Suspension Plasma Sprayed Thermal Barrier Coating Systems – Modelling
and Performance Characterization Under Isothermal and Cyclic Oxidation
Conditions

by

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Abstract

The oxidation behavior of a vertically cracked thermal barrier coating (TBC) deposited by suspension plasma spraying (SPS) technique was studied in this research under isothermal and cyclic conditions. A peak temperature 1080°C and the durations of 400, 800, and 1300 hours/ cycles were utilized. Two different Ni-based substrates, INCONEL 625 and HAYNES 233, were first characterized at 1080°C for the purpose of material selection. INCONEL 625 was selected because of its superior oxidation performance under this condition. The TBC system consisted of an INCONEL 625 substrate, a NiCoCrAl bond coat, and finally a 7YSZ top coat with vertically cracked structure. During cyclic oxidation test, the TBC samples failed after 800 cycles, however, no evidence of failure was observed under isothermal condition for up to 1300 h. After the oxidation tests, microstructure, phase composition, microstrain, and mechanical properties were examined. Based upon the results obtained, samples under cyclic condition assumed faster sintering rate, which in turn shortened the lifetime of SPS TBCs under cyclic conditions more than that under isothermal conditions. Furthermore, stress distributions within the top coat under cyclic condition were calculated using ABAQUS in order to study the crack initiation and propagation under the influences of different TGO thickness, roughness, and mechanical property degradation of the SPS top coat. Moreover, the results of mechanical properties were utilized to predict the crack density distribution within the top ceramic coat following isothermal exposure, with the application of crack numerical density theory. The outcome of this study provides fundamental understating of the sintering mechanism and coating degradation associated with crack initiation and propagation in vertically cracked SPS TBCs under both isothermal and cyclic conditions.

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Contributions

- 1) Discovered the sintering effects on VCs multiplication, TC microstructure densification, and changes in mechanical properties.
- 2) Realized the different outcomes from sintering under isothermal and cyclic conditions.
- 3) Built a model to predict the probability of CND within the SPS TC under isothermal condition and validated it with experimental data.
- 4) Based on the preliminary study of stresses within the SPS TC, horizontal cracks were found to likely initiate at tips of VC near TGO, and the lifetime could have been extended by crack diversion.

The list of published papers are shown as follows:

- 1) Xiao, B.; et al. (2020) “Sintering resistance of suspension plasma sprayed 7YSZ TBC under isothermal and cyclic oxidation.” *Journal of the European Ceramic Society*, 40(5), 2030-2041.
- 2) Xiao, B.; et al. (2020) “Fracture performance and crack growth prediction of SPS TBCs in isothermal experiments by crack numbering density.” *Ceramics International*, 46(3), 2682-2692.
- 3) Xiao, B.; et al. (2019) “Evaluation of oxidation behavior of two potential coating alloys T14 and T19 for superheated steam and supercritical water power plant application.” *Surface and Coatings Technology*, 370, 69-81.
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Nomenclature

Abbreviation	Description
APS	Air Plasma Spray
BC	Bond Coat
CG	Columnar Grain
CND	Crack Number Density
CTE	Coefficient of Thermal Expansion
DC	Direct Current
DOE	Department of Energy
DVC	Dense Vertical Crack
DS	Directionally Solidified
EB-PVD	Electron Beam Physical Vapor Deposition
EDS	Energy Dispersive X-ray Spectroscopy
FCC	Face Centered Cubic
FEA	Finite Element Analysis
YSZ	Yttria Stabilized Zirconia
SEM	Scanning Electron Microscope
SOD	Stand-off Distance
SPS	Suspension Plasma Spray
SPPS	Solution Precursor Plasma Spray
SUB	Substrate
TBC	Thermal Barrier Coating
TC	Top Coat
TCP	Topologically Close Packed Phase
TGO	Thermally Grown Oxide
VC	Vertical Crack
XRD	X-ray Diffraction
<i>c</i>	Cubic Phase of ZrO ₂
<i>t</i>	Tetragonal Phase of ZrO ₂

m	Monoclinic Phase of ZrO_2
t'	Twinned Tetragonal Phase of ZrO_2

<i>symbol</i>	Description
a	Wavelength of the TC/TGO interface
b	Amplitude of the TC/TGO interface
c	Length of the horizontal crack in the TC
d	d -Spacing in lattice
h	TGO thickness
$\dot{h}$	TGO growth rate
q	Thermal activation energy
t	Time
m	Ratio of volume change by oxidation
n	Distribution function of the numerical density of micro-cracks
n_N	Specific crack nucleation rate
r_c	Critical value of b/a
r_{ii}	Tensor notation of the TGO growth strain
A	Crack growth rate
D	Damage percentage
E	Elastic modulus
E^*	Effective elastic modulus
G	Energy release rate
H	Hardness of the SPS TC
K	Stress intensity factor
K_p	Oxide scale growth rate
R	Undulation radius
R_a	Mean roughness of the TGO
T	Operating temperature
U	Elastic strain energy

α	Shape factor of a Gamma distribution
β	Inverse scale parameter of a Gamma distribution
γ_s	Surface energy
ε	Strain
ε^E	Elastic strain
ε^S	Sintering strain
ε^T	Thermal expansion mismatch strain
$\dot{\varepsilon}$	Strain Rate
σ_y	Yield Stress
σ_{22}	Out-of-plane stress in TC
σ_{TGO}	Stress of TGO
Γ	Fracture energy
ν	Possion's ratio
η	Intermediate crack size
Ω	Atomic volume

1 Chapter: Introduction

Between the late 1940s and 1950s, thermal barrier coatings (TBCs) began to be conceptualized in their function to prolong the service life of gas turbine components such as particularly on the air-cooled turbine blades and vanes. In the mid-1970s, TBC coatings were first applied on turbine components and became an integral part of commercial gas turbine engines by the 1980s [1]. Due to the harsh operating environment, the requirements for the selection of TBC materials are restrictive. They have to meet the following criteria: i) high melting point; ii) no phase transformation during heating and cooling thermal cycles; iii) low thermal conductivity; iv) chemical stability; v) compatibility with the thermal expansion of the substrate; and finally vi) good adhesion ability [2]. To satisfy these requirements, limited number of materials can serve the purpose as ideal protective coatings. Ceramics (e.g. YSZ, mullite, CeO_2 , etc.) are considered to be excellent candidates due to their thermal insulation capabilities, as well as their stable chemical structure [2] [3]. The thickness of the TBC is an important parameter because it influences the performance during turbine operations. Although thicker ceramic coatings provide additional thermal insulation and durability, the increasing dimension accelerates spallation [4]. Nowadays, the gas temperature in combustors can reach 250°C higher than the melting point of Ni-based superalloys and the application of a suitable TBC is essential in all modern gas turbine engines. Newer gas turbine designs will require increased efficiency and reduced emissions, all of which can be achieved by increasing the turbine gas inlet temperatures. As a consequence, the capability of TBCs in providing metallic substrate thermal protection has been gradually increased from 140°C to potentially greater

than 170°C, in combination with cooling schemes to protect superalloy substrate melting [5] [6].

TBC systems consist of four layers: i) superalloy substrate, ii) oxidation resistant metallic bond coat (BC), iii) thermally grown oxide (TGO), and iv) the thermal insulating ceramic top coat (TC) [6]. Yttria stabilized zirconia (YSZ) is the most common TC for aerospace applications because of the relatively higher thermal expansion coefficient among ceramic materials, low thermal conductivity, and good erosion resistance [7]. Most ceramic TBCs are deposited either by air plasma spray (APS) or electron beam physical vapor deposition (EB-PVD), with both methods possessing their benefits and some drawbacks. For example, although APS has higher deposition rate and is cost effective, the porous structure inherited in this process lowers the strength and has a higher thermal expansion mismatch with the substrate. EB-PVD deposited coatings, on the other hand, have better stress tolerance and mechanical properties, but the process time is longer and equipment costs much more. As a compromise, a new coating deposition method - suspension plasma spray (SPS) - with a vertical-cracked structure TC has gained increased applications and is therefore used in this research. SPS can deposit submicron size particles to the bulk substrate, leading to denser coatings as well as specific coating structures, such as columnar and vertical cracked ones which can be realized using specifically modified deposition parameters. These uniquely structured TBC are found to improve strain tolerance particularly at high temperatures.

The performance of TBC systems at high temperatures is influenced by many factors, such as: i) TC degradation due to sintering and zirconia phase transformation [7, 8], ii) thermal expansion mismatch between the layers, iii) Al depletion within the BC [9],

iv) TGO growth stress [10], v) crack initiation and delamination [11], and others. Among these factors, sintering of YSZ leads to microstructure densification and phase decomposition resulting in subsequent changes of elastic modulus, hardness, and fracture toughness [12, 13, 14]. These changes have the likelihood to accelerate the cracking in the YSZ TCs, resulting in shorter YSZ TC lifetimes. As such, the sintering performance of SPS TBCs is studied first. In addition, it has been proved that the failure of SPS TCs is caused by crack delamination within TCs, near the TC/TGO interface, as such horizontal crack growth at high temperatures is another main concern and focus area in this study. For APS TCs, out-of-plane thermal stresses within the TCs and the pre-existing imperfections in TCs (accentuating stress concentrations within TCs) [10] make APS TCs crack and propagate until a final TBC failure. Although SPS TCs contain VCs that do not exist in APS TCs, the bulk of the matrix is similar to a dense APS TC, so SPS TCs are assumed to follow the same general crack behavior but with different crack growth rates due to the presence of vertical cracks (VCs). Under cyclic conditions, thermal mismatch induced stresses between the layers are more important than under isothermal conditions because of the dynamic temperature changes. Under isothermal conditions, thermal expansion mismatch becomes less of an issue because of a steady state temperature. TGO growth in isothermal conditions is; however, more critical as it is a reaction between oxygen in the air and the metallic BC at the elevated temperature. TBCs expose longer under isothermal conditions at the elevated temperature, so TGO grows thicker under isothermal conditions than under cyclic conditions within same durations. In this study, both cyclic and isothermal oxidation experiments are conducted.

This thesis is composed of: i) a comprehensive literature review including TBC materials, various TBC deposition methods, failure mechanisms, and existing life prediction modelling methods; ii) materials selection of each layer within TBC systems, and experiment designs required to assess the oxidation performance of SPS TBCs; iii) a discussion on the sintering mechanisms of SPS TCs after isothermal and cyclic conditions; iv) stress distribution simulations in SPS TCs under the cyclic condition by finite element analysis method to understand the crack growth mechanism(s) in the coating; and v) growth of horizontal cracks within TCs under isothermal conditions is predicted by crack number density.

SPS can be used to create nano-structured VC YSZ coatings with improved strain tolerance and mechanical properties. In order to quantify the performances of VC-structured SPS TBCs, such as phase transformations and mechanical property changes, including elastic modulus, hardness, and micro-strain accumulated within the lattice, samples should be exposed for various durations under isothermal and cyclic thermal conditions. The changes in mechanical properties are mainly caused by the TC sintering. In fact, D. Zhou et al. [14] estimated sintering behavior of 5YSZ VC structured SPS TBCs on IN 738 plates in cyclic burner rig thermal exposures at the highest possible temperature of 1400°C. It was found that the porosity within the columns was decreased while the vertical cracks expanded at high temperatures, and meanwhile fracture toughness became anisotropic with the time caused by the texture and residual stress in the coating. However, this reference did not discuss about how VCs influence the sintering performances of TBCs. For this reason, the effects of VCs on sintering, under isothermal and cyclic thermal conditions, are investigated.

With regard to the function of VCs on fracture resistance [15, 16], most existing researches assume that the interface between TC and TGO is flat, ignoring the influence from the interface geometry. However, the interface is assumed as a wavy-shape, hence the impact of VCs on the stress distributions is actually geometrically localized. In this case, VCs at various positions within the TCs and their influence on the stress distributions within TCs are here studied by finite element analysis (FEA) method, particularly with the use of ABAQUS software. The effects of associated changes in TC material properties on localized stresses are also investigated.

Lastly, the long-term durability of SPS TBCs is experimentally examined and is modelled by predicting it using crack number density (CND) theory. CND theory was originally proposed by Fang et al. [17] and was used to describe fatigue cracks in steels. In 2019, Wu [18] applied this theory on APS-TBCs by assuming that crack nucleation followed a Gamma-distribution. Because the theory is based on the crack propagation with a fixed rate and a given nucleation rate, it was assumed in this study to be applicable to SPS-TBCs, with certain modifications. After the probability of different crack sizes is determined and the largest crack size with a certain probability is identified, the life of SPS TBCs can be then predicted. The prediction is compared to the experimentally measured crack distribution to validate the revised model.

2 Chapter: Literature Review

2.1 Gas turbine

The gas turbine, also commonly called a combustion turbine, is one of the most ingenious inventions of our time, affecting many industry sectors including power generation, aerospace, and maritime, as well as other domestic industries [19]. In 1791, John Barber first patented the design of a thermodynamic cycle of the gas turbine with three basic components: a compressor, a combustion chamber, and a turbine [20]. As seen in Figure 0-1, the compressor draws air into the engine, pressurizes it, and feeds it to the combustion section. The combustion process burns a mixture of pressurized air and fuel at an elevated temperature ($>1093^{\circ}\text{C}$), pressurizing the compressed gas. The high-pressure, hot-combustion gas enters the turbine, or rotor section, which consists of a complex array of alternate stationary and rotating airfoil blades, resulting in the rotation of the turbine blades. Work generated by the rotating blades is used to power the compressor to draw more air; any excess work can be used to propel a generator to produce power, drive a fan, or run an industrial pump depending upon the applications [21]. Although all gas turbines operate with the same basic mechanisms, the operating environment and the power requirements may lead to design and system modifications. This section will focus on the applications for land-based power generation and aerospace propulsion.

Figure 0-1 Rolls Royce jet engine [19].

Land-based gas turbines have a wide array of applications ranging from power generation (300 MW combined cycles) to industrial applications such as pumping fluids and cogeneration (less than 30 MW). The turbine inlet temperature (TIT) must be maintained in the range of 1371°C – 1427°C in order to mitigate NO_x pollution problems. Therefore, most of the land-based gas turbines need to improve thermal efficiency at this TIT level. In 1995, the H-series engines manufactured by GE power Systems associated with U.S. Department of Energy (DOE) utilized a closed-loop steam-cooled nozzle with TBC to reduce the gas temperature drop through the first-stage nozzle (Figure 0-2). In this case, the TIT can be increased to produce more energy with the same combustion temperature [10].

Figure 0-2 H-engine hot gas parts [22].

There are two types of land-based gas turbines: heavy frame engines and aero-derivative engines. Heavy industrial frame engines were designed after World War II and entered into the market in the early 1950s. The industrial engines have 15 – 25 stage axial-flow compressors with multiple can-annular combustors (Figure 0-3 (a)). Each combustor is connected to the other by crossover tubes. The main advantage of this type of gas turbine is the long service lifetimes that can be achieved due to their robust mechanical design.

They are mainly utilized in electrical utilities and as independent power producers [20]. Aero-derivative engines, derived from aircraft engine technology as the name implies, are also used in some industrial applications. They are designed for quick removal and replacement, in an effort to improve unit availability and flexibility. They are mainly used for load requirements up to 66 MW, in applications that require a small footprint, as well as in the marine industry due to their relatively low weight [20]. The main components of the aero-derivative engines are an aircraft-derivative gas generator and a free-power turbine (Figure 0-3 (b)). The gas generator produces high temperature gases at high pressure. Usually, an aircraft engine is modified for ground-based applications by adding a couple of stages of compression in front of the existing low-pressure compressor, and the fan section is commonly removed. High-pressure and low-pressure turbines are connected by three shafts with independent speeds in a spooled configuration. The gas generator produces high-pressure, high-temperature gas which enters the power turbine.

Figure 0-3 Land-based gas turbines (a) heavy frame GE MS5002 [23], and (b) GE LM 6000 engine [20].

An aero-engine gas turbine is the propulsion system used to generate thrust to enable an airplane to move through the air. Current aero-engine gas turbines are all based on the Brayton thermodynamic cycle (Figure 0-4). In theory, the inlet slows the air stream

entering the compressor at station 2. The decreasing air stream velocity associated with the aircraft velocity increases the static pressure of the air. Ideally this compression process is isentropic, so entropy remains constant. The combustion process occurs at constant pressure from station 3 to 4. The temperature rises due to the burning of fuel and air. The hot exhaust is then passed through the turbine in which enthalpy is converted to work from station 4 to 5. In an ideal cycle, the work created by the turbine is equal to the work consumed by compressor, and the temperature changes are the same as well. The nozzle brings the flow isentropically back to the free stream pressure from station 5 to 8 [24].

Figure 0-4 Brayton cycle (a) T-S diagram, and (b) P-V diagram [24].

Aero-engines can be further divided into four major categories: turbojet, turboprop, turbofan, and afterburning turbojet (Figure 0-5). They have many components in common: combustion section (red), compressor (cyan), turbine/rotor (magenta), inlet and nozzle (grey). The compressor, burner, and turbine are referred to as the core of the engine.

The turbojet is the first and simplest type among the four. It has a centrifugal compressor to give the gas a high velocity. The burner is located at the exit of the compressor to provide additional energy to the gas required to perform the work in the turbine section in order to generate the sufficient thrust to propel the airplane. The turboprop was originally designed based on the turbojet. It uses additional turbines to

absorb part of energy that is normally expanded in the exhaust nozzle to form a higher velocity jet. Turbofan engine has an engine core with a fan section located in the front of the engine and an additional turbine stage located at the rear. The fan pressurizes and captures air at the inlet. Some of the air enters the engine core to produce the thrust, similar to the principle utilized by a turboprop engine. Most of the air by-passes the engine core and is ejected through a fan nozzle, working like a propeller to produce additional thrust. And lastly the afterburning turbo engines are usually used on supersonic aircraft like jet fighters and supersonic transport aircraft. The afterburner is a duct between the turbine and exhaust nozzle, consisting of fuel injectors and flame holders. In the main burner section, the combustion products are air-rich, so the afterburning can raise the temperature of the exhaust gas and reach a higher stream velocity [24].

Figure 0-5 Computer drawings of four different variations of a gas turbine [24].

2.2 Combustor types

The purpose of the combustion system of aircraft gas turbine engines is to enhance the thermal energy of the gas. The combustion chamber design is very complex, because it is required to perform the following multiple functions: complete combustion; reduce total pressure loss; maintain a stable combustion process; ensure in-flight reliability; assume a

smaller size as possible; and realize correct thermal distribution. This can be problematic as each of these requirements are often in a conflict with one another. The ability to balance these requirements has always been a challenging issue in the design of an efficient gas turbine system [25]. Presently, there are three basic types of combustors used in industry: tubular (can), tubo-annular and can-annular [26], and the main differences among the three combustors are shown in Figure 0-6.

Figure 0-6 Schematic of three combustor types [26].

The tubular (can) combustor is composed of a series of cylindrical liners mounted concentrically inside a cylindrical casing. This type of combustor is no longer used in the aircraft field because of the weight and volume limitations, but they can be used in land-based applications where accessibility and maintenance are the top priorities. The tubo-annular (cannular) combustor consists of individual tubular liners within an annular casing. The concept is to combine the compactness of the annular chamber with the mechanical strength of the tubular chamber. The annular combustor contains an annular liner concentrically within an annular casing. The clean aerodynamic layout results in a compact unit with lower pressure loss and minimum diameter [26, 27].

2.3 Survey of Alloys for Combustors

2.3.1 Ni-based superalloys

Among the various superalloys, Ni-based superalloys are widely used in gas turbines because their intrinsic face centered cubic (FCC) crystal structure make them both tough and ductile. Also, they are relatively thermodynamically stable from ambient temperature to almost the point of melting, rendering them as excellent candidates for a wide range of applications in high temperature environments. The microstructure of Ni-based superalloys consists of different phases described as follows [28, 29]:

- i. Gamma phase (γ) which is the FCC solid solution matrix phase. It contains additional solid solution elements such as Co, Cr, Mo, Ru, etc.
- ii. Gamma prime precipitate phase (γ') which is FCC and coherent with the γ -matrix. This precipitate phase exhibits an $L1_2$ structure with Al, Ti and/or Ta as the primary constituents, and of the compound form $Ni_3(Al, Ti)$ (Figure 0-7 (a)).
- iii. Carbides and borides. Up to 0.2 wt. % carbon combines with reactive elements such as Ti, Ta, and Hf to form MC carbides. The MC carbides decompose to $M_{23}C_6$ and M_6C which reside on the grain boundaries as boundary strengtheners. B can combine with Cr or Mo to form borides which have similar function as carbides (Figure 0-7 (b)). For single crystal alloys, no grain boundary strengthening agents are needed.

In order to gain additional alloy strength via precipitation hardening, the early-day quaternary Ni-Cr-Al-Ti alloys have been modified by adding extra precipitation elements to increase the volume fraction of γ' . In addition, because of the electronic structure, the FCC Ni lattice has a large solubility for additional solid solution strengthening via distortion of the lattice; here, larger atomic size differences between Ni and solid solution

elements enhance the lattice cohesion and helps reduce diffusion at service temperatures [30].

Figure 0-7 Microstructure of (a) fully heat-treated Nimonic 80, showing a grain boundaries carbide ($M_{23}C_6$), and uniform dispersed γ' in a γ matrix, and (b) fully heated Udimet 700 showing cubical γ' [28].

The effects of various alloying elements are summarized in Table 0-1. Cr and Al enhance corrosion resistance and also strengthen the matrix. Heavy elements, Mo and W together with Nb and Ta are the most efficient matrix hardeners, but they increase the density of the gas turbine materials, thus increase weight and affect fuel efficiency. Topologically close packed (TCP) phases such as σ and μ have good oxidation resistance and creep strength, but exhibit brittle mechanical properties. As a result, the content of Cr, Mo and W should be controlled to reduce TCP phase formation. Although Co has little influence on strengthening, it modifies the solubility of γ' and raises the solidus temperature. This leads to a higher volume fraction of γ' at relatively low temperatures [30].

Table 0-1 Effects of the major alloying elements in Ni-based superalloys [30].

Element	Matrix strengthen	Increase in γ' volume fraction	Grain boundaries	Other effects
Cr	moderate	moderate	$M_{23}C_6$ and M_7C_3	improves corrosion resistance, promotes TCP phases
Mo	high	moderate	M_6C and MC	increase density
W	high	moderate		promotes TCP phases
Ta	high	large	NbC TiC	promotes γ' and δ phases
Nb	high	large		
Ti	moderate	very large		
Al	moderate	very large		
Co	slight	moderate		raises solidus, may raise or lower solvus
Re	moderate		retards coarsening, increases misfit	
C	moderate		carbides	
B, Zr	moderate			inhibit carbide coarsening, improve grain boundary strength, improve creep strength and ductility

Ni-based superalloys can be formed by various methods, such as casting, forging, powder metallurgy and machining. Casting is a commonly used fabrication process for Ni-based superalloys because of enhanced creep performance seen in certain cast alloy microstructures and provides possibility to create single crystal alloys with no grain boundaries [31]. The castings can be equiaxed, columnar grained or single crystal, as shown in Figure 0-8. In equiaxed alloys, diffusion and creep deformation usually occur at grain boundaries, followed by void formation and cracking eventually. To reduce this effect, the directionally solidified (DS) casting method can be used to reduce or even remove grain boundaries from the cast microstructures [31]. The columnar grain (CG) structure requires two condition: i) unidirectional heat flow to make grains grow in one direction, and ii) no nucleation in the melt at the advancing interface. The preferred growth

direction $\langle 001 \rangle$ happens to be the direction with greatest resistance of creep and thermal fatigue. To obtain single crystal superalloys, the same directional solidification casting process is used, however, a "pigtail" seeding method is added to the casting mold in order to eliminate all but one grain, the single fastest-growing grain in the preferred $\langle 001 \rangle$ direction.

Figure 0-8 Turbine blades in (a) equiaxed, (b) columnar, and (c) single-crystal forms [29].

2.3.2 Co-based superalloys

Co-based alloys are suitable for applications requiring moderate high temperature creep and fatigue resistance, such as non-rotating components in gas turbines where the stress levels are relatively lower comparing to rotating components. Hence, Co-based alloys are often utilized as turbine vanes and static turbine components as such combustors. In addition, Co-based alloys generally have a lower coefficient of thermal expansion and have better thermal conductivity than Ni-based alloys, which make them better suited for applications where thermal fatigue is a critical life limiting factor [32].

Co-based superalloys contain 30-60 wt.% Co, 10-35 wt.% Ni, 20-30 wt.% Cr, 5-10 wt.% W, and less than 1 wt.% C. They are primarily strengthened by carbide precipitation

rather than intermetallic compounds. Carbides are complex in structures because they can upgrade or degrade alloy properties based on their location, chemical composition, and shape. The primary MC type carbides are formed as dispersed blocky particles or eutectic phases during casting and they possess the FCC structure. Secondary Cr-rich M_7C_3 and $M_{23}C_6$ carbides are commonly situated along the grain boundaries. $M_{23}C_6$ carbides, also rich in Cr, are the most common secondary carbides in Co-based alloys. They control the grain size during service and can provide microstructural refinement during cooling, but carbides may provide potential crack initiation sites or favorize crack propagation paths. In addition, because the secondary carbides contain high amounts of Cr, they usually cause local depletion of Cr from the matrix and result in stress-corrosion or oxidation induced cracking in certain environments due to desensitization [30].

2.4 Thermal barrier coatings

2.4.1 TBC systems

Typically, a TBC system consists of four layers with different functional materials used for each layer. As shown in Figure 0-9, these layers are: 1) superalloy substrate, 2) metallic bond coating (BC), 3) thin, thermally grown oxide (TGO), and 4) thermal insulation ceramic top coating (TC) [6].

The substrate is usually a Ni- or a Co- based superalloy with 5 to 12 additional elements to enhance high temperature strength, oxidation resistance and phase stability [33]. As an integrated system, the TC, the BC and the substrate should be designed simultaneously to ensure compatibility. Internal stresses/strains for spallation arise due to the differences of coefficients of thermal expansion (CTEs) among the four layers [34]. Also, interdiffusion between the BC and the superalloy potentially degrade the integrity of

the TBC system. For example, when a Pt diffusion BC is deposited onto the Ni-based single crystal alloy CMSX4, elemental Al in the BC is replaced by Ti from the substrate under high temperature, leading to oxide formation with poor adhesion properties [35].

The BC plays as a critical role in ensuring the durability of the TBC system. It offers adhesion of the ceramic TC to the substrate. Also, the BC can protect the metal bulk from oxidation via the formation of α -Al₂O₃ [36]. BCs can be divided into two main categories: i) MCrAlY (M=Ni, Co, or NiCo) coatings and ii) Pt-modified diffusion aluminide coatings [37]. MCrAlY coatings are considered to have better ductility than aluminide coatings due to its lower Al content (5-12 wt.%). Also, this BC can be compositionally tailored with respect to different operating conditions by incorporating different solid solutions (γ -Ni(Fe,Co), etc.) [38]. Pt-modified diffusion aluminide coatings are fabricated by electroplating a thin layer of Pt on the substrate and then aluminized by implementing a chemical vapor deposition (CVD) process. The Pt additions improve the oxidation resistance and reduce the growth of voids at the interface of TGO/BC [39]. Aluminide coatings can have two to three layer: inward grown layer by the Al internal diffusion, outward grown layer by the Ni and other substrate elements external diffusion, and an intermediate layer between the two layers [40, 41] Recently, research focus has shifted from β -(Ni, Pt)Al phase to γ/γ' - (Ni, Pt)₃Al bi-phase coatings because the latter can provide a more robust α -Al₂O₃ layer, however γ' -(Ni, Pt)₃Al phase is very sensitive to oxidation temperatures and substrate compositions [42].

The TGO is a thin oxide layer (1-10 μ m) formed between the TC and BC during thermal exposure. The oxygen constituent is obtained from the hot gas medium via existing porosity and microcracks in the ceramic TC, as well as oxygen ions interdiffusing through

coatings themselves. The main constituents of TGO are α -Al₂O₃ along with other transition metal Cr/Ni-rich oxides. α -Al₂O₃ is considered as an ideal phase to protect the substrate from further oxidation [43] due to its low defect concentration [44]. However, when Al concentration falls to <8 at. % due to oxidation and interdiffusion, Al-depletion occurs. The integrity of the TGO is very crucial to TBC durability [36].

Figure 0-9 TBC system [45].

2.4.2 TC (7YSZ)

Zirconia (ZrO₂) has been the most widely used TC material, due to its high CTE, low thermal conductivity and good erosion resistance. However, pure zirconia is rarely used because it is susceptible to crack during cooling as a result of phase transformation. A metal oxide or dopant with a cation valence less than that of the Zr atom can be added to stabilize the charge balance, rendering zirconia more resistant to phase transformation cracking [7].

Pure ZrO₂ assumes three phases as a function of different temperature at ambient pressure (Figure 0-10): cubic (*c*) at temperatures higher than 2300°C, having a fluorite structure with cubic anions (O²⁻) and a face-centered cation (Zr⁴⁺); cubic transfers to tetragonal (*c*→*t*) at 2300°C, where anions displace and lattice distort to the tetragonal structure; tetragonal *t* transfers to monoclinic phase (*t*→*m*) when the temperature is further

decreased to 1050°C, where the cation is in sevenfold coordination. During the transformation from *t* to *m*, the volume is increased due to the cell doubling, causing doubling of the length of lattice parameters [46].

Figure 0-10 Zirconia phases, (a) cubic (*c*), (b) tetragonal (*t*), (c) monoclinic (*m*) [46].

According to the phase diagram (Figure 0-11), the temperature for phase transformation from *t* to *m* decreases with increasing amount of Y_2O_3 . Zirconia with 2.5-7.5 mol.% Y_2O_3 (5-15 mol.% $YO_{1.5}$) has *c* + *t* phase structure above 600°C, and *c* + *m* at room temperature, which is called partially-stabilized zirconia (pure *c* phase at room temperature is called fully-stabilized zirconia) [47].

Figure 0-11 $YO_{1.5}$ phase diagram [47].

When partially stabilized zirconia containing metal oxide dopants such as Y_2O_3 is quickly cooled from high temperature, there is no time for diffusion to occur, leading to the formation of the twinned tetragonal phase (t'). t' phase has the same crystal structure as t but with higher yttria content. The metastable t' is also identified as a non-transformable phase [48]. The t' - ZrO_2 has good strength and crack resistance at high temperature, but if it is reheated to above 1200°C , t' - ZrO_2 will decompose to $c+t$ phases and the newly formed t phase experiences a martensitic phase transition to monoclinic m phase [49].

2.5 Deposition methods

2.5.1 APS

APS TBC coatings first came into application in 1970 [50]. The microstructure features: i) a splat grain morphology with inner splat boundaries and cracks parallel to the metal/ceramic interface rendering for a lower thermal conductivity to APS TBC and ii) 15-25 vol.% of porosity leading to low elastic modulus and also low thermal conductivity. In the plasma spraying process, the powder is injected into the high temperature plasma jet where, the ceramic material is melted and then carried towards to the substrate by the carrier gas. The molten droplets striking the substrate rapidly solidify and are flattened to form a deposit. The cooling rate is reported to be near $10^6^\circ\text{C}/\text{sec}$. Since the ceramic coatings are mechanically adhered to the substrate, the BC should be roughened enough to provide good adhesion. As shown in Figure 0-12 (a), the schematic diagram illustrates the air plasma spray process. Argon or other inert gas passes through a nozzle and is ionized

by a direct current (DC) electrical arc to form hot plasma (8300°C). This electrical arc current produced between the cathode and the anode ranges between 800 – 1000 amps [51].

Figure 0-12 (a) Schematic of the plasma spray process [51], and (b) Photomicrograph of an APS TBC [52].

Plasma sprayed coatings are produced by continuously melting particles with a diameter between 5 – 50 μm into splats. During the solidification process, grains grow in a direction perpendicular to the substrate and parallel to the heat flux direction during spraying, as thus the splats are parallel to the surface of the coating. These splats have microcracks caused by the thermal stress from the mismatch of CTEs between the coating and the substrate/BC. The microstructure is influenced by various spraying parameters, the most important one being the cooling rate. For low substrate surface temperatures (<500°C), splats are loosely bonded, because high tensile stresses generated by the large temperature drop between the coating droplet and the substrate, which create cracks individually in each splat and splat boundaries are weak. At higher substrate temperatures (~ 650°C), splats between each other have higher bonding strength, so the strong bonding increases grain sizes with reduced amount of grain boundaries [53]. Figure 0-12 (b) shows

the cross-section microstructure of an APS deposited TBC. A porous microstructure with splats parallel to the substrate surface is evident. Standard porosity of APS TBCs is controlled to 10 – 20% in order to lower the thermal conductivity coefficient while maintaining suitable mechanical properties [52].

2.5.2 EB-PVD

Physical vapor deposition (PVD) was developed as an alternative commercial deposition method to APS for TBCs [50]. EB-PVD of zirconia-yttria coatings was developed by the OEM, Pratt & Whitney, in the late 1970s. In its early years (1980s), this process technology suffered from poor reproducibility due to variation in coating microstructure, limited differences in processing parameters, but these problems had been largely solved in recent years [50]. Current TBCs produced by EB-PVD show good strain and thermo-shock tolerance due to their inherent columnar microstructures. Also, EB-PVD coatings benefit from their excellent surface finish and good erosion resistance properties. However, their thermal conductivity is often higher than APS coatings (of the same composition) due to the columnar microstructure [54].

The basic process of EB-PVD is to use a high-energy electron beams to melt and evaporate ingots/targets, as well as preheat the substrate in a vacuum chamber. Figure 0-13 is the schematic of a Sciaky EB-PVD unit. It has six electron beam guns, four to evaporate the coating materials and two to preheat the substrate for better coating adhesion [55]. As mentioned previously, TBCs deposited by EB-PVD have unique columnar microstructures along with pores as shown in Figure 0-14 (a), and the surface tends to have stepped flat plains, as presented in Figure 0-14 (b). Due to the independent columnar microstructure, cracks initiated in one column will not propagate to others, hence the coatings assume good

strain tolerance. Columnar microstructures also give rise to good erosion resistance as the column boundaries act as crack inhibitors. TBCs with smaller columns have a lower erosion rate, due to less relative material loss for one cracked column.

Figure 0-13 Schematic diagram of the ion beam assisted, EB-PVD unit [56].

Figure 0-14 Microstructure characteristics of TBCs obtained by EB-PVD, (a) cross-section, and (b) surface [57].

2.5.3 SPS and SPPS

Currently thermal plasma spraying is the most commercially viable method to produce TBCs due to its low cost and wide availability. Due to the powder injection mechanism, the powder size is usually centered in the 10-20 μm range, making nano-structured TBCs impossible. However, more recently, a suspension plasma spray process (SPS) was developed to overcome this limitation and enabled the deposition of nano-sized particles.

The SPS deposited coatings have a novel structure with either vertically cracked (VC) or EB-PVD-like columnar structures. In this process, nano-sized powders are dispersed into a suspension (a liquid carrier such as water or alcohol) and injected into the plasma torch, usually axially or tri-axial nozzles [58].

During the SPS deposition process, droplets of slurry go through the following stages (Figure 0-15): aerodynamic breakdown; liquid evaporation; sintering of fine solids; melting of fine solids and agglomeration to larger size; further evaporation of liquid material; and finally, deposition on to the substrate [59].

Figure 0-15 Stages that suspension droplets undergo during the plasma spraying [59].

Solution precursor plasma spray (SPPS) is a relatively newer technology specifically developed for TBCs. This deposition method was first patented by Karthikeyan et al. [60] in 1997. In 2007, this deposition process was further evaluated and improved by the University of Connecticut and Inframat Corporation [61]. The SPPS process deposits molten material onto the substrate, similar to standard plasma spraying deposition method; however, the feedstock material by SPPS is in the form of liquid rather than powder suspension [62].

Figure 0-16 Schematic of the solution precursor plasma spray delivery system [62].

Figure 0-16 shows the SPPS process where an atomizing injector is located just outside of the nozzle. The power input is usually between 35 – 45 kW. And argon or another inert gas are used as ionization and shielding gasses. Depending on the heat transferred in the plasma, some or all of the following processes take place: precursor solvent evaporation, droplet breakup, precursor solute precipitation, pyrolysis, sintering, melting, and crystallization. Key coating properties such as porosity, density, and hardness can be controlled by varying spray parameters [62]. SPS and SPPS have similar liquid feed mechanism with the same injection device, however; the former one uses liquid medium as a carrier for the fine powders, but the later one makes the coating material synthesized directly into the hot gas stream, after the solvent has been evaporated. SPS process deposits melted coating particles onto the substrate, but SPPS process has different deposition mechanisms depending on whether the material reaches the substrate before the synthesis is complete, because solution precursor has larger liquid drops, which needs higher thermal energy to process droplets [63].

Because of the small powder size used in SPS process, the microstructure varies greatly with deposition parameters. For example, an increased velocity leads to a greater density of interlamellar pores [64]. The standard SPS microstructure is shown in Figure 0-17, a 5YSZ coating with $\sim 250 \mu\text{m}$ in thickness. Compared to the traditional APS coatings, this microstructure has thinner lamellae and weaker inter-splat bonding [65]. Both columnar and dense vertical cracked (DVC) microstructures can be obtained by SPS deposition by varying the substrate temperature, plasma torch temperature, droplet sizes, etc. Similar to columnar structures, vertical cracks within the ceramic layer help to reduce the thermal stresses caused by the thermal expansion difference of the coating and the substrate, rendering the coating more strain tolerant [66].

Figure 0-17 5YSZ structure of a SPS coating, (a) columnar structure, and (b) vertical cracked [65].

2.6 Failure mechanisms

2.6.1 Thermal stress

The TIT and the compressor discharge pressure are usually increased to improve the performance of a gas turbine. Hot components, especially combustion liners, which have a direct interaction with the hot gases experience the highest thermal loads [67]. Temperature differences between the hot combustion gases and the combustion chamber walls, with a

chamber pressure of above 18 MPa, lead to a high heat flux as well as temperature gradients through the chamber wall [68]. There are several ways to decrease the chamber wall temperature. Film cooling technologies utilize discrete minute holes on the outer and inner walls to introduce cold air into the flame tube where a film layer is formed on the inner side of the wall, separating the hot gas from the wall and reducing the convection and radiation heating from the hot gas [69]. In addition, TBCs can be applied on the flame side to insulate metal substrates.

However, because a BC between a TC and a substate typically has a higher CTE than the two, it experiences localized thermal stress, due to the thermal expansion mismatch. Figure 0-18 lists the thermal stresses within the TBC system. During the heating process, TC and TGO experience the in-plane tensile stress, and BC and SUB experience the in-plane compressive stress, because BC and SUB have higher CTE than the one of TC and TGO. During the cooling process, the stresses convert. The stress analysis is based upon the flat interfaces. However, the interface between TC and BC is wavy since the manufacturing process, so out-of-plane stresses are induced.

Figure 0-18 Thermal stresses within the TBC system.

This phenomenon causes the BC surface to roughen under cyclic conditions (Figure 0-19 (a)) because of tensile stresses developed during cooling in the BC having a higher CTE than that of the superalloy. Generally, the as-deposited BC is considered to be at a

stress-free state at high temperature before cooling down to room temperature, but it will experience a tensile plastic strain during cooling and a compressive plastic strain upon heating back to the oxidation temperature. Usually the duration at oxidation temperature (OX) has minimal effect on the plastic deformation, but the wavelength of the undulation continues to increase with the increasing thermal cycles, hence time-dependent creep deformation is involved [70]. As shown in Figure 0-19 (b), segments $1 \rightarrow 2$ and $5 \rightarrow 6$ are elastically deformed when the thermal stress is lower than the yield stress. However, when the accumulated stress in the BC is no longer zero, plastic deformation (creep deformation in nature) occurs on both cooling and heating processes, presented by $2 \rightarrow 3$ and $6 \rightarrow 7$, respectively. The subsequent creep relaxation at the end of heating (point 7) depends on the isothermal duration. The strain at the end of the exposure, $\Delta\epsilon$, can be expressed as:

$$\Delta\epsilon = \frac{\sigma_y}{E} - \epsilon_{creep} \quad (2.1)$$

$$\dot{\epsilon}_{creep} = -5.6 \times 10^{-16} \sigma^7, \text{ at } 1150^\circ\text{C} \quad (2.2)$$

where σ_y is the yield stress of the BC at T_{ox} , E is the elastic modulus, σ is the stress on the BC. When the isothermal holding period is long enough, creep relaxation can complete and the state returns to the original point 1, otherwise the new cycle will start at point 1' instead. The creep relaxation can be described by:

$$\frac{1}{E} \frac{d\sigma}{dt} = -5.6^{-16} \sigma^7 \quad (2.3)$$

$$\epsilon_{creep}(t) = \frac{\sigma_y - \sigma(t)}{E} \quad (2.4)$$

Figure 0-19 Roughening caused thermal mismatch, (a) SEM image of bond coated samples after 100 cycles at 1150°C with a cycle length of 3 h, and (b) strain diagram where yield stress at T_{ox} is not zero [70].

However, some experiments showed that power law creep should be in a form where the exponent n is equal to 1.5 instead of 7, and σ_y may be as high as 70 MPa [70]. In reality, time dependent deformation is often inconsistent and highly influenced by other processes, for example, increased roughness, higher yield stress, grain sizes and the creep relaxation might influence the plastic deformation.

2.6.2 BC degradation

The two main types of BCs (PtAl and MCrAlY) suffer from different failure modes. Based upon the observation, the failure of TBC is usually by spallation of the TC at the interface of TGO/PtAl BC [71]. The commercial PtAl BC has a unique microstructure with a network of ridges, as shown in Figure 0-20. The presence of the ridges modifies the localized stress field and generates out-of-plane tensile stress at peaks and in-plane tensile stress at flanks [71]. The out-of-plane tensile stress at asperities can be sufficiently high to

crack the TGO, thus accelerating oxidation in the BC grain boundaries. In thermal cycling, the stresses around the ridges lead to in-plane and out-of-plane cracks in the TGO [71]. These cracks then admit oxygen to the BC surface and favor the downward oxidation at grain boundaries of the BC. At service temperature, the BC and oxide formed are stress-free. During cooling, tensile stresses and plastic deformation occur in the BC, hence the cavities are enlarged by the CTE mismatch between the BC and the oxide. During reheating, the expanding BC forces the oxide into tension, and the tensile stress eventually develops and subsequently causes cracking in the oxide. Once the cracks start the newly exposed BC is oxidized rapidly, and the crack propagates further from the tip, leading to voids formation near the bottom of the cavity, as demonstrated in Figure 0-21 [71].

Figure 0-20 SEM image of as-received bare PtAl BC [71].

Figure 0-21 PtAl BC failure mechanism in thermal cycling [71].

PtAl BCs also suffer from phase transformation, induced by composition changes. PtAl BCs are primarily consisted single β phase, but they transfer to $\beta - \text{NiAl} + \gamma' - \text{Ni}_3\text{Al}$

structure after operation due to the Al depletion arising from alumina formation. The phase transformation involves a volume change, which produces out-of-plane stress in the BC, hence leading to rumpling and cracks at the TGO/BC interface. Based on Equation 2.5, the calculated volume expansion is 28% when alumina is formed [72]. The martensitic phase transformation from β to γ results in tensile stresses at the interface as well, but it has a minor negative effect on the service hours due to less than 2% volume change [72]. In addition, differences in CTEs of various phases introduce further stresses in the TGO, which in turn induce tensile stress in the BC.

On the other hand, a common failure mechanism in MCrAlY BCs is often described as a chemical failure. A representation of the MCrAlY TBC failure is presented in Figure 0-22. After cooling to room temperature, the Al_2O_3 exhibits some undulation and sustains residual stresses; once it is detached, it creates a path for oxygen to ingress to the BC. When Al is sufficiently rich within the BC, it will be able to reform Al_2O_3 , but when there is an Al depletion zone beneath the cracked alumina, Cr and other metallic elements within the BC are more active because of higher element concentrations in the Al depletion zone. As a result, the metallic elements diffuse outward through the path to form Cr-rich oxide (usually spinel and chromia) externally.

Figure 0-22 Schematic of Al depletion mechanism.

Both Al_2O_3 and Cr_2O_3 acts as protective barriers for metallic substrates because of the oxides are highly stable, continuous, slow growing related to the stoichiometric structure [73, 74]. However, Al_2O_3 is more desirable because Cr_2O_3 is unstable if the operating temperature is higher than 871°C . Cr_2O_3 decomposed by the reaction (2.6) at very high temperature, so the scale is susceptible to accelerate degradation [74].

Spinel $(\text{Ni, Co})(\text{Al, Cr})_2\text{O}_4$ at the surface is yielded by previously formed Cr_2O_3 , CoO , and NiO [75]. The formation of spinel is not desirable, because it companies the volume expansion of 105% as calculated from molar volumes compared with Al_2O_3 . In this case, a marked increase in out-of-plane displacements is formed [72]. In addition, spinel is porous, brittle, without the capability in antioxidation [76], so it is the most undesirable oxide among the three.

Eventually the curved spinel and chromia oxides would lead to the cracking of TC because the thicker and more undulated TGOs produce higher localized stresses in the TC [9]. As shown in Figure 0-23, based on a published research, after 256 h at 1121°C , the TBC was observed to have cracked and buckled [9]. Based on the phase evolution in TGO, Al_2O_3 was mixed with the spinel and α -chromia after 256 h. In addition, the alumina phase is discontinuous after 384 h oxidation and then the TGO assumed primarily spinel and α -chromia.

Figure 0-23 SEM image of cracking and buckling of the TBC [9].

2.6.3 TC degradation

As deposited, TBCs are inherently porous in the as-manufactured condition, however, the ceramic TC experiences sintering effect. High temperature exposure has the potential to heal cracks, bond splats, and grow grains at high temperatures, such phenomenon is defined as sintering effects. Sintering results in changes in the mechanical and physical properties. The elastic modulus, strength, and work of fracture will increase after high temperature exposure; yet, sintering deteriorates strain-tolerance capability and increases thermal conductivity [8]. SEM analysis of polished surfaces of TCs after annealing at 1316 °C with different exposure times (Figure 0-24) shows evidence of microcracking and/or pore healing as a result of sintering [8]. With longer exposure time, the porosity level would reach a certain level and remain stable; however, the surfaces of the annealed specimens became smoother and microcracks disappeared. In terms of mechanical properties, Sung Beck et al. [77] used Equation 2.7 to express the relationship between the elastic modulus (E) and dwell time (t_D) at high temperature:

$$E_{TC} = E_{TC,0} \left[1 - \exp\left(\frac{-N \cdot t_D}{\tau_{sinter}}\right) \right], \tau_{sinter} = H \cdot (T_{max})^l \quad (2.7)$$

where E_{TC} is the elastic modulus after thermal exposure, $E_{TC,0}$ is the initial elastic modulus, T_{max} and τ_{sinter} are time constants for sintering, H and l are appropriate parameters. Keyvani et al. [78] simplified this equation as:

$$E_{TC} = E_{TC,0} + e \cdot t_D^f \quad (2.8)$$

where e and f are constants determined from the experimental data. When the TC begins to sinter, lateral shrinkage occurs and develops extra in-plane tensile stresses because of the constraint of the substrate, leading to reduced lifetimes [11].

Phase transformation can influence the stresses as well because of the associated volume changes [79]. The detailed phase transformation of YSZ has been discussed in the Section 2.4.2.

Figure 0-24 Polished surfaces of plasma sprayed 8YSZ TBCs by SEM annealed at 1316 °C in air at different times t , (a) $t = 0h$, (b) $t = 100 h$, and (c) $t = 500 h$ [8].

2.6.4 Crack growth and delamination in TCs

The ceramic TC also suffers from several other micro-mechanic failure mechanisms, which mainly differ in where the cracks are assumed to nucleate and the path of the growing crack. The crack growth mechanisms of APS and EB-PVD TBCs can be quite different. The failure of APS TBCs is usually manifested by the spallation of the ceramic coat, as result of crack formation in TCs [80]. EB-PVD failures, on the other hand, occur at the TGO/BC

interface because the EB-PVD TC is more strain-tolerant. During thermal cycling, initial cracks and damage occur at the TC/BC interface in a typical EB-PVD TBC system due to the rumpling mechanism and in the vicinity of embedded Ni/Co rich oxides. Voids then form near the interface of TGO/BC, and oxygen penetrates through the original TGO and forms spinel. Due to the voids and brittle Ni/Co rich oxides, failure eventually occurs due to spallation [81].

Figure 0-25 Failure mechanisms (a) APS [82], and (b) EB-PVD [81].

Under both isothermal and cyclic conditions, APS TBCs failed by crack propagation at the imperfections near the interface of TC/TGO within the TC. Under isothermal condition, the cracking is dominated by TGO growth stresses [10]. As shown in Figure 0-26, there is a gap between the TC and TGO. During high temperature thermal exposure, the gap is filled by TGO and its thickness is increasing with time; however, the surrounding layers try to push TGO back to its original shape, so TGO experiences out-of-plane compressive stress normal to the interface. Correspondingly, out-of-plane tensile stress is induced within the TC.

Figure 0-26 TGO growth stress under isothermal condition [10].

As shown in Figure 0-25 (a), the peak tensile stress cracks the TC at high temperatures, but the crack does not penetrate through the TGO because of its creep ductility properties at high temperatures. In addition, the TGO and BC are in compression, inhibiting crack growth in the area [82]. When cooling to an ambient temperature, the stress increases due to thermal expansion misfit and out-of-plane stress (σ_{22}) is produced, with tensile in peaks and compression in valleys [9]. The crack penetration through the TGO is a critical step. Once it occurs, the tensile stress developed is normal to the interface and

will separate the TGO from the BC. The TGO becomes brittle at intermediate temperatures, so the tensile stress is sufficient to result in fracture [82].

D. R. Clarke et al. [83] simplified the relationship between the stress in TGO and out-of-plane tensile stress:

$$\sigma_{22} = \frac{2\sigma_{TGO}h}{R} \quad (2.9)$$

where h is the TGO thickness, and R is the undulation radius. To determine whether the crack is able to grow in the last step shown in Figure 0-25 (a), the fracture criterion is given in Equation 2.10, where E_{TGO} is the elastic modulus of TGO, Γ is the fracture energy of the interface of TGO/BC, c is the crack length, and B is the constant of the order of unity. The right side of the equation is the crack driving force and the left is the fracture resistance.

$$\frac{\pi R^2 E_{TGO} \Gamma}{2Bh^3 \sigma_{TGO}^2} < [1 - e^{-\frac{c}{h}} \cos \frac{c}{R} + e^{-\frac{c}{h}} \frac{R}{2h} \sin \frac{c}{R}] \quad (2.10)$$

The right side of Equation 2.10 is plotted in Figure 0-27 (a) for different h/R values, and the left side is presented by several straight lines. When c/R is smaller than c_0/R , the crack will not propagate, otherwise it will grow until the intersection point (c^*/R) and that be arrested by the TGO. Based on this plot, the relationships between h/R and c/R as well as c_0/R are obtained and summarized in Figure 0-27 (b). The required crack length to cause propagation is reduced with the increasing TGO thickness. It should be noted that when c/R is greater than 1, the tensile stress becomes compressive, so no separation will occur at the interface [9].

Figure 0-27 (a) Plot of various h/R and c/R followed by the fracture criterion, and (b) critical crack length c_0 and c^* with the function of h/R [9].

Under cyclic condition, however, cracking is dominated by TGO ratcheting [10]. During the cooling process, TGO experiences in-plane compressive stress. This thin layer wants to lengthen itself through out-of-plane displacement to release the energy if it is in compression. In this case, TGO ratchets under cyclic condition, and it moves downward at valleys (Figure 0-28 (a)). ϵ_{zz} initiates imperfections at the valley within the TC in the valley region, and then the imperfections delaminate until final delamination, as shown in Figure 0-28 (b).

(a) (b)
Figure 0-28 (a) TGO ratcheting, and (b) TC cracking under cyclic condition [10].

Cracks may also form in the TCs in the form of isolated cracks or edge delamination when a TBC experiences a high heat-flux environment [11]. The two main categories of cracks are shown in Figure 0-29. An isolated crack parallel to the interface experiences an energy release rate due to the thermal gradient. It may occur within the TBC or from the edge. A shrinkage crack is caused by sintering of the TC of the TBC. Regarding the isolated crack, the energy release rate for the crack is described in Equation 2.11, where $K_I^{\Delta T}$ and $K_{II}^{\Delta T}$ are stress intensity factors defined by Equation 2.12:

$$G^{\Delta T} = \frac{1}{2} \left(\frac{1}{\bar{E}_{TBC}} + \frac{1}{\bar{E}_{substrate}} \right) (K_I^{\Delta T} + K_{II}^{\Delta T}) \quad (2.11)$$

$$\begin{aligned} K_I^{\Delta T} &= c_{21} F / \sqrt{h} + 2\sqrt{3} c_{22} M / h^{3/2} \\ K_{II}^{\Delta T} &= c_{11} F / \sqrt{h} + 2\sqrt{3} c_{12} M / h^{3/2} \end{aligned} \quad (2.12)$$

where c_{ij} are coefficients as functions of b/h and $\alpha_D = (\bar{E}_{TBC} - \bar{E}_{substrate}) / (\bar{E}_{TBC} + \bar{E}_{substrate})$, h is the thickness of TC, b/h is the relative crack length to the thickness of TC, F is the in-plane force, M is the moment. When $b/h \gg 1$, G reaches the limiting steady-state value:

$$G_{ss}^{\Delta T} = \bar{E}_{TBC} (\alpha_{TBC} \Delta T)^2 h / 6 \quad (2.13)$$

When the sintering stress $\sigma_s = \gamma_s k$ (where γ_s is the surface energy) grows large enough, sintering cracks form. The steady-state energy release rate is:

$$G_{ss}^{sinter} = 0.343 \sigma_s^2 H / \bar{E}_{TBC} \quad (2.14)$$

Figure 0-29 Three potential modes of delamination of a TBC being exposure to a thermal gradient [11].

2.7 Existing life prediction method

Since coating failure results in overheating of the substrate metal component and produces accelerated oxidation, it is crucial that the expected duration of TBC life is well established before components are put into service. In the following sections, the existing TBC life prediction methods are discussed in detail.

2.7.1 Life prediction based on oxide layer growth and Al consumption

There are three types of protective oxide scale growth relationships as a function of time:

i) parabolic, ii) cubic and iii) logarithmic:

$$h^2 = K_p t \quad (2.15)$$

$$h^3 = 2K_c t \quad (2.16)$$

$$h = K_l \ln (at + 1) \quad (2.17)$$

where K_p , K_c , K_l are rate constants, h is the thickness, t is the time. The oxidation rate of alumina scale is considered as a parabolic growth in various studies [84, 85, 86]. However, K_p is an instantaneous parameter influenced by the diffusion coefficient and grain size of the oxide. It follows the equation of:

$$K_p = \frac{4\delta D_{gb,o}}{G} \left(\frac{\Delta\mu_o}{RT} \right) \quad (2.18)$$

Here δ is the grain boundary width, which is usually considered as 1 nm, G is the grain size of the oxide scale, $D_{gb,o}$ is the oxygen grain boundary diffusion coefficient, and $\Delta\mu_o$ is the oxygen chemical potential change across the oxide scale. The grain size change is determined by:

$$G = G_0 \times \left(\frac{t}{t_0} \right)^m \quad (2.19)$$

where G_0 is the grain size at time $t = t_0$. Equation 2.18 and Equation 2.19 are substituted into Equation 2.15 to arrive at:

$$\frac{\Delta m}{A} = K \times t^n \quad (2.20)$$

W. J. Quadakkers et al. [84, 85] established a simple model to predict the service lifetime of MCrAlY based on the consumption of Al in the alloy. It was assumed that a flat specimen with a thickness of d and surface area of A obtained Δm due to oxide scale growth. If the surface oxide is pure Al_2O_3 , the Al/O weight ratio is assumed to be 1.124. Al mass in the oxide is:

$$\Delta m(\text{Al})^{ox} = 1.124 \times A \times K \times t^n \quad (2.21)$$

Considering the volume of the specimen is $\frac{1}{2} A \times d$, the amount of Al consumed to form the oxide scale after a period of t is:

$$1.124 \times A \times K \times t^n = \frac{(C_0 - C_t)}{100} \times \rho \times \frac{1}{2} A \times d \quad (2.22)$$

where ρ is the density of the alloy, C_0 is the initial Al wt.% and C_t is the remaining Al wt.% at time t . Given C_B^* is the Al content when the scale starts to break, the time for the failure is:

$$t_B = [4.4 \times 10^{-3} \times (C_0 - C_B^*) \times \frac{\rho \cdot d}{k}]^{\frac{1}{n}} \quad (2.23)$$

C_B^* is a governing factor for Equation 2.23. The critical molar fraction of Al required to form a continuous scale is given by:

$$N_B^* \geq [0.3N_o(D_o/D_{Al})(V_m^{alloy}/V_m^{oxide})^{1/2}] \quad (2.24)$$

Here D_o and D_{Al} are diffusivities of O and Al in the alloy, V_m^{alloy} and V_m^{oxide} are the molar volumes of metal and oxide formed, and N_o is the solubility of oxygen in the alloy [87]. The above calculation assumes that the alloy is homogeneous during the oxidation process. However, the concentrations of oxygen and metallic elements vary continuously with the distance from the interface to the interior of the material due to the diffusion.

During the oxidation process, Al diffuses to the surface to form a protective alumina scale. This process continues until the Al concentration becomes insufficient to maintain a continuous alumina scale, resulting in an Al depletion near the surface. It is necessary to know the Al diffusion coefficients in MCrAlY and the substrate [88].

Having defined the Al diffusion coefficient and the oxide growth rate, the Al profile can be determined using Wagner's equation [89]:

$$C(x) = C_s + (C_b - C_s) \frac{\operatorname{erf}\left(\frac{x}{2\sqrt{2D_{Al}t}}\right) - \operatorname{erf}\left(\sqrt{\frac{K_p}{2D_{Al}}}\right)}{\operatorname{erfc}\left(\sqrt{\frac{K_p}{2D_{Al}}}\right)} \quad (2.25)$$

where $C(x)$ is the Al concentration at the distance x from the metal/oxide interface; C_b is the Al concentration in the substrate; C_s is the Al concentration at the metal-oxide interface; D_{Al} is the Al diffusion coefficient in the alloy (cm^2/s); t is the oxidation time in s.

But there is still a number of uncertainties here as the concentration of Al at the interface is unknown. Also, during the oxidation process, the interface moves toward the substrate as oxygen consumes the metal via oxidation and meanwhile an oxide layer forms on the surface [90]. As shown in Figure 0-30, $x=0$ defines the original metal surface, the oxide thickness d_{ox} can be divided into external d_E (formed by metal outward diffusion) and internal d_I (from oxide inward diffusion) oxides. The value of d_I can be expressed by:

$$d_I = \frac{V_{Al}^m}{V_{Al_2O_3}^m} d_{ox} \quad (2.26)$$

Figure 0-30 Schematic of the oxidation mechanism [90].

In a small increment of time, dt , the oxygen consumes the substrate with a thickness of $d(d_I)$, and $C_s \cdot d(d_I)$ represents the Al depleted from the substrate. However, the oxide receives $C_{Al}^{ox} \cdot d(d_{ox})$ during this time, where C_{Al}^{ox} is the Al concentration in the oxide. The effective Al flux then becomes:

$$C_{Al}^{ox} \cdot d(d_{ox}) - C_s \cdot d(d_I) \quad (2.27)$$

Based on Fick's first law:

$$D_{Al} \frac{\partial C_{Al}}{\partial x} \big|_{x=d_I} = C_{Al}^{ox} \cdot \frac{d(d_{ox})}{dt} - C_s \cdot \frac{d(d_I)}{dt} \quad (2.28)$$

where $\frac{\partial C_{Al}}{\partial x}$ is the slope of Al concentration vs. location from the original interface. If the slope at the interface is known, then C_{Al}^{int} can be predicted. Equation 2.24 is used to estimate the shape of the Al concentration vs. location. Although C_{Al}^{int} is unknown in Equation 2.25, the combination of Equation 2.25 and Equation 2.28 can be used to solve the problem.

2.7.2 Physics-based life prediction method

E.P. Busso et al. [91] developed a life prediction method based on a statistical treatment of the TBC's morphological characteristics and a continuum mechanics framework to quantify the local TBC stresses for crack nucleation and growth. The TBC system used in this work consisted of an EB-PVD YSZ TC and a low-pressure plasma spray (LPPS) BC on a CMSX-4 substrate. In the first stage, they quantified the damage percentage via non-destructive inspection methods, namely piezo-spectroscopy and thermographs, as shown in Figure 0-31, where the darkened area denotes the crack area. In order to link the damage percentage D with the accumulated time, Equation 2.29 is used to express the damage fraction with the accumulated time t_{acc} , highest temperature θ_{max} and lowest temperature θ_{min} .

$$D = \widehat{D}(\theta_{min}, \theta_{max}, t_{acc}) \quad (2.29)$$

Figure 0-31 Damaged area maps measured in TBC systems (MCrAlY BC and YSZ TC on CMSX4 substrate), (a) photograph of a coated tested sample after 700 h at 1000 C, (b) SEM image of a failing TBC system, (c) stress maps measured by piezo-spectroscopy, and (d) the corresponding thermographs [91].

The undulation geometry of the TGO was critical because it generated the thermal stress leading to the TBC failure. Over 100 measurements were taken at the EB-PVD TBC/LPPS BC interface to obtain the geometry of b and b/a (Figure 0-32). It was assumed that the measured damage occurred only at the regions having the value of b/a greater than the critical value r_c . In this case, the damage measurement, represented by the accumulated time, can be associated with r_c by Equation 2.30, where $f(x)$ is the probability density function of b/a , as shown in Figure 0-33 (b).

$$D = \int_{r_c}^{\infty} f(x) dx \quad (2.30)$$

Figure 0-32 Roughness geometric parameters a and b [91].

Figure 0-33 (a) Measured fraction of damaged area against time from measured stress maps, (b) critical value r_c as determined from the statistical normal distribution of the b/a values [91].

Subsequently, using a two-dominant failure mechanism, the stress leading to nucleation and propagation of interfacial cracks, and then the stress driving nucleation and propagation of cracks within the TGO were calculated. Analyzing the results shown in Figure 0-33, the relationship between accumulated time t_{acc} and r_c can be correlated. FE calculation was used to solve the stresses. The geometry and the thickness of TGO for each accumulated time along with the meshed FE (Figure 0-32) were input into the software for the calculation and the results are shown in Figure 0-34. When the estimated stress reached the global failure value, σ_f , the TBCs are said to have reached failure stage.

Figure 0-34 Illustration of the interpolation to obtain TBC failure time and the remaining lifetime for a coating whose failure is controlled by (a) the peak normal traction on the TGO-BC interface and (b) peak maximum principal stress within the TGO [91].

The above method assumed that the thickness of the TGO was consistent; however, in reality the TGO is uneven due to composition/microstructure variations and the formation of other oxides such as spinels [92] and chromia. As discussed in section 2.6.2, MCrAlY type BC forms protuberances, resulting in the formation of non-protective oxides and a risk of premature chemical failure. The chemical failure is defined as the process where an Al depleted zone is formed, and non-protective oxides are formed beneath the protective alumina due to the thermodynamic instability (Figure 0-35). In the research carried out by Busso et al. [92], the thickness of TGO was separated into two parts: h_1 as alumina, and h_2 as non-protective oxides. It should be noted that the thickness at the apex and valley of a protuberance varies because Al depletion at valley occurred later than at apex, hence the non-protective oxide thickness is different from apex to valleys. At 1100°C , the calculation for the two thicknesses follows Equation 2.31 to Equation 2.36, where t_b is the exposure time when protective oxide breaks down and t is the actual exposure time.

$$h_{apex} = h_1^{apex} + h_2^{apex} \quad (2.31)$$

$$h_1^{apex} = 5.72 \times 10^{-9} t^{0.5}, \quad 0 \leq t < t_b \quad (2.32)$$

$$h_2^{apex} = 2.78 \times 10^{-11} (t - t_b), \quad t \geq t_b \quad (2.33)$$

$$h_{valley} = h_1^{valley} + h_2^{valley} \quad (2.34)$$

$$h_1^{valley} = 5.72 \times 10^{-9} t^{0.5}, \quad 0 \leq t < t_b \quad (2.35)$$

$$h_2^{valley} = 2.78 \times 10^{-12} (t - t_b), \quad t \geq t_b \quad (2.36)$$

Figure 0-35 An example of the chemical failure at BC protuberances in a MCrAlY/APS-YSZ system [92].

After modifying the thickness of the TGO in this manner, FE calculation was then utilized again to obtain the stress in this system [92]. Assuming the secondary TGO formed after a 200 h isothermal test at 1100°C, the stresses in the TBC system with different surface roughness at operation temperature and after cooling to the room temperature were obtained and are summarized in Figure 0-36. As shown, the maximum stress resides at the interface between TC/TGO, which gradually decreases, from apex to valley. The stress in the TC is much lower in the relatively flat surface than that in the rougher areas due to the reduced deformation at the apex. In the cooling process, the YSZ TC experiences higher out-of-plane stress than in the isothermal process.

Based upon the literature view, the failure mechanisms and life predictions of traditional APS TBCs were studied. The sintering mechanisms, cracking scenario under isothermal and cyclic conditions, and life prediction methods are also useful when evaluating SPS TBCs.

Figure 0-36 Out-of-plane stress (a) which developed at 1100°C after 200 h oxidation, and (b) cooled down to 25°C after 200 h heating at 1100°C, both with two wavelength [92].

3 Chapter: Material and Experimental Methods

The objectives in this research, as well as designed methodologies were summarized in Figure 0-1.

Figure 0-1 Materials and methodologies.

3.1 Material selections

Initially, two candidate substrate alloys were investigated in this research to determine suitability as a substrate alloy for this research. They were INCONEL 625 and HAYNES 233. The nominal chemical compositions for each are listed in Table 0-1. INCONEL 625 is a wrought, solid-solution Ni-Cr based superalloy. Carbides in the form of MC and M₆C (rich in Ni, Nb, and Mo) are present in INCONEL 625 as grain boundary strengtheners. The formation of a chromia scale enhances its high temperature resistance. This alloy is commonly used for manufacturing gas turbine combustion components [93]. HAYNES 233 is a newly developed Ni-Co-Cr-Mo-Al superalloy by Haynes International; it offers

good oxidation resistance at temperatures up to 1149°C due to the formation of an alumina scale. Also, this alloy has a high creep strength due to the solid solution and carbide strengthening mechanisms. The microstructures of as-received alloys are shown in Figure 0-2.

Table 0-1 Chemical compositions of two substrate alloys.

HAYNES 233	Ni Bal.	Cr 19	Co 19	Mo 7.5	Ti 0.5	Al 3.3	Fe 1.5	Mn 0.4	Si 0.2	C 0.1	Ta 0.5	W 0.3	Y 0.025	Zr 0.03
INCONEL 625	Ni Bal.	Cr 20	Mo 8	Ti 0.4	Al 0.4	Fe 5	Si 0.5	C 0.1	Mg 0.5	S 0.015	P 0.02	Cu 0.5	Nb+Ta 4

Figure 0-2 Microstructures of as-received (a) INCONEL 625, and (b) HAYNES 233.

The oxidation behaviour of the two substrate alloys was evaluated at 1080°C. The results showed that INCONEL 625 was superior to HAYNES 233 under this thermal condition, and as a result, only INCONEL 625 was selected as the ideal substrate in the TBC system. In addition, a NiCoCrAl BC with a thickness of 150 µm and a 7YSZ TC with a thickness of 300 µm (both coatings provided by Northwest Mettech Corp, Vancouver, Canada) were applied to INCONEL 625 as other main components of the chosen experimental TBC system. All coatings were sprayed using the Axial III high power

plasma torch and Nanofeed 350 suspension feed system. With a 3-anode/3-cathode DC plasma torch, coating powders in the suspensions were injected into the hot zone of the plasma directly along the central axis. A mixture of Argon, Hydrogen and Nitrogen were employed as process gases with a total gas flow of (200-300) SLPM. A rotating fixture was used to mount the samples while rotating at a speed of 2 m/s. Suspension feed rate was set to 45 ml/min. The structure of the TC was achieved by controlling the stand-off distances (SOD). In this study, a VC TC was selected and manufactured using a SOD less than 50 mm SOD. The INCONEL 625 substrate were circular in shape with 1" in diameter and 0.06" in thickness. The surface and cross-sectional microstructural images are shown in Figure 0-3. To be noted, VCs are hard to tell from the surface image because of the low magnification, and the sample was sputter prior to the SEM.

Figure 0-3 Microstructure of as-received SPS TC on (a) the as-sprayed surface, and (b) cross-section.

3.2 Experimental considerations

3.2.1 Sample preparation procedures

Before oxidation tests, the as-received samples (both substrate alloys and TBCs) were cleaned ultrasonically with an alkaline solution and an acetone solution, separately for 20 minutes. The bare INCONEL 625 and HAYNES 233 alloys were polished using 600 grit before cleaning. The samples were then heated in the furnace at 200°C for 1.5 h to remove

any moisture. After the oxidation tests, one sample from each thermal exposure period was cold cast with EpoFix epoxy resin (Struers) before cutting to protect and conserve the oxide layers and ceramic coatings during the subsequent sectioning process. For the bare substrate samples, samples were copper coated (Quorum Q150T ES) before mounting in order to protect the oxide layers on the surfaces. After mounting, the samples were sectioned using a Buehler Isomet 2000 precision saw equipped with a Beta Diamond wafering blade at a rotating speed of 500 rpm and a load of 250 g. Subsequently, the sectioned samples were polished using a Buehler Ecomet 4 automatic grinding/polishing machine with an Automet 2 power head. Samples were consecutively polished with 240, 400, 600, 800, 1200 grit silicon carbide papers. Then samples were subsequently polished using 3 μm diamond abrasives and final polishing (0.05 μm) was accomplished with MasterMet colloidal silica polishing suspension and distilled water. Samples were ultrasonically cleaned between each step during the grinding procedure. Before microstructural analyses, the mounted coupons were coated by carbon to provide better conductivity under SEM. The equipment used in the sample preparation is shown in Figure 0-4.

(a)

(b)

Figure 0-4 Equipment for sample preparations (a) Buehler Isomet 2000 precision saw, and (b) Buehler Ecomet 4 automatic grinding/polishing machine with Automet 2 power head [94].

3.2.2 Oxidation test of substrate alloys

For INCONEL 625 and HAYNES 233 bare alloys, oxidation tests were carried at 1080°C for various period of time in a box radiant furnace (SNOL 6,7/1300). The size and shape of the HAYNES 233 samples was round with 1” in diameter and 0.04” in thickness. The INCONEL 625 samples used in the bare alloy oxidation performance evaluation were cut from rectangular sheet and had a rectangular shape of 0.8” in width, 1.1” in length, and 0.06” in thickness. For HAYNES 233, the test durations were 10 h, 30 h, 50 h, 100 h, 200 h, and 300 h. For INCONEL 625, the durations were 100 h, 200 h, and 300 h. Because HAYNES 233 showed early oxide layer spallation in the first 100 h of testing, incremental testing durations were implemented to track the reason for early oxide layer spallation. On the other hand, INCONEL 625 performed well in the first 100 h and did not require early inspection steps for spallation examination. Two samples of each alloy for each test duration were used: one for surface investigation, and the other for cross-sectional evaluation. The samples were weighed using a Metler Toledo AG285 (10-5g precision) scale three times and averaged, before and after oxidation tests to determine the associated weight changes. A scanning electron microscope (SEM) and energy dispersive X-ray spectrometer (EDS) were used to analyze sample surfaces and to determine elemental compositions. The equipment used is shown in Figure 0-5.

(a)

(b)

Figure 0-5 Equipment used for oxidation experiments of substrate alloys (a) SNOL 6,7/1300 high temperature box furnace, and (b) VegaII-XMU SEM [94].

3.2.3 Oxidation experiments of TBC systems

For the samples coated with SPS TBCs, both isothermal and cyclic oxidation tests were conducted. For isothermal tests, holding times were 400 h, 800 h, and 1300 h. The isothermal oxidation test was conducted at 1080°C using a SNOL 6,7/1300 high temperature box furnace. After the predetermined durations, the furnace was stopped, and the TBC samples were left in the furnace and cooled at rate of 4°C/min. For cyclic oxidation, the cycle consisted of a 10 min. ramp to 1080°C, 30 min. soak and 20 min. air cooling period. The heating and cooling rate was ~50°C/min. Samples were removed and examined following 400, 800 and 1300 cycles. The cyclic oxidation test was conducted in air using a CM furnace (Rapid Temp Furnace supplied by Bloom Field, N. J., USA in Figure 0-6).

After 800 cycles, the TBC samples had more than 30% of surface showing delamination at the interface between TC and BC; however, the cyclic test continued until 1300 cycles in order to compare the sintering performance under isothermal and cyclic

conditions of the same durations. It should be noted that, the TBC samples did not fail after 1300 h under the isothermal condition. One sample after each thermal exposure period was examined. Surface analyses were conducted first on samples, and then cross-sectional analyses were conducted. The microstructural analyses were conducted using SEM equipped with EDS.

Figure 0-6 CM Rapid Temp Furnace for cyclic oxidation tests [94].

3.3 TBC microstructural characterization and mechanical property assessment

3.3.1 TBC microstructural characterization

Several TBC parameters were determined during SEM examination: i) the vertical crack densities of as-received and tested samples; ii) TGO thickness and roughness; and iii) crack sizes within TC at the interface between TC/TGO after isothermal tests.

To characterize the vertical crack density, cross-sections of samples before and after isothermal and cyclic tests were scanned from end to end at 200 $\times$ magnification (> 10

frames for each sample). The number of vertical cracks were counted and divided by the scanning distance to obtain the density.

For TGO thickness measurement and crack sizes determination, only isothermally exposed samples were examined in SEM at 1000× magnification. Each sample had approximately 60-70 images in total were captured in order to measure the length of submicron cracks. Shown in Figure 0-7 (a), all cracks near the interface between TC and BC, within the TC, in every frame were measured by ImageJ from tip to tip as a straight line. The TGO was divided into two regions: uniformly dark oxide Al_2O_3 , and uneven, grey colored spinel ($\text{Cr}_2\text{O}_3 \cdot \text{Ni}(\text{Cr}, \text{Al})_2\text{O}_4 \cdot \text{NiO} \cdot \text{Co}_3\text{O}_4$) [92]. In order to determine the thickness of these two layers, SEM images were post-processed by Photoshop to render Al_2O_3 in black, spinel in grey, and the rest in white (Figure 0-7 (b)). Then the processed images were imported into OpenCV to measure the area of black and grey sections, as well as the length at the interface of the two layers. The thickness h is then calculated by Equation 4.1.

$$h = \frac{\sum \text{cross sectional TGO area}}{\sum \text{cross sectional length of TC/TGO interface}} \quad (4.1)$$

Figure 0-7 Schematics of the sample after 400 h of thermal exposure. (a) crack size measurement and (b) TGO thickness measurement.

Since the TGO roughness influences the stress distribution and fracture behaviors of the TC [95, 96]; hence, it is necessary to determine the roughness parameters. Based on the ISO standard [97, 98, 99], exterior surface roughness is measured using a profilometer.

After the profile acquisition, the measured data is post-processed with high-pass and low-pass Gaussian filters based on wavelengths. The controlled cut-off wavelengths are $\lambda_f > \lambda_c > \lambda_s$. For this study, roughness profile (R-profile) is set to be within the range of $\lambda_c > \lambda_s$. λ_c cut-off wavelength is related to the waviness wavelength of the studied specimen. Setting λ_c is to make the R-profile capture mainly the interface characteristics. λ_s cut-off wavelength is usually set to a value related to the dimension of the stylus tip. Since a physical stylus tip cannot be applied onto the surface of the TGO due to the presence of TC, image analysis of cross sections is utilized instead. The process is illustrated in Figure 0-8. The microstructural images of the TGO are converted to binary images to render the TC as a black zone and the rest of the parts as a white zone. Then a semicircular stylus with 5 μm in radius is simulated by OpenCV to assess the interface. After profile acquisition, R-profile is obtained by Gaussian filtering and establishes the mean line of R-profile (where $\lambda_s = 10 \mu\text{m}$, $\lambda_c = 800 \mu\text{m}$ [96]). However, the roughness calculations for samples after isothermal and cyclic tests are different. For samples after isothermal tests, the TGO roughness did not change as much as the samples after cyclic tests. The roughness of the TGO can be considered as semi-circular cycles as shown in Figure 0-25 (a), so the arithmetic mean value of the absolute z-coordinates Ra is calculated as:

$$Ra = \frac{1}{L} \int_0^L |z(x)| dx \quad (4.2)$$

where L is the length of the mean line, $z(x)$ is the value on vertical axis as illustrated in Figure 0-8. Let the radius of imperfections R be equal to the average of Ra for the CND model, which will be discussed in details in Chapter 8. For samples after cyclic tests, the change of waviness of TGO during each cycle influences stress distributions within TCs,

so the parameter should be more accurate. The shape of TGO is usually simplified as periodic array of wavy-type segments featured by cosine interface in FE model [100], so peaks and valleys were marked in the acquired R-profile as seen in Figure 0-8, to obtain the amplitude (b) and wavelength (a).

Figure 0-8 Schematics of roughness parameter determination.

3.3.2 Mechanical properties tests

Elastic modulus (E) and hardness (H) of TCs were determined by a nanoindentation tester (NHI) [101]. The principle is based upon the depth-sensing indentation technique. A load of 100 mN was applied at a 200 mN/min loading and unloading rate, with a holding time of 15 seconds. A curve of the indentation load versus the corresponding penetration depth of the indenter is then generated for each loading/unloading cycle. Assuming that unloading is fully elastic, the reduced elastic modulus E_r is evaluated from the unloading curve by:

$$E_r = \frac{\pi^{1/2}}{2} \cdot \frac{S}{a^{1/2}} \quad (4.3)$$

where S is the stiffness at the maximum loading point, a is the contact area. Then the elastic modulus E can be calculated by:

$$\frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_s^2}{E} \quad (4.4)$$

where ν_i and ν_s are the Poisson ratios of the indenter and specimen, E and E_i are the elastic modulus of the specimen and indenter. Ten indentations were made on the lateral regions far away from VCs to avoid direct crack influence. The effective elastic modulus (E^*) of tested material was calculated by:

$$E^* = \frac{E}{1 - \nu^2} \quad (4.5)$$

where $\nu = 0.3$ is the assumed Poisson's ratio.

To measure the fracture toughness (K_{IC}), a Vickers hardness tester (CLEMEX) was used. Generally, when the localized in-plane stress intensity approaches its fracture toughness (K_{IC}), a crack starts to nucleate. Here, a load of 1000 gf was applied to generate cracks at four tips as shown in Figure 0-9, and K_{IC} was estimated by the following equation [102]:

$$K_{IC} = 0.046(EH)^{1/2} \frac{\left(\frac{d}{2}\right)^2}{c^{3/2}} \quad (4.6)$$

where $c = (c_1 + c_2)/2$ represents average length of the tip cracks; H is the hardness of the TC; $d = (d_1 + d_2)/2$ is the average value of the two diagonal lengths of the residual indentation. In this study, K_{IC} of SPS TCs under isothermal conditions is evaluated.

Figure 0-9 Schematic diagram of Vickers indentation on the lateral region.

3.3.3 XRD

X-ray diffraction (XRD) was carried out using a Bruker AXS D8 Discover diffractometer, controlled with Bragg-Brentano configuration and Cu K_α radiation produced at 35 kV and 40 mA (Figure 0-10). The samples were scanned from 25-80° (of 2θ angle) with a step size of 0.02°/step and a count time of 1 s per step. In this study, XRD was used to identify the phase compositions after each duration as well as the residual strains within crystals. Following Bragg's law, d -spacing was calculated for every test condition [103] by Equation 4.6:

$$d = \frac{n\lambda}{2\sin\theta} \quad (4.7)$$

where $\lambda = 1.5406 \text{ \AA}$, the wavelength of the incident x-ray beam; n is a positive integer. The residual strain is calculated by $\frac{d-d_0}{d_0}$, where d_0 is the spacing in untested condition and d is the spacing after thermal tests. Generally, a uniform lattice strain applied to a grain will lead to the XRD patterns to shift to left (in tension) or right (in compression), while a nonuniform lattice strain such as bending will lead to the XRD patterns broadening [104].

Different phases of zirconia were determined by the XRD patterns. In addition, the yttria content in the tetragonal phase, in particular, was calculated using Equation 4.6 [105], where c and a are the unit cell dimensions expressed in Å.

$$\text{YO}_{1.5} \text{ (mol\%)} = \frac{1.0225 - c/\sqrt{2}a}{0.0016} \quad (4.8)$$

Figure 0-10 Bruker AXS D8 Discover diffractometer for XRD [94].

3.3.4 Thermography

The damage fractions of the cyclic samples were determined by thermography. The pulsed thermography (PT) experiments were carried out using an Echotherm system, which is a commercial PT system designed by Thermal Wave Imaging. The system is powered by 2 x 2400J capacitor, for a total power of 4800J. The surface temperature of the specimen was monitored by a Flir ThermaCam SC 3000 infrared (IR) camera, that is sensitive to long wavelengths (8–12 μm). The acquisitions of thermal images were carried out at 60 Hz.

4 Chapter: Oxidation Behavior of Bare Alloys

4.1 Visual and weight changes of alloys

In order to select a more suitable substrate of the TBC system for this study, HAYNES 233 and INCONEL 625 were first investigated to determine their oxidation behavior under isothermal conditions only. Figure 0-1 summarizes the visually observed changes of the two alloys after various durations of up to 300 h at 1080°C. All samples lost their original metallic shine after exposure, turning dark due to oxide formation. HAYNES 233 showed partial oxidation after 10 h of thermal exposure, and then a dark green oxide gradually formed over a larger surface area. However, the oxide failed to cover the entire sample due to oxide partial spallation after the oxide formation. INCONEL 625 generated a dark grey oxide layer in general. After 200 h of thermal exposure, the oxide layer uniformly covered the whole surface area. However, the oxide layer debonded after 300 h, as metallic substrate was subsequently observable.

(b)
Figure 0-1 Visual inspections of (a) HAYNES 233, and (b) INCONEL after isothermal tests.

Figure 0-2 compares the weight change per unit surface area of HAYNES 233 and INCONEL 625 after isothermal exposure, and the results are consistent with the visual observations. As shown in the figure, the HAYNES 233 exhibits weight loss from the early stage of testing. The weight reduced quite significantly in the first 50 h, yielding a weight loss per unit area up to -1.1869 mg/cm^2 ; subsequently, weight loss returned to -0.1904 mg/cm^2 after 300 h. It is believed that greater metal loss occurred in the first 50 h before a protective oxide layer formed, and then the weight gradually increased as more oxides began to form on the surface. INCONEL 625, on the other hand, shows positive weight gain in all the intervals. The weight gain reached the highest value after 200 h and then a decrease in weight gain to 0.3766 mg/cm^2 after 300 h of exposure, based on the observation of Figure 0-2. As revealed by visual inspection, the oxide layer separation at 300 h contributes to the weight gain reduction between 200 h to 300 h.

Figure 0-2 Weight change of HAYNES 233 and INCONEL 625 after isothermal oxidation tests.

4.2 Microstructural analyses

The SEM images in Figure 0-3 show that oxide layers formed on HAYNES 233 after 10 h to 300 h of exposure at 1080°C. Based upon the surface observation results, the top surface layers were porous and uneven from the first 10 h of exposure. In addition, the alloy shows evidence of spallation at an early onset as well, which explains the reason for the observed weight loss. Furthermore, HAYNES 233 formed flat oxides with pitting (location 1), spheroid oxides (location 2) and oxides located beneath the spheroid oxides (location 3) after 10 h of thermal exposure, as shown in Figure 0-3 (a). Based upon the chemical compositions summarized in Table 0-1, locations 1 and 2 are enriched in Cr, indicating the formation of chromia. Location 3 has similar concentrations of Cr, Co, and Ni, an indication of a mixed spinel $\text{Cr}_2\text{O}_3 \cdot \text{NiCr}_2\text{O}_4 \cdot \text{NiO} \cdot \text{Co}_3\text{O}_4$. After 30 h (Figure 0-3 (b)), the sample was covered by blackish oxides (location 4) and grey oxides (location 5). Both oxides exhibit more Al content than the oxides observed after 10 h. This suggests that Al

gradually diffused outward to the surface forming alumina partially. In fact, the content of Al detected is not sufficient to form exclusive, protective Al_2O_3 . After 50 h (Figure 0-3 (c)), the porous oxide (location 6) exhibits a similar spinel composition again. HAYNES 233 formed similar surface oxides during 100 h to 300 h (Figure 0-3 (d) to (f)): porous oxides (location 7, 9, and 11) partially spalled off at location 8 and 10 to reveal relatively denser, inner oxides near the substrate. Both inner oxides have higher Al content (respectively 28.1 wt.% and 15.7 wt.%) than the outer oxides (respectively 9.4 wt.% and 3.0 wt.% of Al), indicating the likelihood of Al_2O_3 formation near the substrate. This will further be elaborated in the cross-sectional analyses.

Figure 0-3 Surface microstructure of HAYNES 233 after (a) 10 h, (b) 30 h, (c) 50 h, (d) 100 h, (e) 200 h, and (f) 300 h of isothermal conditions.

Table 0-1 Chemical compositions on various locations of HAYNES 233 under isothermal conditions.

Duration	Location	Chemical compositions (wt.%)								
		Al	Cr	Co	Ni	Ti	Si	Mn	Mo	O
10 h	1	0.5	45.8	10.4	12.7	2.1	0.7	----	----	27.8
	2	----	52.9	2.9	4.2	3.9	----	4.1	----	32.0
	3	----	21.3	20.6	29.2	0.6	----	1.7	----	26.6
30 h	4	13.3	20.1	7.7	21.4	----	0.4	----	1.4	35.7
	5	6.2	11.8	7.3	25.9	----	----	----	15.0	33.8
50 h	6	2.2	36.9	12.6	16.9	1.0	----	----	----	30.4
100 h	7	9.4	14.4	7.3	37.3	0.5	0.8	----	----	30.3
	8	28.1	8.5	4.3	21.0	----	----	----	----	38.1
200 h	9	3.0	36.8	11.8	17.2	0.8	0.6	----	----	29.8
	10	15.7	20.2	8.5	22.1	----	----	----	----	33.5
300 h	11	2.8	36.7	11.8	15.4	0.7	----	0.9	----	31.7

The surface microstructure of INCONEL 625 and compositions are summarized in Figure 0-4 and Table 0-2. In the first 100 h, as shown in Figure 0-4 (a) INCONEL 625 is covered by a flat and dense oxide (location 12) as well as a porous oxide (location 13). With further exposure, then porous oxides became denser (location 14) and covered the whole surface after 200 h (Figure 0-4 (b)). At the end of the test (Figure 0-4 (c)), oxides spalled off partially, as highlighted in yellow enclosure, representing top oxides (location 16) and bottom oxides (location 15). During the 300 h of thermal exposure, the chemical compositions at all locations have more than 60 wt.% Cr (Table 0-2); Cr₂O₃ is believed to be primary phase present under this condition.

Figure 0-4 Surface microstructure of INCONEL 625 after (a) 100 h, (b) 200 h, and (c) 300 h isothermal oxidation tests.

Table 0-2 Chemical compositions of various locations on the surface of INCONEL 625 after isothermal oxidation tests.

Duration	Location	Chemical compositions (wt.%)			
		Cr	Ni	Ti	O
100 h	12	63.9	0.8	0.7	34.6
	13	68.3	1.1	0.5	30.1
200 h	14	64.2	0.3	0.8	34.7
300 h	15	62.7	----	0.4	36.9
	16	62.3	0.6	----	37.1

SEM images from the cross sections of HAYNES 233 are shown in Figure 0-5, and the chemical compositions at various locations are shown in Table 0-3. From these images, a dense dark oxide layer can be seen to have formed after 10 h, and then a subsequent grey oxide layer formed on top. According to the chemical compositions, the internal dark oxide layers CX-1, CX-3, CX-10, and CX-12 have significant amount of Al (> 30 wt.%), as such they are assumed to be Al_2O_3 . Although alumina started to form after 10 h with thickness of about 1 μm , as shown in Figure 0-5 (a), it is only found in a small localized region. Combined with the visual investigation results shown in Figure 0-1 (a), Al_2O_3 did not seem to have covered the whole surface in the first 10 h. With continued exposure, an external grey oxide layer formed after 30 h, to bring the total oxide layer thickness to around 7 μm . Compared to the chemical composition results of the external oxide CX-2 and the internal oxide CX-3, CX-2 has less Al but more Cr and Ni. This indicates that Cr and Ni diffused

outward through Al_2O_3 , and reacted with oxygen to form Cr, Ni, Al-enriched oxides. In addition, there is an internal oxidation zone with an observed maximum depth of 6 μm . After 50 h, the external oxide layer thickened, and the external CX-4 layer has more Cr (38.6 wt.%) and Co (13.8 wt.%) but less Al (3.3 wt.%) than these at CX-2. It suggests that more spinel forms on CX-4. The internal oxide, CX-5, contains only 18.9 wt.% Al, suggesting the oxide may not be Al_2O_3 inclusively. Figure 0-5 (c) shows that a grey oxide mixed within the internal oxide layer containing 32.5 wt.% Ni, indicates the onset of Al depletion after 50 h. Meanwhile, the Al content of the internal layer reached 44 wt.% (CX-12) from 100 h to 300 h. At 200 h, the external oxide layer became increasingly porous (CX-8) and partially peeled off. Meanwhile, the internal oxide formed pegs at the interface between the internal oxide layer and the substrate. At 300 h, the oxidation can be seen to have attacked deeper into the substrate, as shown in the SEM image Figure 0-5 (f). Although a clean and dense Al_2O_3 is found at the location represented by CX-12, the protective oxide could not effectively impede oxygen diffusing inward. The total thickness of oxides fluctuated from 50 h to 300 h, indicating the simultaneous oxide spallation and reformation.

Figure 0-5 Cross-sectional microstructure of HAYNES 233 after (a) 10 h, (b) 30 h, (c) 50 h, (d) 100 h, (e) 200 h, and (f) 300 h of isothermal oxidation tests.

Table 0-3 Chemical compositions on various locations of HAYNES 233 after isothermal oxidation tests.

Duration	Location	Chemical compositions (wt.%)						
		Al	Cr	Co	Ni	Mo	Si	O
10 h	CX-1	32.7	11.0	8.4	19.4	----	----	28.5
30 h	CX-2	29.4	8.6	5.0	24.5	6.4	----	26.1
	CX-3	43.4	5.3	5.2	11.9	----	----	34.2
50 h	CX-4	3.3	38.6	13.8	20.2	----	1.7	22.4
	CX-5	18.9	15.1	9.3	32.5	----	1.0	23.3
100 h	CX-6	9.8	17.1	10.5	20.4	2.4	2.0	37.8
	CX-7	22.9	7.4	7.9	22.5	----	0.6	37.8
200 h	CX-8	1.7	42.1	13.0	21.3	----	0.8	21.1
	CX-9	22.8	15.1	7.1	25.9	----	0.5	28.6
	CX-10	33.1	10.2	7.0	26.4	----	----	23.3
300 h	CX-11	22.4	10.0	5.9	29.5	----	1.2	31.0
	CX-12	44.0	4.5	3.5	11.4	----	----	36.6

The SEM images in Figure 0-6 reveal that the oxide layer on INCONEL 625 increased its thickness from 4 μm to 17 μm between 100 h and 300 h. The outermost oxide CX-15 became porous and peeled off after 300 h. According to Table 0-4, the chemical compositions of the oxides located at CX-13, CX-14, CX-15 and CX-16 are consistent of chromia in nature as time progresses. In addition, the internal oxidation along the grain boundaries can be seen to occur after 100 h of thermal exposure, with subsequent internal oxidation resulting in the formation of voids in the substrates.

Figure 0-6 Cross-sectional microstructure of INCONEL 625 after (a) 100 h, (b) 200 h, and (c) 300 h isothermal oxidation tests.

Table 0-4 Chemical compositions of various locations on INCONEL 625 after isothermal oxidation tests.

Duration	Location	Chemical compositions (wt.%)					
		Cr	Si	Nb	Ni	Ti	O
100 h	CX-13	60.1	0.4	----	13.5	----	26.0
200 h	CX-14	65.5	0.4	----	7.3	----	26.8
300 h	CX-15	62.2	0.5	----	6.2	0.5	30.6
	CX-16	53.6	----	3.0	8.3	0.7	34.4

4.3 Comparison of oxidation behaviors between the two alloys

In this screening test, HAYNES 233 and INCONEL 625 were evaluated at 1080°C for up to 300 h. Based upon the weight changes (Figure 0-2), HAYNES 233 lost significant

weight within the first 50 h, and then partially regained weight thereafter. However, the total weight change remained negative for the test duration. INCONEL 625, on the other hand, exhibited weight gain at all times, except for a partial weight decrease from 200 h to 300 h of exposure. Weight loss was a result of the initially formed oxide spallation, while weight gain was a manifestation of oxide formation. The weight gain did not explicitly mean that no spallation had occurred, rather the oxide formation rate was faster than the spallation rate. The results from the visual observation were consistent with the weight changes, i.e., no uniform oxide covered the HAYNES 233 samples at all times; whereas, INCONEL 625 successfully formed a uniform oxide layer at 200 h, with evidence of localized oxide separation set in at 300 h (Figure 0-1).

SEM microstructural analyses also indicated that HAYNES 233 suffered from early oxide spallation (Figure 0-4). Combining surface and cross-sectional investigation results, HAYNES 233 was believed to form an internal dense oxide Al_2O_3 layer, and an external porous mixed oxide or spinel layer enriched in Ni, Cr, Co. The external layer became increasingly porous with the prolonged exposure and spalled progressively while new oxide being reformed during the thermal exposure. Both surface (Figure 0-4) and cross-sectional (Figure 0-5) microstructures illustrated bright particles omnipresent on external oxide layers in 300 h. Further SEM analysis was conducted at higher magnification of the sample with 200 h of thermal exposure. As shown in Figure 0-7 and Table 0-5, these particles contain 4.5 wt.% Ta. Although the measured concentration of Ta is low, the value is highly influenced by the surrounding compositions as the size of these particles is too small to quantify precisely. Furthermore, 4.5 wt.% exceeds the nominal Ta concentration (0.5 wt.% in Table 0-1), thus indicates that these particles are indeed enriched in Ta. Ta, in

form of presumably Ta_2O_5 [106], is believed to contribute to the weakening of oxide bonding and the early onset of spallation as large growth stress has been observed during oxidation of Ta [107]. Also, the main oxidation product Ta_2O_5 initially formed in an adherent scale, but eventually detached [106]. This explains why the top oxide layer spalled on such a large scale, as Ta_2O_5 precipitated on most of the surface and resulted in detachment of the top oxide. Many pores with the similar size to these bright particles were also found in Figure 0-7, suggesting that the detachment of Ta_2O_5 particles during spallation left behind the craters where the particles were situated, causing an increased fraction of surface porosity.

Figure 0-7 Microstructure of HAYNES 233 after 200 h exposure.

Table 0-5 Chemical composition of bright particles.

Cr	Co	Ni	Mo	Ta	Ti	Al	Si	O
31.0	14.8	11.7	0.2	4.5	1.2	3.1	0.6	32.9

In general, Al_2O_3 is a desirable constituent because its dense structure inhibits oxygen penetration, thus reducing the rate of oxidation [108]. However, the observed Al_2O_3 did not cover the entire surface required to protect the substrate. In addition, the alumina did not prohibit oxygen penetrating into the substrate, and other metallic elements such as

Cr, Co, and Ni diffused outward through the alumina to form external oxide layers. Park S. J. et al [74] found that additions of Si, and Cr were beneficial to the formation of dense and adherent Al_2O_3 , on the other hand, minor elements such as W, Ta, Nb, Ru, Ti and Mo inhibited the formation of Al_2O_3 in Ni-based alloys. When the elements such as W, Ta and Ti were incorporated in the formation of Al_2O_3 , Al_2O_3 became discontinuous [74]. In this study, Mo was detected within the oxide after 30 h thermal exposure (Table 0-1 and Table 0-3), and Ta-particles were observed to disperse everywhere on the surface. As a result, for this alloy under the investigated conditions, Al_2O_3 did not protect the substrate well.

INCONEL 625, on the other hand, formed pure Cr_2O_3 and the thickness of Cr_2O_3 increased steadily during the isothermal oxidation test. Although INCONEL 625 also contained minor elements, such as Ta, Mo, Ti, and Nb, these elements did not deteriorate the stability of the scale at the temperature used in this study, unlike what was observed for HAYNES 233. One reason might be that the Cr concentration (20 wt.%) in the alloy is sufficiently high to form a more exclusive chromia, reducing the influences from these minor elements. However, some voids formed within the substrate near the interface between the oxide layer and the substrate after 200 h thermal exposure. These voids may be resulted from Ti diffusion from the substrate to the oxide scale, as 0.5 - 0.7 wt.% Ti was detected within the scale after 300 h of thermal exposure (CX-15 and CX-16 in Table 0-4) but it was not found in the scale in the first 200 h. Ti outward diffusion created voids within the substrate, rendering the interfacial area with increasing oxygen activity due to voids, thus oxidation growth rate was believed to accelerate based on the literature [109]. In addition, observing the chemical composition at CX-16 in Table 0-4, it was seen that Nb was present at the interface of the oxide layer and the substrate after 300 h thermal

exposure. This phenomenon is consistent with the finding in the ref. [110], where INCONEL 625 was tested at 1000°C in air for 240 h. A Cr depletion zone was formed beneath chromia due to chromia formation. This Cr depletion zone changed the thermodynamic stability of the phases and was enriched in Nb. As a result, Nb started to diffuse outward towards the surface oxide.

4.4 Summary of the comparison between the substrate alloys

Combining the results of visual observation, weight change, and microstructural analyses, INCONEL 625 performed better than HAYNES 233 at 1080°C due to the formation of a protective Cr_2O_3 layer covering the entire surface region. On the other hand, HAYNES 233 failed to form a uniform oxide layer on the entire sample surface, and a continues weight loss was manifested. In light of these observations, INCONEL 625 was selected as the substrate for the TBC system for further study.

5 Chapter: Sintering Behavior of SPS 7YSZ TBCs under Isothermal and Cyclic Conditions

Sintering of YSZ with exposure to high temperatures can lead to densification, cracking, and phase transformation. Subsequently, elastic modulus, and hardness change with time, and accelerate the failure of the TBC coatings. The sintering performance of APS and EB-PBD deposited TCs have been well documented [111, 112], but there is limited information on how VC-structured TCs sinter under high temperature. In this chapter, the effects of thermal exposure on sintering, mechanical properties, phase transformations, and microstructures of VC-structured SPS TCs are reported. Both isothermal and cyclic thermal conditions are considered, after 400 h/cycles, 800 h/cycles, and 1300 h/cycles.

No evidence of failure was observed for SPS TCs after isothermal oxidation tests. As shown in Figure 0-1 (a), the appearances of tested TBCs under isothermal conditions did not show significant changes with exposure time. On the other hand, the SPS TBCs turned darker gradually during cyclic oxidation, as shown in Figure 0-1 (b). The SPS TCs failed at 800 cycles, judged by more than 30% of the TC debonded. The implicated region was determined by the pulsed thermography and the result is presented in Figure 0-1 (c). The yellow part stands for the spalled area. Although the appearance of the coating after 800 cycle did not show significant visual evidence of debonding or cracking in Figure 5-1 (b), the SPS TC had actually debonded from the substrate when using the 30% surface area criteria based on PT observation in Figure 5-1 (c).

Figure 0-1 Visual changes of SPS TBCs after (a) isothermal tests, (b) cyclic tests, and (c) damage fractions of SPS TBCs after cyclic tests.

5.1 Microstructure evolution of TCs

Surface microstructure of SPS 7YSZ after isothermal and cyclic oxidation tests for different durations/cycles is summarized in Figure 0-2. Comparing the samples after either isothermal or cyclic tests, the cyclic tested samples feature a smaller cluster size with a greater number of subcracks in each cluster. After 1300 cycles, some of the micro-cracks within the clusters healed, as seen in Figure 0-2 (f). These micro-cracks are characterized by a typical mud-cracking pattern at the surface as arrowed in Figure 0-2 (a), so these cracks are named as mud-cracks. To quantify how these changes occurred during exposure, VC density was calculated from the cross-sectional images since mud-cracks start at the surface and penetrate through the thickness in the form of VCs. The method of the VC

density measurement has been introduced in Section 3.3.1. The VC density in fact increased with time, from 7.14 /mm to 9.44 /mm under isothermal conditions from 400 h to 1300 h. The VC density increased to 9.49 /mm after 800 cycles, but decreased to 8.48 /mm after 1300 cycles, as shown in Figure 0-3.

Figure 0-2 Surface microstructure of isothermally tested samples after isothermal and cyclic oxidation tests.

Figure 0-3 Vertical cracks density of TCs after isothermal and cyclic oxidation tests.

The sintering effect on the porosity of TCs was also investigated by SEM at higher magnifications, with images shown in Figure 0-4. After isothermal tests, the size of micropores gradually decreased, and the elongated pores turned into spherical shape. When comparing the cyclic and isothermal samples, it is apparent that the porosities of samples after cyclic tests decreased much faster than after isothermal tests; the total exposure time

at the peak temperature was only 50% of that under isothermal conditions, indicating faster sintering rate under cyclic thermal conditions. There is no significant difference between samples after 400 cycles and 800 cycles, but the sample after 1300 cycles exhibited pore coarsening. As reported in ref. [113], both surface and grain boundary diffusion were activated at 1100°C in plasma sprayed 7YSZ, resulting in reduction of intralamellar cracks and interlamellar pores. In addition, grain boundary diffusion can also lead to pores coarsening due to the volume change [14].

Figure 0-4 Porosities in the untested and tested coatings.

5.2 Micro-strains within TCs

The XRD diffraction patterns of isothermal and cyclic conditions tested samples are summarized in Figure 0-5. Under isothermal conditions, there is no obvious peak shifting after 400 h and 800 h; however, after 1300 h, all peaks shifted to higher angles, approximately 0.6° . Under cycling conditions, however, all peaks shifted to higher angle by 0.5° , after 400 cycles and then gradually returned to the initial position as shown in Figure 5-5. The movement of peaks may be attributed by phase transformation, however, a constant $\Delta 2\theta$ shift of all peaks reflected the change of the d -spacing of the hkl plane at all 2θ , hence the existence of uniform external stresses [114]. In this study, the stress generated within the TCs was considered as a thermal misfit stress due to the difference between the CTEs of the TBC and the bond coat/substrate. On heating, the TBC experienced a general in-plane tensile stress from the substrate as the substrate expanded faster than the ceramic TBC. With the increased duration, the tensile stress can be relaxed by creep. During cooling, on the other hand, the TBC experienced a generally compressive stress. However, it should be noted that stress states at the interface of the BC and TC can be affected by the local surface roughness.

The peak for $\{1\ 0\ 1\}_t$, near 30.2° , was chosen in this research to calculate the lattice deformation because it is the peak with the highest intensity (Figure 0-6). By using this stronger intensity peak, the background noises interference generated by amorphous impurities and background radiation was limited. As shown in Table 0-1, the lattice experienced -1.76% strain after 1300 h of isothermal oxidation test, indicating a residual compressive stress generated during cooling. Under the cyclic condition, the lattice was

subjected to -1.42% strain after 400 cycles, similar to the value after the 1300 h isothermal condition. The nature of the cyclic condition contributed to a high compressive thermal stress during cooling [115]. The diffraction peaks shifted back for the 800 cycles sample, indicating that the delamination started, releasing the residual stress.

Figure 0-5 XRD results for TBCs after (a) isothermal, and (b) cyclic oxidation tests.

Figure 0-6 XRD patterns of YSZ with 2θ between 29.6° - 31° after (a) isothermal, and (b) cyclic tests.

Table 0-1 XRD and strain information for YSZ after thermal exposure.

		Isothermal (h)	
	untested	400	800
$2\theta (^{\circ})$	30.1681	30.1894	30.1381
d -spacing (nm)	0.2959	0.2957	0.2962
strain (%)	----	≈ 0	0.097
		Cyclic (cycles)	
	400	800	1300
$2\theta (^{\circ})$	30.6148	30.4446	30.1681
d -spacing (nm)	0.2917	0.2933	0.2959
strain (%)	-1.42	-0.89	≈ 0

5.3 Phase transformations

As shown in Figure 0-11, ZrO_2 can assume tetragonal (t), cubic (c), and monoclinic (m) structure, as determined by the concentration of Y_2O_3 , the cooling rate and the temperature [47]. According to the binary pseudo-phase diagram, 7YSZ assumes $t + c$ phase at 1080°C and may transfer to $m + c$ during cooling. However, this phase diagram only shows transformations under equilibrium state; in fact, rapid cooling rate often leads to the formation of the metastable twinned tetragonal phase (t') [48].

As shown in Figure 0-5, the XRD pattern of as-deposited coating exhibited pure t' -YSZ phase. Under all testing conditions, phases of $t'/t/c$ were detected by XRD. With respect to m phase, it is present after 1300 h of isothermal holding at 1080°C , and after 800

cycles, the m phase could not be detected after 1300 cycles. Most diffraction peaks representing $t'/t/c$ phases overlap due to the similar crystallographic parameters, however, they can be differentiated using $\{2\ 2\ 0\}_{t,t'}$, $\{2\ 2\ 0\}_c$ and $\{0\ 0\ 4\}_{t,t'}$ in the 2θ range of 72° - 76° (Figure 0-7) [116]. The two peaks of t phase overlapped, but the gap between $\{2\ 2\ 0\}_t$ and $\{0\ 0\ 4\}_t$ is wider than the corresponding peaks of t' phase. A new peak between $\{2\ 2\ 0\}_{t,t'}$ and $\{0\ 0\ 4\}_{t,t'}$ represents the formation of c -YSZ phase. After 400 h and 800 h isothermal exposure, a small amount of phase transformation, from t' to t , has occurred, as $\{0\ 0\ 4\}$ shifted to left for 0.1° (Figure 0-7 (a)). After 1300 h, peaks for $\{2\ 2\ 0\}$ and $\{0\ 0\ 4\}$ representing t/t' phases widened, indicating more t' to t phase transformation. In addition, there are no observable patterns presenting $\{2\ 2\ 0\}_c$ in all isothermally tested samples, however, m -YSZ is detected after 1300 h. For cyclic tested samples, peaks at $\{2\ 2\ 0\}_{t,t'}$ and $\{0\ 0\ 4\}_{t,t'}$ have split into two after 800 cycles (Figure 0-7 (b)), indicating the formation of t -YSZ phase. There is a small peak of c -YSZ formed after 1300 cycles.

Figure 0-7 XRD patterns of YSZ with 2θ between 72° - 76° after (a) isothermal, and (b) cyclic tests.

5.4 Mechanical properties

The changes of hardness and effective elastic modulus of SPS TCs as a function of time were evaluated by nanoindentation method and the results are summarized in Figure 0-8

and Figure 0-9. It should be noted, E in Figure 0-8 is the tested elastic modulus by nanoindentation, but the E^* in Figure 0-9 represents the effective modulus after calculation by Equation 4.3, hence the values are different in the two figures. There is an apparent trend in mechanical property changes for samples tested under both conditions. Under isothermal condition, E^* and H increase from 146.2 GPa / 10.4 GPa in the ‘as received’ condition to 181 GPa / 12.7 GPa after 800 h, before reaching 248.9 GPa/17.6 GPa after 1300 h; this indicates an accelerated rate between 800 h and 1300 h. For cyclic tested samples, E^* and H vary with the number of cycles. Both values increase initially to 208.2 GPa/15.7 GPa after 400 cycles, then decrease to 184.7 GPa/13.6 GPa after 800 cycles; this is followed by another increase to 262.8 GPa/17.6 GPa between 800 to 1300 cycles. The increase in E^* and H values is a result of sintering, including improved bonding between the splats, pore reduction and the healing of micro-cracks [117, 14]. On the other hand, the decrease of E^* and H could be induced by the formation and propagation of macro-cracks induced by the thermal stress [117, 80]. Comparing the samples after experiencing isothermal and cyclic oxidation tests, it is obvious that thermal cycling has accelerated the sintering rate.

Figure 0-8 Measured elastic modulus by nanoindentation after (a) isothermal, and (b) cyclic tests.

Figure 0-9 Mechanical properties of SPS YSZ after isothermal and cyclic tests, (a) effective elastic modulus, and (b) hardness.

5.5 Discussion

5.5.1 SPS TC sintering behavior under isothermal and cyclic conditions

The SPS 7YSZ TCs have been observed to form more VCs in the form of mud-cracks at surface, and with wider crack gaps after thermal tests, as shown in Figure 0-2. When a 7YSZ TC is exposed to a high temperature environment, the sintering leads to lateral shrinkage. The shrinkage induces extra in-plane tensile stress in TC while being constrained by the substrate [11, 118]. When the stress reaches a critical sintering stress value σ_s , shrinkage slows down and the stress generates a new VC throughout the thickness of the TC [11]. In addition, as seen in Figure 0-10, as ceramic based 7YSZ TC has a much lower CTE (α) than that of INCONEL 625 metal substrate and BC, the distances between the averaged center of VCs (L) are bound by the expansion of the substrate because the substrate is much thicker than the coating. The individual ceramic columns (R) expands less than the distance L at high temperature as such the average width of individual VC becomes wider. Similar observations were reported with respect to EB-PVD TCs with

columnar structure [12]. The volume shrinkage induced by the sintering process leads to VCs opening.

Figure 0-10 Schematics of VC widening.

Furthermore, concerning the porosities of SPS TCs after isothermal and cyclic conditions (Figure 0-4), samples under cyclic thermal condition show apparently faster densification than ones under isothermal conditions. As a result, more and wider VCs under cyclic conditions are generated due to more volume shrinkage (as density increases) and higher in-plan stresses.

The sintering process is considered as a diffusion process along the interfaces. The interfacial diffusivity D is temperature dependent, as shown in Equation 6.1 [119]:

$$D = \frac{\delta\Omega}{kT} D_0 \exp(-q/kT) \quad (6.1)$$

where D_0 is a reference diffusivity; Ω is the atomic volume; δ is the interface thickness; q is the thermal activation energy; T is the temperature in K; and k is a Boltzmann's constant. Based upon Equation 6.1, SPS TCs under isothermal conditions should have higher extent of diffusion, because the samples experienced static thermal dwell at 1080°C under isothermal conditions, while cyclic thermal exposure took place between 80°C and 1080°C, with only half of the durations at high temperature.

Sintering processes consist of two outcomes: densification and grain growth. Fundamentally, these two processes coexist due to the same driving force and mass transport mechanisms [120], but a difference lies in the diffusion paths of the two processes. Surface diffusion is a non-densifying process, which redistributes materials around pores for spheroidization and grain growth. However, grain boundary diffusion is a densifying process, which leads to volume shrinkage and pore elimination [121, 122]. When surface diffusion is energetically favored, the resulting driving force balance will lead to a reduction in grain boundary diffusion [121]. As reported in [122], high heating rates enhance the densification of ceramic powders because the surface diffusivity is slower. There is in fact a relatively new sintering technique named field-activated sintering (FAST) which uses pulsed direct current to enable high heating rates (up to 700°C/min), thus enabling fully-densified ceramic powders within 10 min [122]. In this study, although the heating rate is not as high as FAST, the densification is nevertheless accelerated in every cycle, as such the samples under cyclic conditions densified much faster than that under isothermal conditions.

Besides the heating rate, different planar stresses within the TCs under isothermal and cyclic conditions lead to different sintering behavior as well. Under the isothermal condition, TCs experience tensile stress during heating and at elevated temperature, as such the tensile stress within TCs is gradually reduced because of TGO creep-plastic behavior [123], and finally the stress changes into compressive state during cooling. This process is repeated in the cyclic samples, however, there is much less time for stress reduction due to creep-plastic behavior, hence, the TCs experience tension to compression fatigue loading every hour. Generally, sintering is accelerated by smaller tensile stress and larger

compressive stress in the form of reducing elastic strain energy, as reported by Hutchinson R.G. et al [119]. As shown in Equation 6.3, the elastic strain ε^E is composed of two parts: thermal expansion mismatch strain (ε^T) and sintering strain (ε^S). The ε^E can be positive (tension) or negative (compression). In Equation 6.2, α_{TC} and α_s are the CTEs of TC and the substrate, and T_D is the TC deposition temperature during manufacturing, while ε^S becomes an increasingly negative value with time. Tension leads to higher ε^S than that under compression, so the elastic strain energy U (Equation 6.4) is lower during the cooling stage than that during the dwell stage. As a result, the frequent cooling steps under cyclic conditions accelerate sintering.

$$\varepsilon^T = \alpha_{TC}(T - T_D) - \alpha_s(T - T_D) \quad (6.2)$$

$$\varepsilon^E = -(\varepsilon^T + \varepsilon^S) \quad (6.3)$$

$$U = \frac{E}{1 - \nu} (\varepsilon^E)^2 \quad (6.4)$$

Finally, as mentioned in the Section 5 Chapter., certain micro-cracks were healed after 800 to 1300 cycles, indicating an accelerated sintering process. The SPS TC reached failure at round 800 cycles with 20% of the surface area showing delamination of TC from BC; once delamination has begun, the TC can be considered to be in a free sintering state instead of a sintering constrained by a substrate. Previous literature has shown that free sintering has a higher rate of crack closure than that of a constrained sintering because tensile planar stress during the heating process retards crack closure [124, 125, 126]. As a result, sintering accelerates after reaching 800 cycles when delamination commences.

5.5.2 Phase compositions

In the as-coated condition, the SPS TCs assumes metastable t' -YSZ phase. The t' phase can decompose to $t + c$ phases driven by the yttrium redistribution [127] during prolonged thermal exposure where Y^{3+} and O^{2-} ions diffuse out of t' phase to form t phase which contains less $YO_{1.5}$ (4 – 13 mol.%) and c phase which contains more $YO_{1.5}$ (12 – 25 mol.%) [47]. This process continues and the c phase formation increases with time. During cooling, the t phase has the potential to transform to m phase depending on the $YO_{1.5}$ concentration, stress state and cooling rate [127, 128, 129], while c phase remains. The formation of m phase is undesirable, because this phase transformation is accompanied by high shearing strain and volume increase which results in macro cracks within crystals [130] as well as much higher thermal conductivity than t phase [131].

Comparing samples after isothermal and cyclic conditions, more t' -YSZ decomposed to t -YSZ under cyclic conditions than that under isothermal conditions as more prominent dual peaks at $\{2\ 2\ 0\}_{t,t'}$ are observed (Figure 0-7). The concentration of $YO_{1.5}$ within t -YSZ was calculated following Equation 4.8, and the results are summarized in Figure 0-11. It is apparent that $YO_{1.5}$ depleted faster in t' -YSZ under cyclic conditions than that under isothermal conditions. Thermal cycling effectively accelerated $YO_{1.5}$ diffusion to c phase, as a result, diffraction peaks for $\{2\ 2\ 0\}_c$ are more obvious under cyclic conditions.

Figure 0-11 Yttrium concentration in tetragonal phases after isothermal and cyclic tests.

For $t \rightarrow m$ phase transformation, the following factors have been observed to be influential by various researchers:

- i) When yttria in t -YSZ depletes to a critical level, t -YSZ undergoes martensitic transformation to a m -YSZ [127];
- ii) Budiansky et al. [128] evaluated how stresses influenced phase transformation in ZrO_2 . They found that at a fixed temperature, decreasing applied shear stress favored the $t \rightarrow m$ phase transformation while increasing applied shear stress reversed this transformation;
- iii) VanValzah J. R. et al. [129] evaluated the cooling rate effect on $t \rightarrow m$ phase transformation. The results showed that air quenched PSZ ($1000^\circ\text{C}/\text{min.}$) produced 2-5 times less m phase at room temperature than the furnace cooled ($10^\circ\text{C}/\text{min.}$) material. Moon J. et al [132] found similar results based on their experiments, because the higher amount of oxygen vacancies formed at high

temperature remained at room temperature due to the fast cooling rate, which suppressed the martensitic transformation and in turn stabilized the *c*-phase.

Comparing samples under isothermal and cyclic conditions, *m*-phase was observed on cyclically tested samples after 800 cycles, earlier than that under the isothermal condition (1300 h). Although cyclic tests using the equipment described previously have much faster cooling rate than isothermal tests (50°C/min in cyclic tests vs. 4°C/min in isothermal tests), it is not sufficiently fast to retain oxygen vacancies as that in the air quenching. On the other hand, faster diffusion of YO_{1.5} from *t*-YSZ and frequent cooling process accompanied by decreasing stress accelerate the formation of *m*-YSZ. After delamination occurred during 800 – 1300 cycles, the constraint from the substrate was released, the likelihood of *t*→*m* due to stress was diminished and finally the reversed transformation of *m*→*t* occurred during the heating and dwell processes. Under isothermal condition, however, the lattice experienced compressive deformation during furnace cooling as discussed in section 5.2, which is likely due to the creep-plastic behavior of TGO, generating additional compressive stress. With lower cooling rate and YO_{1.5} diffusion out of *t*-YSZ after 1300 h, *m*-YSZ was formed.

5.5.3 Sintering resistance of SPS TCs

Based upon previous studies, in addition to the changes in porosity and grain size, the sintering resistance of TBCs can also be evaluated by measuring the changes in E^* [133, 134], and H values [135]. Generally speaking, both the values of E^* and H increase by the sintering process due to the densification, as a result, slower rates of changes in these two mechanical properties indicate better sintering resistance of the coating. Based upon Figure 0-9, the rate of change in the mechanical properties were obtained and are summarized in

Table 0-2. Under isothermal conditions, sintering rate is slower, up to the first 800 h with gradually increased VCs density; the sintering rate is subsequently accelerated when VC density reached a saturation point. Under cyclic conditions, the sintering rate is much greater during 0 - 400 cycles and 800 - 1300 cycles, which is consistent with the changes in porosity, the reasons for this greater rate have been discussed in section 4.1. An interesting find is the reduction of the sintering rate in the range of 400-800 cycles, just prior to coating failure, as shown by the reduction in E^* and H . In these samples the greatest VC density is observed, it is therefore surmised that the macro cracks in both horizontal and vertical directions in the samples tested under cyclic conditions quickly undermined the splat boundaries and lowered E^* , a similar phenomenon was observed in [117]. In summary, sintering resistance is greater during the first 800 h under isothermal conditions, and sintering resistance is also higher under isothermal conditions than under cyclic conditions.

Table 0-2 Summary of mechanical properties and VC density change rate during isothermal and cyclic tests.

Isothermal				Cyclic			
Durations (h)	ΔVC density (/mm·h)	ΔE^* (GPa/h)	ΔH (GPa/h)	Durations (cycles)	ΔVC density (/mm·cycle)	ΔE^* (GPa/cycle)	ΔH (GPa/cycle)
0-400	3.5×10^{-3}	0.052	3.8×10^{-3}	0-400	3.8×10^{-3}	0.16	0.013
400-800	2.3×10^{-3}	0.035	2×10^{-3}	400-800	2.05×10^{-3}	-0.06	-5.25×10^{-3}
800-1300	≈ 0	0.097	7×10^{-3}	800-1300	-1.44×10^{-3}	0.11	5.71×10^{-3}

As the mechanical properties are influenced by the presence of cracks under cyclic conditions and density changes, it is difficult to predict the trend. Here the emphasis will be placed on the behavior under isothermal conditions. Sintering stress (σ_s), which is also termed as sintering potential, is the product of the interfacial energies of pores and grain boundaries [136]. Sintering occurs at elevated temperature and σ_s increases with increasing

sintering strain (compressive). Meanwhile, the volume shrinkage and the increase in E^* give rise to the in-plane stress (tensile) within the material. When sintering stress and in-plane stress become equal, the sintering process will be greatly reduced. If the material has a high E^* , in-plane stress from the substrate constraint will be released by cracking along the imperfections. After the constraint is released and the in-plane stress reverts again to less than σ_s , sintering will continue [137]. For SPS TCs, the initial E^* (146 GPa) is higher than APS TCs (usually $\ll 100$ GPa [138, 139, 140]), so the in-plane stress can build up quickly to hinder sintering; this also explains why VCs are easier to form in SPS TCs. In addition, during the first 800 h at the elevated temperature, the in-plane tensile stress is high enough to generate fresh VCs and to impede sintering. However, during the period of 800 – 1300 h, TGO creep may occur at a certain point to release part of tensile thermal misfit stress within the coating, therefore VCs stop forming and the reduced in-plane stress accelerates sintering.

Comparison of this study with those on APS TCs, and SPS TCs illustrates different sintering performances. Li G. R. et al [141] evaluated sintering performance of APS TC coated stainless-steel substrate at 1150°C for up to 500 h. Although the substrate and the evaluated temperature were different from this study, E was observed to increase rapidly within the first 20 h from 20 GPa to 45 GPa ($\Delta E = 1.25$ GPa/h), then the value became stable to around 55 GPa at 500 h (0.02 GPa/h). As the initial E value of APS is small due to inherently higher porosity, sintering was fast in the first stage with low in-plane stress in place. In addition, as shown in Figure 0-12, the lamella and porous structured APS TC enhanced inter-lamellar bonding during the first 20 h, then the porosity began to decrease. As APS coatings are known to have many inter-splat pores with multi-connections, hence

high surface energy and rapid healing by sintering. The result was that the inter-lamellar bonding was enhanced within the first 20 h. In the second stage, only inter-splat pores with single connections were left behind, requiring longer period of time to heal. For SPS TCs, on the other hand, its change in E is relatively stable at first and then increases. With higher density and less inter-splat pores in SPS TCs, the imperfections contribute marginally to the mechanical property changes driven by sintering.

Figure 0-12 APS TCs microstructure changes during thermal exposure at 1150°C after (a) 0 h, (b) 20 h, (c) 200 h, and (d) 500 h [141].

1.1 Summary of sintering performances under isothermal and cyclic conditions

- 1) After high temperature exposure, the porosity in SPS TCs decreased due to the sintering, accompanied by more and wider vertical cracks due to the volume shrinkage and thermal strain. These changes subsequently influenced the mechanical properties and led to increased elastic modulus and hardness.
- 2) SPS TCs densified more rapidly under cyclic thermal condition than under isothermal conditions, despite a reduced high temperature residence time (50% less) than that under isothermal conditions. This was attributed to the repeated heating and

cooling processes, favoring material densification. In addition, larger amount of m -ZrO_{1.5} was measured under cyclic conditions due to faster diffusion rate of YO_{1.5} from t -ZrO_{1.5}.

- 3) Measurement of the mechanical properties of the TC indicated an accelerated sintering rate within the first 400 h/400 cycles. The buildup of tensile stresses within the TC led to a decrease in sintering rate. This trend was once again reversed following stress relaxation due to TGO creep leading to a third period of accelerating sintering rate.
- 4) Vertical cracks aided SPS TCs in terms of enhancing the tolerance of volume shrinkage caused by sintering, enabling coatings with higher elastic modulus to survive longer than traditional APS TCs.

6 Chapter: Stress Distributions within the SPS TCs under the Cyclic Condition Simulated by ABAQUS

In this chapter, stress distribution in the SPS TC under the cyclic condition is simulated using ABAQUS in order to quantitatively evaluate the mechanical property degradation and the influence of VCs on the behavior of TBCs under cyclic thermal exposure. The cyclic thermal condition is considered to be more detrimental to coating systems than the isothermal condition because of faster sintering rate and mechanical degradation, as well as associated thermal fatigue, which all lead to an acceleration of TBC failure. In addition, isothermal oxidation tests have longer dwell times at high temperature, which involve time dependent inherent behavior such as creep damage. Required creep parameters are available through other cited references; however, data may not be accurate or applicable for this current study. For the cyclic condition, because of the inherently shorter dwell times at elevated temperature, the inaccuracy caused by such borrowed creep parameters is decreased. Here the simulation is conducted to generate a trend in order to facilitate future coating structure designs and coating selections.

6.1 Methodology to model TBC stresses

6.1.1 Mechanistic considerations

Although TCs produced by different deposition technologies have varied failure modes [15, 81], these failure modes are all essentially caused by thermal expansion mismatch between different layers, mechanical properties degradation, TGO growth, TGO undulation and finally TC sintering [142, 91]. Among these, the stress and strain generated by the TGO growth and undulation are considered to be the most influential factors for TBC failure [142]. As shown in Figure 0-1, stresses and tractions in a TBC system were

plotted schematically by E. P. Busso et al. [91]. The out-of-plane stress, which is parallel to X_2 -axis, is the driving force to generate micro-cracks lying in the X_1 - X_3 plane within the TC near the TC/TGO interface. Here the out-of-plane stress (σ_{22}) is the object of this study.

Figure 0-1 Schematic diagram of the TBC system with relevant stresses and tractions [91].

6.1.2 Identification of TGO geometric parameters

The stress distribution within the TC is highly influenced by the TGO geometry, so the parameters should be determined based upon the experimental data initially. To assess the TGO roughness, the method to determine the amplitude (b) and wavelength (a) of TGO has been introduced in Section 3.3.1. In addition, the critical value of b/a (r_c), introduced in Equation 2.30, must be determined as well. Based upon the method explained by E. P. Busso et al. [91], r_c is solved by the cumulative probability function replotted in Figure 0-2. In this study, the known damage fraction after 800 thermal cycles is assumed to be 0.3, so the corresponding value of $r_c = 0.5$. The value of a is determined by averaging of all measurements carried out previously.

Figure 0-2 Determination of the critical b/a from the cumulative distribution function.

6.1.3 Finite element model

The Standard/explicit module of ABAQUS is used to create a two-dimensional planar deformable shell structure. In this study, the bonding between the layers is assumed to be perfect, which means no sliding or debonding occurred during the thermal exposure. As the failure of the SPS TBC systems occurs within TCs, the stress distribution within the TC is of prime importance in this simulation. The initial stress of the TBC system is considered as zero with no defects and horizontal micro-cracks in the TBC.

6.1.3.1 TGO growth

When the TBC system experiences the “dwell” step at 1080°C, TGO is expected to grow following the parabolic oxidation law. The oxide layer growth is materialized by writing the subroutine CREEP with SWELLING option in Abaqus/standard. The initial thickness of TGO is set to be 1 μm . The growth rate $\dot{h}$ is calculated by Equation 6.1, where t_D is the holding duration at high temperature. In order to determine the oxidation constant k_p , the TGO thickness is measured by the method explained in the Section 3.3.1. According to

Figure 0-3, the TGO growth rate K_p was determined to be $0.073 \mu\text{m}^2/\text{h}$ for the total TGO growth including $\text{Al}_2\text{O}_3 + \text{spinel}$. It should be noted, the data in Figure 0-3 was measured from the isothermal samples as an approximation because the samples in cyclic conditions generated too many interface cracks, making the measurements highly inconsistent. Assuming that TGO growth is activated at high temperature and the growth rate is controlled by the evaluated temperature only, TGO growth under the cyclic conditions can assume the same k_p , but the testing duration t to account for dwell duration t_D must be included.

$$h^2 = 2k_p t_D \Rightarrow \dot{h} = \frac{k_p}{h} \quad (7.1)$$

Figure 0-3 TGO thickness growth with time.

The oxide growth rate $\dot{h}$ is calculated for the initial TGO thickness based upon Equation 6.1 and kept constant throughout the simulation. Here the growth rate is gradually decreased as a function of TGO thickness. For the simulation, a growth strain rate $\dot{\epsilon}_{gh}$ is given by [143]:

$$\dot{\varepsilon}_{gh} = \frac{\dot{h}}{h} \quad (7.2)$$

In the model, the oxide growth is an anisotropic parameter. The growth is mainly in the thickness direction, while lateral growth is ignored. As a result, the growth strain rate in tensor notation can be written as:

$$\dot{\varepsilon}_{ii}^{gh} = r_{ii} \frac{1}{3} \dot{\varepsilon}_{gh} \quad (7.3)$$

where r_{ii} , $i = 1, 2, 3$, is the local coordination with X_1 and X_2 axes shown in Figure 0-1. In this study, $r_{11} = r_{33} = 0$ and $r_{22} = 3$ are set to fix oxide growth solely in the X_2 direction.

6.1.3.2 Identification of the geometric model

The geometry for the model (Figure 0-4) consists of the SUB (substrate), BC, TGO and TC. In order to study how VCs influence stress distribution within the SPS TCs, a geometry without VCs is also considered here as a baseline. The thicknesses of TC, BC, and SUB are assumed to be 300 μm , 150 μm and 1.5 mm, respectively. The initial TGO thickness is set as 1 μm , and then grows to the value of 10 μm . The cosine function of the interface is shown:

$$y(x) = \frac{b}{2} \cos\left(\frac{\pi x}{a}\right) \quad (7.4)$$

where $a = 110 \mu\text{m}$, based upon the averaged measurements of this study; $b = 55 \mu\text{m}$, to give the critical $b/a = 0.5$. In order to understand how the interfacial roughness influences the TC stress distribution, another value of $b = 110 \mu\text{m}$ ($b/a = 1$) is also assumed and modelled.

Figure 0-4 TBC model for finite element analysis

Regarding the VCs within the SPS TCs, the positions of VCs are assumed to be situated mainly at the valley and the sloped regions, near the interface (Figure 0-5). In this case, VCs at these two positions (position ① and ② in Figure 0-4) are simulated. The stress and magnitude VC at each position are respectively 250 μm , and 270 μm . As shown in Figure 0-5, the VCs did not propagate further towards the interface, rather became wider after thermal exposure. As such, the VCs were assigned as “Seam” in the crack function in ABAQUS, ensuring that the assigned VCs could open but they did not propagate in simulation. In order to reflect the stress concentration at the crack tip, the mesh around the crack tip is refined (Figure 0-6). The J-integral for these VCs were estimated from ABAQUS using the domain integral method [15].

Figure 0-5 Microstructural images of the sample after 400 cycles, (a) VCs at the slope, and (b) VCs at the valley.

Figure 0-6 Mesh at the vertical crack tip.

6.1.3.3 Thermal load and boundary condition

The thermal loading of TBCs is assumed to be a homogeneous (i.e., constant temperature) for the whole system immediately following heating, dwell, and cooling steps within each cycle. During thermal cycling, the max-min thermal load is defined as one cycle, but the dwell time is assumed to be a 0.5 h multiplied by the number of cycles. This yields:

$$t_D = n_{cycle} \cdot 0.5 \text{ h} \quad (7.6)$$

where t_D is the dwell time, and n_{cycle} is the number of cycles. Based upon $\dot{\epsilon}_{gh}$, n_{cycle} is set to be 200 to reach a TGO thickness value of 10 μm , which was found to be the total oxide thickness at the failure. The overall thermal load is shown in Figure 0-7.

For the boundary conditions, the horizontal displacement at the left boundary is fixed to get a symmetric condition and the bottom boundary is constrained in the vertical direction. Furthermore, the right boundary is restricted by using Equation Constraint, which allows nodes to move freely but simultaneously in the X_I direction. Lastly the meshing element type of 4-node bilinear quadratic plane strain elements (CPE4) are used. The size of mesh is controlled to be 0.5 on each sides, with refined meshing elements at the crack tip to be 0.2 within the cycle.

Figure 0-7 Thermal load during cyclic test

6.1.3.4 Material properties

All layers within the TBC system are considered as homogeneous and isotropic. Since gas turbine components are always exposed to elevated temperatures, elastic modulus (E), Poisson's ratio (ν) and CTEs (α) of each layer are temperature dependent and these parameters at various temperatures are summarized in Table 0-1. In addition, in this simulation, it is assumed that the E of TC at high temperature is about 30% of the value at ambient temperature [144]. And the ambient E value is assumed to be that of the as-sprayed SPS TC (Figure 0-8).

Table 0-1 Elastic properties and CTEs of materials

Temp. (°C)	TC [145, 146]			TGO [145]		
	$\alpha \times 10^{-6} (^{\circ}\text{C}^{-1})$	E (GPa)	ν	$\alpha \times 10^{-6} (^{\circ}\text{C}^{-1})$	E (GPa)	ν
20	9.68	130	0.3	5.1	380	0.27
100	--	--	0.3	--	--	0.27
200	--	--	0.3	--	--	0.27
400	9.7	--	0.3	--	353	0.27
600	--	--	0.3	--	--	0.27
700	9.88	--	0.3	--	--	0.27
800	--	--	0.3	--	338	0.27
900	--	--	0.3	--	--	0.27
1000	10.34	42	0.3	--	312	0.27
1165	--	--	0.3	9.8	--	0.27

Temp. (°C)	BC [145]			SUB [147]		
	$\alpha \times 10^{-6} (^{\circ}\text{C}^{-1})$	E (GPa)	ν	$\alpha \times 10^{-6} (^{\circ}\text{C}^{-1})$	E (GPa)	ν
	--	183	0.3	--	204	0.3
20	10.34	--	0.3	13	200	0.3
100	11.3	--	0.3	--	193	0.3
200	12.5	152	0.3	--	180	0.3
400	--	--	0.3	14	172	0.3
600	--	--	0.3	--	--	0.3
700	14.3	55	0.3	--	--	0.3
800	16	--	0.3	16	147	0.3
900	--	--	0.3	--	--	0.3
1000	--	--	0.3	--	--	0.3

Besides the substrate, which is considered as elastic material, the other layers are all assumed as viscous and elastic material. Although the metallic substrate has viscous behavior at high temperatures, its creep response has little influence on the residual stress presented in ceramic TCs [148]. For BC, TGO and TC, the creep behavior follows the basic Norton power-law as shown in Equation 7.7:

$$\dot{\varepsilon}_{cr} = B\sigma^n \quad (7.7)$$

where $\dot{\varepsilon}_{cr}$ is the creep strain rate (s^{-1}), B is the pre-factor ($\text{s}^{-1} \cdot \text{MPa}^{-n}$), σ is the equivalent von Mises stress (MPa), and n is the power-law creep exponent. The detailed parameters are summarized in Table 0-2 [143, 95]. This is to be noted that several researchers consider BC as visco-plastic material [143, 149], but since the plasticity is ignored in this simulation

to reduce computation time, a visco-elastic material is assumed for the BC. This is justified because creep relaxation within the BC impedes the stresses growing large enough to cause plasticity at elevated temperature [144].

Table 0-2 Creep properties of materials [143, 95]

	$B \left(\frac{\text{MPa}^n}{\text{s}} \right)$	n	$T (^{\circ}\text{C})$
TC	1.8×10^{-7}	1	1000
TGO	7.3×10^{-7}	1	1000
BC	6.5×10^{-19}	4.57	≤ 600
	2.2×10^{-12}	2.99	700
	1.8×10^{-7}	1.55	800
	2.15×10^{-8}	2.45	≥ 850

6.1.3.5 TC sintering

TC sintering has been discussed in detail in Chapter 6. However, the elastic modulus E of any coating can only be tested at ambient temperature; as such, there is no information readily available on the elastic property at higher temperatures. In this case, E at 1080°C was assumed to reduce to 30% of the value at the ambient temperature after each duration used in this study, i.e., after 400, 800, and 1300 cycles. Using this method, the time dependent E at room and elevated temperatures after each interval is shown in Table 0-3. Furthermore, the experimental datapoint for the 800 cycles sample decreased significantly to 185 GPa because of the formation of macro-cracks, therefore the data cannot truly represent the real matrix elastic modulus. For this reason, the E of 800 cycles TC is obtained from linear interpolation between 400 and 1300 cycles.

Table 0-3 Time dependent elastic modulus of SPS TCs

	400 cycles (room temp.)	800 cycles (room temp.)	1300 cycles (room temp.)	400 cycles (1080°C)	800 cycles (1080°C)	1300 cycles (1080°C)
E (GPa)	187	227	263	56	68	79

Equation 2.8 is used to relate the E value after sintering and the corresponding dwell time. The values of e and f are determined using Figure 0-8. The sintering behavior of the TC is materialized by writing a UMAT subroutine.

Figure 0-8 The relationship of elastic modulus vs. dwell time at 1080°C.

6.2 Results and discussion

In this chapter, the objectives are to identify: i) how different structures of VCs influence the stress distribution within the TC and the stresses along the interface of TC/TGO; ii) how TGO growth influences the stresses along the interface of TC/TGO; iii) how TC sintering influences the stresses along the interface of TC/TGO; iv) how TC creep influences the stresses along the interface of TC/TGO; and v) how TGO roughness influences the stresses along the interface of TC/TGO. The detailed plan for this parametric study is described in Figure 0-9.

Figure 0-9 Plan for the parametric study of SPS TCs.

6.2.1 Parametric study of the TBC system without vertical cracks

Influences of TGO growth and roughness

As shown in Figure 0-10, the out-of-plane residual stress σ_{22} within the TC is analyzed with and without TGO growth with smooth TC/TGO interface ($b/a = 0.5$) as well as rougher TC/TGO interface ($b/a = 1$) without TGO growth. σ_{22} has the most influential effect on the crack delamination and the eventual failure. In this section, it is assumed that the TC does not creep or sinter. The TGO growth is assumed to only be activated during the dwell step, as a result, the stress distributions within the TC with and without TGO share the same stress distribution in the heating step. The symbols “+” and “-” in Figure 0-10 stand for the tensile stress and the compressive stress, respectively.

As shown in Figure 0-10 (a), the TBC system without TGO growth generates tensile stress (in red) along the interface of TC/TGO after heating. Subsequently the tensile stress gradually moves toward the peaks, and meanwhile the compressive stress (in blue)

is concentrated at valleys. After cooling, the values of these stresses sharply increase to a maximum of 219 MPa (in tension) and a minimum of -188 MPa (in compression). With TGO growth (Figure 0-10 (b)), the stresses become higher. Due to the oxidation of the BC and the thickening of the TGO, the maximum tensile stress moves from near the peaks toward the flanks, and the stress at the peaks is converted from tension into compression during the dwell step. After cooling, the maximum σ_{22} at the flanks and above the peaks increases to 225 MPa. As proposed by Bäker et al. [150], the BC and TGO play opposite roles on the stress state. BC has a larger CTE than the TC, but the CTE of TGO is smaller than that of the TC. As a result, a compressive stress state can be induced at the TC valley and a tensile stress state at the TC peak by BC-induced stresses, but TGO-induced stresses cause a tensile stress state at the TC valley and a compressive stress state at the TC peak. This explains why stresses at peaks and valleys are converted with gradual TGO thickening during dwell step. Similar findings were also observed by M. Ranjbar-Far, et al. [143]. Comparing the stresses in Figure 0-10 (a) and (c), the stress distributions are similar, but rougher TGO value results in higher stress levels after heating, dwell and cooling steps.

After
dwell

After
cooling

(a)

With TGO growth (σ_{22} , MPa)

After
heating

After
dwell

After
cooling

(b)

Figure 0-10 Stress distribution comparison of no-VCs TC between (a) without, (b) with TGO growth with $b/a=0.5$, and (c) $b/a=1$ geometry without TGO growth.

6.2.1.1 Influences of TC creep and sintering

After assigning the time-dependent material properties to TCs with BC oxidation, the residual stress distributions changed as well. Figure 0-11(a) presents the influence of TC sintering (i.e., change of E), and Figure 0-11(b) presents another scenario where TC creep was taken into consideration. The TC sintering does not seem to influence the tensile and compressive stress distribution, but increase the stress values by 20%. On the other hand, creep in TC redistributes the stresses within the coating in dwell. The tensile stress

concentrates at valleys instead of flanks, and the compressive stress moves towards the peaks. After cooling, the tensile stress bridges the neighboring asperities, giving rise to the potential for horizontal cracks to propagate. However, these values of stresses are significantly decreased by creep during the thermal exposure, from heating to cooling, due to the stress relaxation effect.

(b)
Figure 0-11 Influences of TC (a) sintering, and (b) creep on the stress distribution within the SPS TC.

6.2.2 Parametric study of TBC with vertical cracks

6.2.2.1 Basic structural analysis

In order to study the effects of different VC positions on stress distributions within the TC, the VC TBC system without TGO growth or TC property changes (due to sintering) were first studied, and the results are summarized in Figure 0-12. In general, the tensile stress concentrates at the tips of the VCs (in grey) during the heating and dwell steps, whereas such stress switches into a compressive state after cooling. Because the localized tensile stress at the VC tips reaches as high as 2 - 3 GPa after heating and cooling, such high tensile stress level can readily initiate horizontal cracks at the tips. After cooling, the previous compression region converts to tension, having the potential to accelerate the crack growth and to enable delamination.

Comparing the two SPS TCs with VCs located differently, the one with the VC at the valley has lower maximum tensile stress than the other one within a thermal cycle. The main difference between these two structures is that the VC at the valley has a symmetric geometry, and the VC at the slope configuration has an asymmetrical shape. The stresses within the TBC systems are mainly caused by thermal mismatch between different coating layers, as such the load is assumed to be uniform if the TC geometry is symmetric. However, if the geometry is asymmetrical, it leads to an **antisymmetric** stress distribution, resulting in an extra stress moment on one side and a higher stress on the other side in order to balance the stresses within the TC. Consequently, the highest tensile stress (grey part in Figure 0-12 (a)) leans to the right side and arrives at a higher stress value at the same time when comparing it to the stresses in the TC with VC at the valley (Figure 0-12 (b)).

Figure 0-12 Influences of VC at (a) slope, and (b) at valley on the TC stress distributions without the change of TC material properties.

To better understand how VCs operate during service, further analysis was carried out to place focus at the tip locations of the VCs. With reference to Figure 0-13 (a), the stresses in most of the regions near the VC at the slope are in tension after heating, where

the crack could initiate near the tip. In the dwell step, the crack may propagate upward or downward, but it has higher resistance to grow horizontally because of the compressive stress on the right. In the cooling step, the crack near the VC has no potential to grow as stresses in most regions are compressive in nature. According to Figure 0-13 (b), an initiated crack due to tensile stress after heating at the tip of a VC situated at the valley could grow horizontally in the dwell step, but the crack size would be limited by the surrounding compressive stress field. In the cooling step, the normal stresses are released through the VC as $\sigma_{22} = 0$ MPa at the tip of VC. The peak compressive stress reaches -716 MPa at the bottom as indicated by arrows in Figure 0-13 (b). In this case, any defects near the VC tip are more likely to grow in the heating step, rather than the dwell and cooling steps. After multiple thermal cycles, these cracks may reach sufficient size and link, leading to the final delamination and ultimate TBC system failure.

Figure 0-13 Stress distributions at tips of VCs in the (a) VC at slope SPS TC, and (b) VC at valley SPS TC.

Although the overall stresses within SPS TCs with VCs are much higher than that in the TBC without VCs, VC structured TCs nevertheless demonstrate longer lifetimes than that of APS TCs [140]. The rational for this phenomenon can be further analyzed as follows.

A kinking angle ϕ for crack propagation is defined as an angle between the direction of crack propagation and horizon, and can be determined by mode I and mode II stress intensity factors [151]. As shown in Figure 0-14 and Equation 7.8, cracks under pure mode I (opening) stress will grow horizontally, while cracks with pure mode II (shearing) stress will grow with a $\phi = 77^\circ$ towards the surface of the TBC. When a horizontal crack meets VCs (at the valley) σ_{22} has a chance to fully relax in the cooling step, which brings K_I to 0; the horizontal crack can change the propagation direction with $\phi = 77^\circ$. In summary, the horizontal cracks are more likely to form in the SPS TCs than in the TCs without VCs but

the propagation direction of the initially horizontal cracks within SPS TCs can be re-orientated, so that these cracks are not likely to form in the same plane. The lifetime is extended in a similar fashion as that in the composite materials where crack deflection helps to render increased fracture toughness [152].

$$\varphi = \begin{cases} \arctan(-2K_{II}/K_I), & \text{for } K_{II}/K_I \rightarrow 0 \\ 77^\circ, & \text{for } K_{II}/K_I \rightarrow \infty \end{cases} \quad (7.8)$$

Figure 0-14 kinked cracks for pure mode I, pure mode II, and mixed mode stresses.

In fact, the experimental results demonstrated the presence of horizontal cracks near tips as shown in Figure 0-15 (a) and Figure 0-5, after 400 thermal cycles. Some of these cracks propagated horizontally through VCs, and some changed directions, moving up or down depending upon different positions of VCs. In Figure 0-15 (a), there are numerous horizontal cracks, not only at the interface, but also in the TC far away from the interface. The stresses around VCs can reach the GPa scale in magnitude during the cooling step (Figure 0-12), so they are sufficient to generate cracks but not to lead to final failure. After 800 cycles, the coating eventually failed due to the crack delamination within the TC near TGO, as shown in Figure 0-15 (b). The delamination is seemed to grow along the tips of VCs. The scenario is assumed to be: cracks initiated at the tips of VCs and propagated with time, until these cracks coalesced to lead to final delamination. In this case, the

simulation and experimental results are in agreement and are considered to be of consistence.

Figure 0-15 Microstructure of (a) horizontal cracks at VC tips and (b) delamination within SPS TCs after 800 cycles.

As shown in Figure 0-16, in order to study how VCs influence the interfacial stresses after heating, dwell and cooling, the relationship between σ_{22} along the nodes at the interface of TC/TGO and the normalized node position $\tilde{x} = x/a$ (ratio of the horizontal distance between nodes and the left edge x over a) are presented in Figure 0-17. The odd values of $\tilde{x}$ (1, 3, 5, etc.) stand for valleys; the even values (2, 4, 6, etc.) stand for peaks. For example, $\tilde{x} = 4.5$ signifies VC on the slope and $\tilde{x} = 5$ for VC at the valley.

Figure 0-16 Schematic diagram of interfacial stresses

Because of the periodic geometry, the stress distribution in the coating without the VCs is periodic (black curves) in three thermal steps. On the other hand, interfacial stress distributions in the two coatings with VCs seem similar, but the TC with VC at the valley has globally lower stress levels in three thermal steps. After heating, the out-of-plane stresses of the no-VC TC fluctuates in the range of -25 MPa to 50 MPa, from peaks to valleys. The coatings with VCs (blue and red curves) assume four to five times higher out-of-plane stress than that in the coating without VCs, at the position $\tilde{x} \in [2.5, 6]$. However, the remaining regions with lower stresses can be observed in TCs with VCs. After dwell, although the TC with VC situated at the valley contributes to the realization of the highest stress (≈ 150 MPa) at $\tilde{x} \approx 4.2$, the stresses at the remaining region are lower than that in the TC without VC. After cooling, stress distributions exhibit different to the heating step. The two VC TCs are subjected to higher out-of-plane stresses than that in the no-VC coating at regions away from the VCs, and the stress gradually decreases to negative values when approaching the VCs. Based on this simulation, the SPS TCs are likely to debond in VC tip regions in the heating step when comparing to that with no VC and then the spallation can dissipate towards the two sides of the crack in the cooling step. Although stresses in VC structured TCs are higher than that in TC without VC, VC TCs sustain a larger area of compressive stress, which means that the size of debonding may be limited due to limited area of tensile stress.

Figure 0-17 Interfacial stress distributions at the interface of TC/TGO including no VC structure, VC situated at the slope and VC at valley.

6.2.2.2 Influences of TGO growth and roughness

Illustrated in Figure 0-18, TGO growth and roughness geometry have shown to increase σ_{22} along the interface of TC/TGO in all three thermal steps, regardless of the types of TC structures. The black curves represent the baseline interfacial stress distributions in the VC TC without TGO growth and $b/a = 0.5$. It is noted that the curves of the baseline (black) and the curves with TGO growth (red) overlap after heating, as TGO growth is activated in dwell. Higher b/a ratios broaden the stress range, particularly in the middle of the range where crack resides, in three thermal steps. Higher TGO asperities decrease the stresses at peaks, and increase the stresses at valley and flank locations. Although VCs contribute to the elevated compressive stress at the center, the accompanied tensile stress near VCs can lead to debonding locally. Comparing the two structures with different roughness, the influence is less for the TC with VC at valley than at the peak, because there is a very little difference in stress between the baseline and that with $b/a = 1$.

Regarding the TGO growth, the stresses at valleys are increased during dwell, while the stress at peaks reduces in the cooling step. Comparing the two VC TCs, the coating with the VC at the valley is subjected to lower stress level than the other, especially during dwell and cooling.

VC at slope After heating

After dwell

After cooling

(a)

(b)

Figure 0-18 Influences of TGO roughness and growth on interfacial stress distributions at the interface of TC/TGO of (a) VC at slope TC, and (b) VC at valley TC.

6.2.2.3 Influences of TC creep and sintering

Figure 0-19 summarized the influences of TC creep and sintering on the interfacial stress distribution in SPS TCs at the TGO/TC interface. The black curves represent the coatings with TGO growth only (i.e., no sintering); the red curves represent the coatings with both TGO growth and TC sintering; the blue curves denote the coatings with TGO growth and TC creep. Sintering is seen to slightly increase the stresses in two coatings of all three thermal steps. Sintering influences stresses at flanks more than at peaks and valleys. On the other hand, creep highly influences the out-of-plane interfacial stresses in dwell. Comparing the interfacial stress distributions in the coatings with either VC at slope or VC (blue curves in Figure 0-19 after dwell) at valley are similar, indicating that TC creep have reduced the disparities arising from the location of the VCs. In order to further validate this observation, interfacial stress distributions with TGO growth and TC creep in (i) TC without VC, (ii) TC with VC at slope, and (iii) TC with VC at valley after dwell are plotted together in Figure 0-20. The three curves are almost overlapped in this figure with illegible differences. It is therefore realized that with the onset of creep in TC, the interfacial stress distribution will not be influenced by the existence of VCs nor the positions of VCs. In the cooling step, TC creep decreases the maximum σ_{22} , to about half of its value in the coating without TC creep.

VC at slope

After heating

After dwell

After cooling

(a)

(b)

Figure 0-19 Influences of time dependent TC properties on interfacial stress distributions at the interface of TC/TGO of (a) VC at slope TC, and (b) VC at valley TC.

Figure 0-20 Interfacial stress distributions at interface of TC/TGO of three types of coatings with TGO growth and TC creep in the dwell step.

1.2 Summary of stress simulation in SPS TCs under cyclic conditions

- 1) Out-of-plane stresses were found to concentrate at the tips of the VCs enabling crack initiation under cyclic conditions. In addition, the high tensile stress accumulated at the peak locations away from VCs during cooling was also considered as preferred crack initiation sites.
- 2) Comparing TCs with or without VCs, those with VCs had a higher maximum tensile stress under cyclic conditions, but at the same time they also induced larger adjacent compressive stress areas, so the sizes of cracks were inhibited.
- 3) Although cracks could easily form in VC TCs, the cracks re-oriented because of the stress relaxation by VCs. In this manner, cracks were less likely to form in the same plane and as such delaying the final delamination due to crack deflection.
- 4) Regarding the influences of TGO, increase of TGO thickness led to the augmentation of the stresses at valley locations after dwell. An increase of TGO asperities also broadened the range of stresses at the interface.

- 5) Finally, the TC sintering marginally raised the stresses after heating, dwell and cooling, in the thermal cycling. TC creep lessened the influences of TC sintering on the interfacial stress distributions in TCs with or without VCs.

7 Chapter: Fracture Performance and Crack Growth Prediction of SPS TBCs in Isothermal Experiments by Crack Numbering Density

In this chapter, the growth of horizontal cracks within SPS TCs under isothermal conditions is predicted using crack number density. As there have not been many published researches on crack growth prediction involving VC TCs, this part of the research is critical in terms of providing tools for future SPS TBC life assessment. Unlike cracks formed under cyclic conditions, there are much less cracks formed after isothermal tests, making it easier and more accurate to characterize. In this chapter, the modelling methodology and results are presented for isothermally tested TBC system with VCs.

7.1 Theory and Calculation

7.1.1 Crack progression

Regardless of coating deposition methods, cracks in the TC experience a similar fracture mechanism. Under an isothermal condition, sphere-wedging cracks are formed and grown by intrinsic stresses introduced by TGO growth, as well established by Evans and He et al. [10]. At elevated high temperatures, the out-of-plane stress in the TC, σ_{22} , increases with TGO thickening, which contributes to the mode I radical crack propagating within the TC and to form cracks in planes which are parallel to the interface between TGO/TC [82]. The crack tip which is propagating outwards from the TGO asperity is considered to be the external tip; and the crack tip at the surface of the TGO asperity is considered to be the internal tip. At elevated temperatures the rate of crack propagation within the TGO is reduced due to stress redistribution and creep, once the TGO is cooled to the room temperature these cracks propagate more readily because of the high stress intensity at the internal tips, and eventually cracks begin to coalesce at the interface between TGO and BC

[10]. To simplify the geometry of the fracture mechanism, as shown in Figure 0-1, it is assumed that the imperfections are modeled as cycles with radius R , the mode I stress intensity factor K_I at the external crack tip for unconnected and fully connected cracks are provided in Equation 8.1 [10].

$$K_I = \begin{cases} \frac{E(m-1)}{3(1-\nu)m} \left(\frac{h}{R}\right) \sqrt{R} \sqrt{\frac{\pi}{2} \left(\frac{c}{2R} - 1\right)} \left(\frac{2R}{c}\right)^{2.4} & (\text{unconnected}) \quad (8.1a) \\ \frac{E(m-1)}{3(1-\nu)m} \left(\frac{h}{R}\right) \sqrt{R} \frac{3}{2(1+\nu)\sqrt{\pi}} \left(\frac{2R}{c}\right)^{\frac{3}{2}} & (\text{fully connected}) \quad (8.1b) \end{cases}$$

where m is the ratio of volume change by oxidation, ν is the Poisson's ratio of TC, h is the thickness of TGO, c is the crack size.

Figure 0-1 Cracking scenario.

7.1.2 CND Model

CND theory describes the evolution of cracks by the following differential equation [17, 18]:

$$\frac{\partial n}{\partial t} + \frac{\partial[An]}{\partial c} = n_N \quad (8.2)$$

where n is a distribution function of the numerical density of micro-cracks at time t , c is crack size, $A = \dot{c}$, the crack growth rate, and n_N is the specific crack nucleation rate. The specific nucleation rate is, in essence, an intrinsic material property which represents the strain energy available for forming new crack surfaces. Where the leftmost term represents the creation of new crack surfaces in the form of crack nucleation and the second left-hand term represents the creation of new crack surfaces in the propagation of current cracks. These two equations form a balance where crack nucleation or propagation being energetically favorable depends upon strain energy available, the crack density and the crack size distribution at that point in time.

The general solution of Equation 8.2 can be rewritten as:

$$n(c, t) = \begin{cases} n_N(c)t, & c < c_0 \\ \frac{1}{A(c)} \int_{\eta}^c n_N(u) du, & c \geq c_0 \end{cases} \quad (8.3)$$

where c_0 is the threshold value below which crack growth is energetically unfavorable, and η is an intermediate crack size evaluated by:

$$t = \int_{\eta}^c \frac{du}{A(u)} \quad (8.4)$$

where u is an intermediate integration variable.

It is also assumed that the growth of total TGO thickness follows the parabolic oxidation law as shown in Equation 2.15.

When the discussed K_I at the crack tips reaches the fracture toughness K_{IC} of the TC, cracks start to propagate. Although there are two equations to describe K_I , only Equation 8.1b for fully connected cracks is utilized in this study for the following reasons: i) Equation 8.1b covers wider range of crack sizes; ii) for life prediction, cracks with critical size which lead to failure are more important, and the critical size is usually much larger than $2R$. In this case, Equation 8.1b is rearranged to:

$$c = 2\left[\frac{(m-1)ERh}{4m(1-\nu^2)K_{IC}\sqrt{\pi}}\right]^{2/3} = Ch^{2/3}, C = 2\left[\frac{(m-1)ER}{4m(1-\nu^2)K_{IC}\sqrt{\pi}}\right]^{2/3} \quad (8.5)$$

Assuming that the fully connected cracks can propagate in two direction, the overall surface energy for cracks to create is doubled compared to one tip growth. As a result, $2K_{IC}$ is involved in Equation 8.5. Combining Equation 2.15 and Equation 8.5, the crack growth rate A can be expressed as:

$$A = 2\dot{c} = \frac{4}{3}k_p C^3 c^{-2} \quad (8.6)$$

Cracks can propagate in two directions, so a constant 2 is shown in Equation 8.6. Although there is a possibility of the existence of stable cracks below a threshold size for growth, these cracks exist only in ideal conditions, not replicable in experimental procedures. As a result, it is reasonable to assume $c_0 = 0$ for this material system and all cracks are considered to be able to propagate. The specific crack nucleation rate is assumed to follow a Gamma distribution, $\Gamma(\alpha, \beta)$ with $\alpha = 2, \beta = 1/(Ch^{2/3})$ giving:

$$n_N = B \frac{\beta^\alpha}{\Gamma(\alpha)} c^{\alpha-1} e^{-\beta c} \quad (8.7)$$

where α is the shape factor and B is a scaling constant.

Substituting Equations 8.6 and 8.7 into Equations 8.3 and 8.4, the crack number density function can be written as:

$$n_N(c, t) = \frac{B}{\Gamma(\alpha)} [\beta(\eta e^{-\beta\eta} - c e^{-\beta c}) + (e^{-\beta\eta} - e^{-\beta c})] \quad (8.8)$$

where η can be expressed based on Equation 8.4 as:

$$\eta = \begin{cases} 0, & c \leq \sqrt[3]{3kC^3t} \\ \sqrt[3]{c^3 - 3kC^3t}, & c > \sqrt[3]{3kC^3t} \end{cases} \quad (8.9)$$

7.1.3 Measurements of Mechanical properties of TC

Based upon the CND model, there is a critical parameter C related to mechanical properties that are to be determined. According to Equation 8.5, C is influenced by E , m , R , ν , and K_{IC} . Assuming $\nu = 0.3$ which remains consistent over the time, the other parameters are determined by experiments after the isothermal tests, and the methods are summarized in Table 0-1. More details can be found in Section 3.3.2.

Table 0-1 Methods for mechanical properties determination.

Parameter	E	K_{IC}	R	m
Method	Nanoindentation	Vickers indentation	Image processing	Image processing

It is important to note that these measurements are carried out after the samples are cooled to ambient temperature. The mechanical properties at elevated temperatures will vary from that measured at ambient temperature. In addition, the real TBC system has a TC/BC interface roughness with variable amplitudes, so the neighboring roughness with a lower or higher amplitude may stop or accelerate crack growth due to lower or higher corresponding tensile stress [95] in the form of influencing the ratio E/K_{IC} . In this case, C is rewritten to

$$C = \lambda \left[\frac{(m-1)ER}{4m(1-\nu^2)K_{IC}\sqrt{\pi}} \right]^{2/3} \quad (8.10)$$

where λ is a fixed constant which will be calibrated using experimental data from varying test durations.

7.2 Results

7.2.1 Parameters determination for CND

The required material parameters are summarized in Table 0-2, Figure 0-8 (a), Figure 0-3, and Figure 0-2. According to Figure 0-3, the TGO growth rate K_p was determined to be $0.073 \mu\text{m}^2/\text{h}$ for total TGO growth ($\text{Al}_2\text{O}_3 + \text{spinel}$), and the relationship between thicknesses of spinel and Al_2O_3 is obtained as well, which helps determine the value of m . The results of nanoindentation and Vickers indentation tests indicate that the elastic modulus E of SPS TCs increases with continuing high-temperature exposure (Figure 0-8 (a)), while K_{IC} decreases. With the increasing oxidation test duration, E increases from 130 GPa to 223 GPa due to the sintering effect. K_{IC} reduces from $5.5 \text{ MPa}\cdot\sqrt{m}$ for the as-received TBC TC sample to $2.0 \text{ MPa}\cdot\sqrt{m}$, but the value is stabilized after 800 h. The roughness R does not change much with time, because there is less thermal misfit stress contributing to the roughness of the TGO under isothermal conditions than under thermal cycling. In this case, an average value of $6.4 \mu\text{m}$ is used as R for the CND model.

Figure 0-2 Vickers indentations after 400 h, 800 h, and 1300 h.

Table 0-2 Summary of parameters

Duration (h)	R (μm)	K_p ($\mu\text{m}^2/\text{h}$)	E (GPa)	K_{IC} ($\text{MPa}\cdot\sqrt{\text{m}}$)
0 h	5	0.073	130 ± 12	5.5 ± 1
400 h	7		154 ± 11	4.3 ± 1.4
800 h	7		165 ± 26	2.0 ± 0.9
1300 h	6		223 ± 7	2.0 ± 1.2
	6.4 (mean)			

As discussed in the previous section, the mechanical properties vary with exposure time and temperature due to sintering, BC oxidation and other microstructural changes; therefore, in this study the parameter C is revised to be a function of thermal exposure duration.

With regard to parameter m , it can be expressed as:

$$m = \frac{V_{TGO}}{V_{metal}} \quad (8.11)$$

where V_{TGO} is the volume of TGO and V_{metal} is the volume of consumed BC to form the TGO. The chemical compositions of TGO were determined by EDS on various locations with different contrasts as shown in Figure 0-3 after 400 h of isothermal test, and the results are summarized in Table 0-3. The grey oxides at the locations 1 and 2 are shown to have high contents of Co, Cr, and Ni, implying the existence of spinel $\text{Cr}_2\text{O}_3\cdot\text{Ni}(\text{Cr},\text{Al})_2\text{O}_4\cdot\text{NiO}\cdot\text{Co}_3\text{O}_4$. The black oxide at the interface of TC/BC (location 3) is enriched in Al, showing the formation of Al_2O_3 . Although specific formulation of the mixed oxides is not constant, NiCr_2O_4 is assumed in this study to represent mixed oxides. The overall reactions for the formation of alumina and the spinel is expressed in (A).

Then m can be calculated by molar volumes, V , as:

$$m = \frac{V_{Al_2O_3} + \Lambda V_{NiCr_2O_4}}{2V_{Al} + \Lambda V_{Ni} + 2\Lambda V_{Cr}}, \Lambda = \frac{h_{spinel}}{h_{Al_2O_3}} \quad (8.12)$$

where h_{spinel} and $h_{Al_2O_3}$ are the thicknesses of spinel and Al_2O_3 respectively.

Figure 0-3 Chemical composition evaluations of TGO after the 400 h isothermal test.

Table 0-3 Chemical compositions of TGO at various locations for the sample after 400 h isothermal test (wt.%)

Location	Chemical compositions (wt.%)					
	Al	Cr	Co	Ni	Zr	O
1	6.2	21.4	18.2	12.7	12.3	29.2
2	7.6	5.8	21.5	33.7	8.8	22.6
3	33.4	5.6	8.7	11.6	7.1	33.6

The molar volumes for each compound are $V_{Al} = 10 \text{ cm}^3$; $V_{Ni} = 6.6 \text{ cm}^3$; $V_{Cr} = 7.2 \text{ cm}^3$; $V_{NiCr_2O_4} = 43 \text{ cm}^3$; $V_{Al_2O_3} = 25.6 \text{ cm}^3$. The calculated $m \approx 1.73$ for the three durations.

When all the parameters are determined, C values can be obtained as shown in Figure 0-4. After fitting C linearly with time using:

$$C = \lambda(qt + s) \quad (8.13)$$

The values are obtained for $q = 0.007$, $s = 4.2$. C can be predicted for longer durations.

Figure 0-4 Parameter C vs. time.

7.2.2 Experimental and modelled CND growth

The CND (Crack Number Density) can now be calculated for the three test durations. The probability of CND is normalized by the total number of cracks at a given exposure time as:

$$\rho(c, t) = \frac{n(c, t)}{N(t)} = \frac{\frac{1}{A} [\beta(\eta e^{-\beta\eta} - c e^{-\beta c}) + (e^{-\beta\eta} - e^{-\beta c})]}{\int_0^\infty \frac{1}{A} [\beta(\eta e^{-\beta\eta} - c e^{-\beta c}) + (e^{-\beta\eta} - e^{-\beta c})] dc} \quad (8.14)$$

As discussed above, parameter C is assumed to linearly increase with time at elevated temperature, so C based upon Equation 8.13 is utilized for the CND model. The value of λ is calibrated based on the experimental data with the shortest duration (400 h) and determines to be $\lambda = 1.2$. Because C is a dynamic parameter varying with time, the density should be normalized with variable C . As shown in Equation 8.15, for a certain duration, the probabilities of CND are summed up with C from 0 h to the respective tested duration with a constant increment, and then divided by the increments. In this study, the increment size is set as $0.2 \mu\text{m}^{1/3}$. As shown in Figure 0-5, cracks measured after 400 h,

800 h, and 1300 h of thermal exposure are plotted as histograms, with dashed lines presenting as calculated results.

$$\tilde{\rho}(c, t) = \frac{\sum_{C|t=0}^{C|t} \rho(c, t)}{N}, N = \frac{C|_{t=0} - C|_{t=0}}{\Delta C} \quad (8.15)$$

Figure 0-5 Crack density growth for samples exposed to 1080°C for (a) 400 h, (b) 800 h, and (c) 1300h.

7.3 Discussion

7.3.1 Crack Propagation Mechanism in SPS TBCs

As shown in Figure 0-6, with an increasing thermal exposure time, the porosity in the TC decreases due to the sintering effect, and sub-micron VCs widen because of energy release.

In the first 400 h, cracks propagate through VC slowly due to the high porosity in YSZ

providing sufficient strain tolerance. With extended exposure time, cracks propagating faster through the VCs are increasingly being diverted to overcome VCs due to the sintering effect. Since mode I dominates the crack growth, especially for the large-sized cracks [153], VC TCs possess outstanding strain tolerance. After 1300 h, cracks start to induce delamination within the TC near the interface between TGO/TC, indicating the onset of failure (by TC spallation). Mode I stress relaxation as well as crack deflection contribute to life extension of SPS TC (vs. APS TC) under the high temperature oxidation condition.

Figure 0-6 Crack propagation in SPS TC after exposure at 1080°C for (a) 400 h, (b) 800 h, and (c) 1300 h. (d) Schematic diagram illustrating crack deflection.

7.3.2 Stress Intensity Factor for Various Crack Sizes

Stress intensity factors, K_I , are calculated for the three test durations used in this study and are summarized in Figure 0-7. The horizontal straight line indicates the critical value $2K_{IC}$, and the right intersection c_{max} indicates the crack size at which the crack is no longer propagating. It is concluded that the larger cracks continue to expand with increasing h/R and exposure time. Although these curves show that the crack growth will stop at c_{max} , cracks with larger size than c_{max} are nevertheless detected in the three isothermal tests. The reasons for the formation of cracks with $c > c_{max}$ are as follows: i) the calculation assumes that R is consistent, but in reality the size of imperfections varies along the interface; ii) Equation 8.1 for K_I assumes that the tensile stress for crack tip opening is caused by a single imperfection with no extra stresses in the space, however the roughness of TGO at the interface between the TC/TGO interface introduces many imperfections resulting in a complicated tension and compression distribution, leading to the K curve repeatedly fluctuating beyond the c_{max} ; iii) the neighboring cracks may coalesce during crack propagation during the time.

Figure 0-7 Stress intensity factor vs. crack size

Assuming no crack coalescence happens and the spacing between the two asperities is large enough to neglect the impact on the stress distribution by the neighboring asperity, c_{max} is the most critical crack size for nucleation. For the nucleated cracks smaller than c_{max} , growth to c_{max} occurs rapidly due to high K_I at crack tips; for the nucleated cracks larger than c_{max} , propagation rates are reduced due to low K_I at tips. This behavior is best represented by a gamma distribution as the nucleation rate with a shape factor, $\alpha = 2$, and the mode of the CND is theoretically determined by c_{max} . Based upon the previous description, the quickest crack nucleation rate occurs at $c = c_{max}$, as such Equation 8.7 is used to take derivation of c at c_{max} :

$$\frac{dn_N}{dc} = e^{-\beta c_{max}} - \beta c_{max} e^{-\beta c_{max}} = 0 \Rightarrow \beta = \frac{1}{c_{max}} = \frac{1}{Ch^{2/3}} \quad (8.16)$$

7.3.3 CND predictions

As seen in Figure 0-4, the initial state of the TBC prior to isothermal exposure contains smaller cracks in the range of 0-100 μm . As the TBC is exposed to elevated temperatures, two factors start to govern the growth of larger cracks: the growth of the TGO and the degradation of the TC properties due to sintering. A dynamic value of C is normalized across the expected C range for each exposure time to account for the fact that C evolves with material property changes but is extremely challenging to measure *in situ*. As the evolution of the crack size distribution is determined by larger cracks over longer durations, the crack propagation term of $\frac{\partial[A_n]}{\partial c}$ in Equation 8.2 is varied as TC degrades. It can be seen in Figure 0-4 that the CND model under-predicts cracks in the 0-50 μm range. This is in part due to the use of stress intensity factor, K_I , for connected cracks in the distribution

prediction as well as the variation in properties between the modelled TC and the actual TC. However, since larger, connected cracks are the primary concern for TBC life-prediction, it is assumed that this aspect of under-estimation is not detrimental.

The traditional FEM method for TC failure prediction is to evaluate whether the cracks can reach a size equal to the distance between two asperities [95]. If cracks larger than this distance develop, the TC approaches the end of its useful life. In this study, the mean value of the asperities distance was determined to be 250 μm which is obtained by the same method as R_a . The probability of cracks with a size greater than 250 μm has been determined by integrating the CND from 250 μm to infinity (shown in Figure 0-8). The predicted probability of a crack reaching 250 μm is calculated to be 0.01%, 2% and 11% for 400h, 800h and 1300h of exposures respectively. Based on this method, the **density** of a crack reaching 250 μm at 1500 h is increased to 15%.

Figure 0-8 Probability of existing cracks higher than the critical size.

7.3.4 Suitability of CND Model for SPS TBC

CND model described above only concentrates on the cracks within the TC, but ignores other failure mechanisms such as interfacial fracture between TGO and BC [81] and Al depletion within BC. Thus, CND is not suitable for EB-PVD TCs, where the failure usually occurs within TGO. Based on the results of this study as well as that discussed ref. [140] on SPS TCs, some cracks within the TC may penetrate through the TGO and propagate within the interface between TGO and BC, however, this will not be considered as the main cause for SPS TBC failure. On the contrary, cracks generated at imperfections of the TGO and propagated horizontally within the TC can lead to the ultimate failure of a TBC system. As such, CND model is ideal for predicting crack progression in SPS TBC systems. Based on the comparison between the computed and experimentally determined values, it can be concluded that the model aligns well with the experimental results. In addition, the CND method over predicts the damage by predicting higher probabilities than the measured values for large-sized cracks, which benefits potential users as it provides a more conservative forecast.

However, it is important to realize that the CND model requires mechanical properties of TC as a function of time (and temperature) in order to determine the parameter C for different exposure temperatures and durations, which makes the crack growth prediction in part experimentally based. When the mechanical properties are determined, only one tested coating sample is required to determine the λ value, enabling the CND model to capture crack behavior up to failure.

7.3.5 Summary of crack growth prediction by CND under isothermal

The application of crack numerical density theory (CND) is used to determine the damage state of a TBC produced by SPS technique. The TBC was exposed to an isothermal temperature of 1080°C for a duration of up to 1300 h with specimens removed for examination at 0 h, 400 h, 800 h and 1300 h. Cross sections of the specimens were examined using an SEM, image editing software was used to detect cracks within the TC and determine the rate of growth and roughness of the thermally grown oxide layer. Micro and nano-indentation was used to further determine material properties of the TC including the elastic modulus and fracture toughness. These properties were used to fit a CND model to predict the crack distribution within the TC following isothermal exposure. Probabilities of cracks developing within the TC that can bridge asperities were determined to be 0.04%, 2% and 8.6% for 400h, 800h and 1300h of exposure at the tested temperature of 1080°C, respectively. Provided that the aforementioned material properties can be determined for future SPS TBCs, this CND method contributes to future life prediction models.

8 Chapter: Conclusion and Future Work

8.1 Conclusion

In this study, the oxidation behavior of two substrate alloys HAYNES 233 and INCONEL 625 under isothermal exposure at 1080°C were evaluated first in order to select a more suitable substrate for a SPS TBC system being investigated. Based upon the results, INCONEL 625 was selected as it was able to form a more protective Cr_2O_3 layer covering the entire surface. Results also showed that HAYNES 233 failed to form a complete protective Al_2O_3 over the whole surface of the material. Moreover, minor elemental additions in HAYNES 233 resulted in localized external oxide layers which resulted in debonding process during early phases of testing. As a result, INCONEL 625 was selected as the substrate for the TBC system.

Subsequently a SPS TBC system was tested under isothermal and cyclic conditions with a peak temperature of 1080°C. This particular TBC system failed after 800 cycles under the cyclic condition, but the samples survived at least 1300 h under the isothermal condition. Based upon the cross-sectional analysis, the TBC failure occurred due to the separations of SPS TCs from the TGO/TC interface. The measurements of mechanical properties further delineated that the SPS TC degraded faster under cyclic conditions than that under isothermal conditions because of faster sintering rates due to dynamic diffusion mechanism. The faster sintering rate under cyclic conditions was a result of repeated heating phases and larger in-plane stresses produced during associated cooling phases.

Based upon the simulation of stress distributions within TCs under the cyclic condition, the absolute out-of-plane stresses were higher in VC TCs than that in the coatings without VCs. The stresses concentrated at the tips of the VCs, which explained the formation of horizontal cracks in this vicinity. In addition, the tensile stress at peak

locations on the interface of TGO/TC, located remotely from the VCs, were also enlarged implying reasons for the formation of horizontal cracks within TCs near the TC/TGO interface. These cracks were considered as the primary cause for final TBC failure. Although VCs increased the overall stresses in the coating, they also aided in reducing part of out-of-plane stresses and allowed re-orientation of horizontal cracks. Consequently, these horizontal cracks had less likelihood to form within the same plane, thereby resulting in extended lifetimes.

Lastly, the crack size distributions within SPS TCs were predicted by CND theory for TBC subjected to isothermal conditions. The theory assumed that the failure of TCs were mainly caused by TGO thickening. The modelling was partially based upon the experimental data, including measured mechanical properties and horizontal crack sizes, in order to calculate the probabilities of cracks that can bridge asperities. The modelling results fitted well with the trends of experimental data, providing a useful tool for future TBC life prediction.

This research systematically studied the oxidation behavior of a SPS TBC system and the mechanisms of TC degradations leading to final failure. Both the actual performance assessment and the tools developed to simulate these stresses and crack growth contributed to enhance the understanding and performance prediction of SPS TBCs in gas turbine engines.

8.2 Future work

In the future, the following tasks are recommended:

- 1) FEA simulation could be further optimized to account for additional parameters.

In this study, the temperature of the TBC system was considered to be uniform,

but in reality, temperature gradients in the TBC experienced during heating and cooling, particularly during cyclic conditions. The thermal gradient highly influences the thermal stresses, this should be added into future FEA simulation research.

- 2) In order to determine the thermal gradient within the TBC, thermal diffusivity of SPS TCs should be measured by a laser flash technique. However, the properties of TGO may be challenging to measure.
- 3) Pre-existing horizontal cracks at tips of VCs should be modelled as well, as they would influence the stress distributions in TC. These cracks are assumed to form at the very beginning of service in the current study.
- 4) Explicitly state that crack propagation under cyclic condition will be modelled once thermal stresses can be solved.
- 5) Stress intensity at the tips of horizontal cracks near the interface can be calculated by ABAQUS to delineate the relationship between the stress intensity and exposure time, improving life prediction accuracy.
- 6) In the future, NDT technologies, such as piezo-spectroscopy and/or ultrasound method can be implemented in order to determine the in-situ elastic modulus E . In addition, other mechanical properties such as hardness, fracture toughness, etc., at the elevated temperature should be determined as well.
- 7) Isothermal and cyclic oxidation under engine environment can be simulated by the burner rig to evaluate the performances of SPS TBCs.

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