D

Figure 38 SEM Micrograph and EDS results for specimen F28 (bare) after 250 hours test.

(a) sulfide formation results in the production of oxide ions that react with Al₂O₃ and Cr₂O₃, sulfur removed from the deposit diffuse into coating and form sulfide

Figure 39 Schematic diagram to illustrate the MSO₄-induced hot corrosion.

(b) Schematic diagram of the formation of porous oxide and sulfides

(c) the formation of porous oxide and sulfides

Figure 39 Schematic diagram to illustrate the MSO₄-induced hot corrosion.

(a) SEM Micrograph for specimen B6 after 250 hours test (low magnitude)

(b) SEM Micrograph for specimen B6 after 250 hours test (high magnitude)

Figure 40 SEM Micrograph for specimen B6 (DC I) after 250 hours test.

(c) EDS results for point E

(d) EDS results for point H

Figure 40 SEM Micrograph for specimen B6 (DC I) after 250 hours test.

(a) SEM Micrograph for specimen B9 after 250 hours test (low magnitude)

(b) SEM Micrograph for specimen B9 after 250 hours test (high magnitude)

Figure 41 SEM Micrograph and EDS results for specimen B9 (DC III) after 250 hours test.

(c) EDS results for point D

(d) EDS results for point F

Figure 41 SEM Micrograph and EDS results for specimen B9 (DC III) after 250 hours test.

(a) SEM Micrograph for specimen B12 after 250 hours test (low magnitude)

(b) SEM Micrograph for specimen B12 after 250 hours test (high magnitude)

Figure 42 SEM Micrograph for specimen B12 (DC IV) after 250 hours test.

(c) EDS results for point D

(d) EDS results for point E

Figure 42 SEM Micrograph for specimen B12 (DC IV) after 250 hours test.

(a) SEM Micrograph for specimen B42 after 250 hours test (low magnitude)

(a) SEM Micrograph for specimen B42 after 250 hours test (high magnitude)

Figure 43 SEM Micrograph for specimen B42 (CoCrAlY+ZrO₂) after 250 hours test.

(a) SEM Micrograph for specimen B45 after 250 hours test (low magnitude)

(b) SEM Micrograph for specimen B45 after 250 hours test (high magnitude)

Figure 44 SEM Micrograph and EDS results for specimen B45 (DC VI) after 250 hours test.

(c) EDS results for point E

(d) EDS results for point F

Figure 44 SEM Micrograph and EDS results for specimen B45 (DC VI) after 250 hours test.

(a) SEM Micrograph for specimen B26 (bare) after 250 hours test (low magnitude)

(b) EDS results for point B

Figure 45 SEM Micrograph and EDS results for specimen B26 (bare) after 250 hours test.

Figure 46 Schematic diagram to illustrate the oxidation at low temperature.

APPENDICES

Appendix A Micrograph for 500 Hours Test

(a) SEM Micrograph for specimen C8 (DC I) after 500 hours test

(b) EDS results for point C

(c) SEM Micrograph for specimen C16 (OC I) after 500 hours test

(d) SEM Micrograph for specimen C22 (DC IV) after 500 hours test (low magnitude)

(e) EDS results for point C for specimen C 8

(f) SEM Micrograph for specimen C22 (DC IV) after 500 hours test (high magnitude)

(g) EDS results for point C for specimens C22

(h) SEM Micrograph for specimen C26 (TBC I) after 500 hours test

(i) SEM Micrograph for specimen C42 (TBC III) after 500 hours test

(j) SEM Micrograph for specimen C10 (bare) after 500 hours test

(k) SEM Micrograph for specimen F6 (DC I) after 500 hours test

(l) SEM Micrograph for specimen F9 (DC V) after 500 hours test

(m) SEM Micrograph for specimen F12 (DC IV) after 500 hours test

(n) SEM Micrograph for specimen F42 (DC II) after 500 hours test

(o) SEM Micrograph for specimen F45 (DC VI) after 500 hours test

(p) SEM Micrograph for specimen F28 (bare) after 500 hours test

(q) SEM Micrograph for specimen B6 (DC I) after 500 hours test

(r) SEM Micrograph for specimen B9 (DC III) after 500 hours test

(s) SEM Micrograph for specimen B12 (DC IV) after 500 hours test

(t) SEM Micrograph for specimen B42 (TBC II) after 500 hours test

(u) SEM Micrograph for specimen B45 (DC VI) after 500 hours test

(v) SEM Micrograph for specimen B26 (bare) after 500 hours test

Appendix B Micrograph for 750 Hours Test

(a) SEM Micrograph for specimen C8 (DC I) after 750 hours test

(b) SEM Micrograph for specimen C16 (OC I) after 750 hours test

(c) SEM Micrograph for specimen C22 (DC IV) after 750 hours test

(d) SEM Micrograph for specimen C26 (TBC I) after 750 hours test

(e) SEM Micrograph for specimen C42 (TBC III) after 750 hours test

(f) SEM Micrograph for specimen C10 (bare) after 750 hours test

(g) SEM Micrograph for specimen F6 (DC I) after 750 hours test

(h) SEM Micrograph for specimen F9 (DC V) after 750 hours test

(i) SEM Micrograph for specimen F12 (DC IV) after 750 hours test

(j) SEM Micrograph for specimen F42 (DC II) after 750 hours test

(k) SEM Micrograph for specimen F45 (DC VI) after 750 hours test

(l) SEM Micrograph for specimen F28 (bare) after 750 hours test

(m) SEM Micrograph for specimen B6 (DC I) after 750 hours test

(n) SEM Micrograph for specimen B9 (DC III) after 750 hours test

(o) SEM Micrograph for specimen B12 (DC IV) after 750 hours test

(p) SEM Micrograph for specimen B42 (TBC II) after 750 hours test

(q) SEM Micrograph for specimen B45 (DC VI) after 750 hours test

(r) SEM Micrograph for specimen F26 (bare) after 750 hours test

Appendix C Micrograph for 1000 Hours Test

(a) SEM Micrograph for specimen C8 (DC I) after 1000 hours test (low magnitude)

(b) SEM Micrograph for specimen C8 (DC I) after 1000 hours test (high magnitude)

(c) SEM Micrograph for specimen C16 (OC I) after 1000 hours test

(d) SEM Micrograph for specimen C22 (DC IV) after 1000 hours test

(e) SEM Micrograph for specimen C26 (TBC I) after 1000 hours test

(f) SEM Micrograph for specimen C42 (TBC III) after 1000 hours test

(g) SEM Micrograph for specimen C10 (bare) after 1000 hours test

(h) SEM Micrograph for specimen F6 (DC I) after 1000 hours test

(i) SEM Micrograph for specimen F9 (DC V) after 1000 hours test

(j) SEM Micrograph for specimen F12 (DC IV) after 1000 hours test

(k) SEM Micrograph for specimen F42 (DC II) after 1000 hours test

(l) SEM Micrograph for specimen F45 (DC VI) after 1000 hours test

(m) SEM Micrograph for specimen F28 (bare) after 1000 hours test

(n) SEM Micrograph for specimen B6 (DC I) after 1000 hours test

(o) SEM Micrograph for specimen B9 (DC III) after 1000 hours test

(p) SEM Micrograph for specimen B12 (DC IV) after 1000 hours test

(q) SEM Micrograph for specimen B42 (TBC II) after 1000 hours test

(r) SEM Micrograph for specimen B45 (DC VI) after 1000 hours test

(t) SEM Micrograph for specimen B26 (bare) after 1000 hours test