Thermal Barrier Coatings
– Durability Assessment and Life Prediction

Robert Eriksson

Linköping University
INSTITUTE OF TECHNOLOGY

Department of Management and Engineering
Linköping University, 581 83, Linköping, Sweden
http://www.liu.se

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During the course of the research underlying this thesis, Robert Eriksson was enrolled in the graduate school Agora Materiae, a doctoral program within the field of advanced and functional materials at Linköping University, Sweden.

Cover:
Fractured plasma sprayed zirconia.

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Abstract

Thermal barrier coating (TBC) systems are coating systems containing a metallic bond coat and a ceramic top coat. TBCs are used in gas turbines for thermal insulation and oxidation resistance. Life prediction of TBCs is important as high-temperature exposure degrades the coatings through mechanisms such as thermal fatigue and the formation and growth of thermally grown oxides (TGOs). This thesis presents research on durability assessment and life prediction of air plasma sprayed TBCs.

The adhesion of thermal barrier coatings subjected to isothermal oxidation, thermal cycling fatigue and thermal shock was studied. The adhesion strength and fracture characteristics were found to vary with heat treatment type.

The influence of interdiffusion between bond coat and substrate was studied on TBCs deposited on two different substrates. The thermal fatigue life was found to differ between the two TBC systems. While fractography and nanoindentation revealed no differences between the TBC systems, the oxidation kinetics was found to differ for non-alumina oxides.

The influence of bond coat/top coat interface roughness on the thermal fatigue life was studied; higher interface roughness promoted longer thermal fatigue life. Different interface geometries were tried in finite element crack growth simulations, and procedures for creating accurate interface models were suggested.

The influence of water vapour and salt deposits on the oxidation/corrosion of a NiCoCrAlY coating and a TBC were studied. Salt deposits gave thicker TGOs and promoted an Y-rich phase. The effect of salt deposits was also evident for TBC coated specimens.

A microstructure-based life model was developed using the Thermo-Calc software. The model included coupled oxidation-diffusion, as well as diffusion blocking due to the formation of internal oxides and pores. The model predicted Al-depletion in acceptable agreement with experimental observations.
Preface

This thesis summarises the work I have done during my time as a Ph.D. student at Linköping University, 2008–2013. The thesis consists of two parts. The second part, which is the main part of the thesis, consists of seven scientific papers that summarises my work during the research project. The first part of the thesis gives background to the research and provides general information about the topics studied more in detail in the appended papers. The first part also gives the necessary knowledge for the non-specialist reader. The introductory parts of this thesis is based on my licentiate thesis *High-temperature degradation of plasma sprayed thermal barrier coating systems* from 2011.

Many thanks to my supervisor, Sten Johansson, and others involved in the research project, Håkan Brodin, Sören Sjöström, Xin-Hai Li and Lars Östergren, for their help and support over the years.

I would also like to thank my many colleagues at the Division of Engineering Materials for contributing to such a nice work environment full of creativity, intellect, curiosity and humour. I would especially like to thank Kang Yuan with whom I have had the opportunity to cooperate during my last years as a Ph.D. student.

Robert Eriksson
List of papers

The thesis is based on the following papers:


Acknowledgements

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Kang Yuan, Mikael Segersäll, Jan Kanesund and Ru Lin Peng are acknowledged for contributing to Fig. 5, 6 and 7.
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>APS</td>
<td>air plasma spray</td>
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<tr>
<td>BC</td>
<td>bond coat</td>
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<tr>
<td>BRT</td>
<td>burner rig test</td>
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<tr>
<td>CTE</td>
<td>coefficient of thermal expansion</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapour deposition</td>
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<tr>
<td>EB-PVD</td>
<td>electron beam physical vapour deposition</td>
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<td>EBSD</td>
<td>electron backscatter diffraction</td>
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<td>EDS</td>
<td>energy dispersive spectroscopy</td>
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<td>FCT</td>
<td>furnace cycle test</td>
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<td>FE</td>
<td>finite element</td>
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<td>FEA</td>
<td>finite element analysis</td>
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<td>FEM</td>
<td>finite element method</td>
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<td>HVOF</td>
<td>high-velocity oxy-fuel spray</td>
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<tr>
<td>InCF</td>
<td>intrinsic chemical failure</td>
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<tr>
<td>MICF</td>
<td>mechanically induced chemical failure</td>
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<tr>
<td>PBR</td>
<td>Pilling-Bedworth ratio</td>
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<tr>
<td>PS</td>
<td>plasma spray</td>
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<td>PVD</td>
<td>physical vapour deposition</td>
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<td>RE</td>
<td>reactive element</td>
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<td>SEM</td>
<td>scanning electron microscope</td>
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<tr>
<td>TBC</td>
<td>thermal barrier coating</td>
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<td>TC</td>
<td>top coat</td>
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<td>TCF</td>
<td>thermal cycling fatigue</td>
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<tr>
<td>TCP</td>
<td>topologically close-packed</td>
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<tr>
<td>TET</td>
<td>turbine entry temperature</td>
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<td>TGO</td>
<td>thermally grown oxide</td>
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<tr>
<td>VPS</td>
<td>vacuum plasma spray</td>
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<td>WDS</td>
<td>wavelength dispersive spectroscopy</td>
</tr>
<tr>
<td>Y-PSZ</td>
<td>yttria partially stabilised zirconia</td>
</tr>
<tr>
<td>YAG</td>
<td>yttrium aluminium garnet</td>
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<tr>
<td>YAP</td>
<td>yttrium aluminium perovskite</td>
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Part I

Background and theory
Introduction

1.1 Background

The technology of gas turbines arose during the early to mid 1900s [1] and is now commonly used for power production and aircraft propulsion. Gas turbines are closely integrated in today’s society and technology, and the development towards higher efficiency and fuel economy is naturally desirable [1–3].

Fig. 1 shows two examples of gas turbines: Fig. 1 a) shows a stationary gas turbine for power production, and Fig. 1 b) shows an aircraft engine. Fig. 1 also marks the major parts of a gas turbine: 1) the compressor, which compresses the air, 2) the combustor, in which air and fuel are mixed and ignited, and 3) the turbine which drives the compressor and provides the power output for, for example, electric power production. The latter two, combustor and turbine, operate in a very demanding high-temperature environment.

1.1.1 Gas turbine development towards higher efficiency

Since the performance of gas turbines depends on the temperature in the turbine part of the gas turbine [4], an increase in efficiency can be achieved by increasing combustion temperature [5–9]. Consequently, the development of gas turbines has driven the service temperature to higher and higher levels. Fig. 2 shows an example from the aircraft industry where the turbine entry temperature (TET) has kept increasing since the 1940s.

Increasing operating temperatures offer several challenges in the field of engineering materials. As the operating temperature is driven to higher levels, material issues such as oxidation, corrosion, creep and loss of strength are inevitable [4, 9–12]. The state-of-the-art metallic materials for high temperature applications, the superalloys, are already operating at their maximum capacity
Figure 1: Gas turbines for power production and aircraft propulsion. a) Land-based gas turbine, SGT 750, for power production, (courtesy of Siemens Industrial Turbomachinery). b) Aircraft engine RM 12, used in JAS 39 Gripen, (courtesy of Volvo Aero Corporation).

and further increase in operating temperature cannot be achieved by further alloy development alone [4, 8, 10, 13–15]. This is illustrated in Fig. 2 which shows the capability of typical superalloys compared to the TET; as seen, the TET now exceeds the material capability.

Furthermore, the increasing demand for a more energy sustainable and environmental friendly society has drawn attention to the use of bio-fuels in gas turbines [16]. The incorporation of bio-fuels in gas turbine technology may cause changes in the operating conditions in the turbine which may also have consequences for the metallic materials used there.
The current and future research on gas turbine technology is therefore largely influenced by the striving for higher fuel efficiency, lower emissions and the ability to use renewable fuels in gas turbines. The Swedish research programme TURBO POWER, of which the research presented in this thesis is a part, aims at achieving this. The programme is run as a collaboration between Siemens Industrial Turbomachinery, GKN Aerospace Engine Systems, the Swedish Energy Agency and several Swedish universities. The research programme TURBO POWER seeks to:

- Improve fuel efficiency of power-producing turbomachines, thereby reducing emissions and decreasing environmental strain.
- Improve fuel flexibility by making possible the use of alternative fuels.
- Reduce operating costs of power-producing turbomachines.

By developing technology and generating knowledge for university and industry, TURBO POWER will contribute to a more sustainable and efficient energy system in Sweden. The research aims at being applicable and governed by needs.

1.1.2 The importance of coatings

As the temperature approaches the upper limit of material capability, phenomena such as creep, loss of mechanical properties, oxidation and corrosion occur.
rapidly and limit the life of metallic materials [7, 9, 10, 13, 17–19]. As an example, Fig. 3 shows the variation of tensile strength with temperature for some common superalloys. As seen in Fig. 3, superalloys cannot maintain their tensile strength at temperatures typical in gas turbine combustors and turbines; the combustion temperature of gas turbines is even approaching the melting temperatures of the base-elements in superalloys (nickel, cobalt and iron), see Fig. 3.

![Figure 3: Tensile strength of some superalloys as function of temperature.](image)

By lowering the temperature below the point at which the alloys lose their engineering properties, they can still be used as structural materials. The high operating temperatures of today’s gas turbines – and the even higher temperatures of tomorrow’s gas turbines – are made possible by the use of air cooling and thermal insulation in the form of thermal barrier coatings (TBC) [4, 8, 10, 13–15]. Air cooling, if too ample, has the disadvantage of reducing the achievable efficiency increase somewhat [13, 20] while thermal barrier coatings offer an effective mean to provide insulation and oxidation resistance [5–8, 14, 18].

Fig. 4 a) shows a schematic drawing of a thermal barrier coating system; the three parts of a thermal barrier system are: 1) substrate (component), 2) bond coat (BC), and 3) top coat (TC); with time at high temperature, a layer of thermally grown oxides (TGO) develops between the bond coat and the top coat [7].

The top coat is made of a ceramic material with low heat conductivity and thus provides the necessary thermal insulation. The metallic bond coat ensures good adhesion of the ceramic coating and provides oxidation resistance [12, 17]. The effect of applying a TBC system onto a gas turbine component is illustrated in Fig. 4 b): the top coat introduces a temperature gradient and
hence enables high combustion temperatures while avoiding high temperature degradation of metallic parts.

The use of TBCs in gas turbines is, however, not entirely without its problems. Since the ceramic top coat and metallic bond coat have different coefficient of thermal expansion (CTE), stresses arise in the bond coat/top coat interface due to temperature variations (such as start and stop of the turbine). Stresses are also introduced in the interface due to growth of the TGO layer. The interface stresses eventually lead to failure of the TBC by spallation of the top coat, which deprives the TBC system of its heat insulating capability.

1.2 Aim of this work

Thermal barrier coating systems currently offer an effective method for increasing gas turbine combustion temperature and thereby increasing efficiency [4, 8, 10, 13, 14]. To fully utilise protective coatings in gas turbines, reliable life prediction of TBCs must be achieved [5, 14, 17]. TBCs are only beneficial as long as they adhere to the metallic parts which they are meant to protect. Understanding of the failure mechanisms of TBCs and the development of life models are therefore important areas of research [4, 5, 12, 17].

The current research project has involved studies that contributed to the understanding of: TBC durability, methods for evaluation of TBC life and durability, and life modelling aspects. The performed research has aimed at developing and improving life models for air plasma sprayed TBCs in gas turbines. For this purpose, the research project has involved testing of several different coating systems as well as the use of diverse testing methods.
Evaluation of durability of TBCs has included: isothermal oxidation, furnace cycling, burner rig test, corrosion test, adhesion tests on thermally degraded specimens, nanoindentation as well as microscopy studies on microstructure and oxide composition and growth kinetics. The study includes the investigation of several degrading mechanisms of TBCs during isothermal and cyclic high-temperature exposure: fatigue damage, interface TGO growth, influence of substrate material on life, influence of BC/TC interface roughness on life, and cracking and sintering of the top coat. Life prediction was tried both from a fracture mechanics point of view and from an oxidation/interdiffusion-based point of view.
2

Materials for high temperature applications

High temperature materials are materials that can operate at temperatures close to their melting temperatures while still maintaining many of the typical room temperature characteristics of engineering materials, such as high strength and microstructural stability [4, 10, 11].

The base material makes up the structural parts of the gas turbine and their chemistry may often be chosen for good mechanical properties rather than resistance to environmental degradation, i.e. oxidation and corrosion [11]. Three classes of alloys: Ni-base, Co-base and Fe–Ni-base, collectively referred to as superalloys, have shown to have good to excellent high temperature properties and are widely used as base material for high temperature applications [4, 10, 11].

2.1 Physical metallurgy of systems containing Ni, Co, Fe, Cr and Al

2.1.1 Base materials

In superalloys, the solid-solution γ-Ni phase – which has the face centred cubic (FCC) atomic arrangement – constitutes the matrix phase. Ni-base superalloys can be solid-solution strengthened, such as Haynes 230 and Hastelloy X, or precipitation hardened, such as Waspaloy and Inconel 738, 939 and 718. As seen in Fig 3, precipitation strengthened alloys typically have higher strength than solid-solution strengthen alloys and are used in more demanding high temperature environments [11]. Solid-solution strengthened materials have ad-
vantages when it comes to processing and have, for example, better weldability [11]; they can also be manufactured in complex geometries from powders through laser melting techniques, see for example Saarimäki [21].

For solid-solution strengthened alloys, the alloying elements are chosen from Fe, Co, Cr, Mo, W, Ti and Al [10]. Al, Cr, W and Mo are potent solid-solution strengtheners largely due to their different atomic radius compared to Ni [10]. For precipitation hardened alloys the alloying elements are typically chosen from: Al, Ti, Ta, and sometimes Nb which promotes the formation of the γ′ or γ″ precipitates in the γ-matrix [4, 10, 11], shown in Fig. 5. In addition, minor amounts of elements like Hf, Re, Zr, C and B may be added for various purposes. The compositions of some common Ni-base alloys are given in Table 1.

Table 1: Composition of some Ni-base alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Co</th>
<th>Fe</th>
<th>Cr</th>
<th>W</th>
<th>Mo</th>
<th>Al</th>
<th>Ti</th>
<th>Nb</th>
<th>Ta</th>
<th>Si</th>
<th>C</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haynes 230</td>
<td>57a</td>
<td>5b</td>
<td>3b</td>
<td>22</td>
<td>14</td>
<td>2</td>
<td>0.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.4</td>
<td>0.1</td>
<td>0.015b</td>
</tr>
<tr>
<td>Hastelloy X</td>
<td>47a</td>
<td>1.5</td>
<td>18</td>
<td>22</td>
<td>0.6</td>
<td>9</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1b</td>
<td>0.1</td>
<td>0.008b</td>
<td></td>
</tr>
<tr>
<td>Inconel 738</td>
<td>61.4a</td>
<td>8.5</td>
<td>–</td>
<td>16</td>
<td>2.6</td>
<td>1.75</td>
<td>3.4</td>
<td>3.4</td>
<td>0.9</td>
<td>1.75</td>
<td>–</td>
<td>0.17</td>
<td>0.01</td>
</tr>
<tr>
<td>Inconel 939</td>
<td>47.3a</td>
<td>19</td>
<td>0.5b</td>
<td>22.5</td>
<td>2</td>
<td>–</td>
<td>1.9</td>
<td>3.7</td>
<td>1</td>
<td>1.4</td>
<td>0.2b</td>
<td>0.15</td>
<td>0.01</td>
</tr>
<tr>
<td>Inconel 718</td>
<td>52.5</td>
<td>1b</td>
<td>18.4b</td>
<td>19</td>
<td>3.1</td>
<td>0.5</td>
<td>0.9</td>
<td>5.1</td>
<td>–</td>
<td>0.35b</td>
<td>0.08b</td>
<td>0.006b</td>
<td></td>
</tr>
<tr>
<td>Waspaloy</td>
<td>58a</td>
<td>13.5</td>
<td>2b</td>
<td>19</td>
<td>4.3</td>
<td>1.5</td>
<td>3</td>
<td>–</td>
<td>–</td>
<td>0.15b</td>
<td>0.08</td>
<td>0.006</td>
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</table>

a) balance
b) maximum

The γ′ phase is an aluminide with formula Ni₃(Al, Ti); the Al and Ti may be substituted by Ta and Nb, and the Ni can, to some extent, be substituted by Co.
or Fe [11]. The \( \gamma' \) phase is an ordered phase with the L1\(_2\) structure. The morphology of the \( \gamma' \) precipitates depends on their mismatch with the surrounding parent lattice and includes: cubical, small spherical particles and arrays of cubes [4, 11]. Modern precipitation hardened alloys may contain \( \gtrsim 60 \% \ \gamma' \) [4, 11]. An interesting characteristic of \( \gamma' \) is its increasing tensile strength with increasing temperature [11].

For Ni–Fe alloys, such as Inconel 718, the addition of Nb may cause the precipitation of \( \gamma''-\Ni_3\Nb \) [10, 11] which acts as the primary strengthening micro-constituent. Alloys that rely on the strengthening from \( \gamma''-\Ni_3\Nb \) are limited to operating temperatures below \( \sim 650^\circ\text{C} \) as the tetragonal \( \gamma''-\Ni_3\Nb \) otherwise will transform to a stable orthorhombic \( \delta-\Ni_3\Nb \) which does not add to strength [11].

The addition of C and B enables the formation of carbides and borides. Carbide formers include Cr, Mo, W, Nb, Ti, Ta and Hf, which form carbides of various stoichiometry, such as MC, \( \M_{23}C_6 \) and \( \M_6C \). Common boride formers are Cr and Mo, which form \( \M_3B_2 \); boron tends to segregate to grain boundaries [10, 11]. Carbon and boron perform an important role as grain boundary strengtheners and are consequently added in greater amounts to polycrystalline alloys [4].

MC carbides typically form at high temperatures, for example during solidification and cooling in the manufacturing process, while \( \M_{23}C_6 \) and \( \M_6C \) form at lower temperatures: 750–1000 °C [10]. The MC carbide typically forms from Ti, Hf and Ta [4, 11], while the \( \M_{23}C_6 \) is promoted by high Cr contents and the \( \M_6C \) is promoted by large fractions of W and Mo [10]. The MC carbide may form within grains as well as at grain boundaries; the \( \M_{23}C_6 \) carbides are preferably formed at grain boundaries.

The MC carbides may decompose to form \( \M_{23}C_6 \) and \( \M_6C \) carbides during high temperature exposure during operation or heat treatment [22, 23]. The following reactions have been suggested [10]:

\[
\text{MC} + \gamma \rightarrow \M_{23}C_6 + \gamma' \quad (A)
\]

\[
\text{MC} + \gamma \rightarrow \M_6C + \gamma' \quad (B)
\]

A group of intermetallics generally considered harmful to Ni-base alloys, are the topologically close-packed (TCP) phases, such as the \( \sigma \) phase. These phases may form in alloys rich in Cr, Mo and W [4]. The \( \sigma \) phase has the general formula \( (\Cr,Mo)_{x}(\Ni,Co)_{y} \) [10]; it may have a plate or needle-like morphology and may appear in grain boundaries, sometimes nucleated from grain boundary carbides [10, 11].
2.1.2 Overlay coatings

**Overlay coatings** are deposited on top of the substrate without interacting much with the substrate [13, 24]. This can be contrasted to **diffusion coatings** which are coatings that are formed through interdiffusion with the substrate and the coating is formed as the coating elements interact with the substrate [13, 24].

Overlay coatings are deposited by methods such as plasma spraying (PS), electron beam physical deposition (EB-PVD) and high velocity oxy-fuel spraying (HVOF). These deposition methods use alloy feedstocks and the deposited coating may therefore have a composition completely different from the substrate. Overlay coatings are often chosen from the MCrAlX family of alloys where M is either Ni, Co or Fe or a combination of them; X denotes additions of reactive elements (RE), which in various ways improve the properties of the coating.

As for the base material, MCrAlX coatings consist of a γ-matrix with the aluminium largely bound in aluminides. The γ′ aluminide may be present in the microstructure, but for such large amounts of Al as are commonly used in MCrAlX alloys, another aluminide forms: β-NiAl [15, 25]. For MCrAlX coatings, most of the aluminium is bound in this phase and the two main microconstituents of many MCrAlX coatings are γ and β. In addition, MCrAlX may contain chromium rich σ–(Cr, Co) and α-Cr [25]. The latter may occasionally precipitate in the β phase [25, 26]. Thus, a typical MCrAlX alloy may have microstructures such as: γ + β or γ/γ′ + β/α both with the possible addition of σ–(Cr, Co) [12, 27–29].

Fig. 6 shows the phases present at high temperature for the Ni–Cr–Al system with different additions of Co. Fig. 7 and 8 shows the microstructure of two MCrAlX coatings which have been cooled in air from high temperature; the figures show how electron backscatter diffraction (EBSD) and energy dispersive spectroscopy (EDS) can be used to identify the γ, γ′, β and σ phases.

2.2 Thermal barrier coating systems

A protective coating for high temperature applications must lower the temperature of the substrate and provide the oxidation and corrosion resistance which the base material lacks. The requirements on a protective coating can be summarised as [13]:

- The coating must have low thermal conductivity.
- The coating needs to have good oxidation and corrosion resistance.
A protective coating must have high melting temperature and retain its structural integrity in the full interval of operating temperatures.

The coating should have a coefficient of thermal expansion close to the substrate on which it is deposited to avoid thermal mismatch.

As no single material possesses all of those properties, protection of superalloys is typically achieved by material systems containing an insulating coating (top coat) deposited on top of an oxidation resistant coating (bond coat). The bond coat also provides adhesion of the top coat to the substrate. A TBC system is shown in Fig. 9.

Figure 6: Phase diagrams for some NiCoCrAl alloys established by Thermo-Calc. a) NiCrAl + 10 wt.% Co at 950 °C b) NiCrAl + 10 wt.% Co at 1100 °C c) NiCrAl + 20 wt.% Co at 950 °C d) NiCrAl + 20 wt.% Co at 1100 °C
Figure 7: Microstructure in a NiCoCrAlY coating analysed by EBSD and EDS: a) electron micrograph, b) EBSD results showing crystal structure, c) EDS results showing Al content, and d) EDS results showing Cr content.

Figure 8: Microstructure in a NiCoCrAlY coating analysed by EBSD: a) electron micrograph, b) phases identified by EBSD.
2.2.1 Top coat materials

The top coat is the part of the TBC system that provides thermal insulation. As any insulation, the top coat must be combined with internal cooling to keep the temperature low in the substrate; the top coat only introduces a steep temperature gradient. The temperature drop in a top coat, 300 µm in thickness, can be as high as 200–250 °C [4, 7, 11, 13].

The 6–8 wt.% yttria partially-stabilised zirconia (Y-PSZ) has arisen as the industry standard for top coat material [30]. This is largely due to its combination of low thermal conductivity and relatively high coefficient of thermal expansion [7, 30]. The software CES provides a convenient tool for illustrating this; Fig. 10 shows a diagram of thermal conductivity and thermal expansion for a number of technical ceramics and some Ni-based alloys; it can be seen that zirconia has the desired combination of low thermal conductivity and high thermal expansion.

Pure zirconia (ZrO₂) is allotropic: monoclinic up to 1170 °C, tetragonal in the interval 1170–2370 °C and cubic up to the melting point at 2690 °C. The tetragonal to monoclinic transformation is martensitic in nature and involves a 3–5% volume increase that induces internal stresses which compromise the structural integrity of the ceramic [13, 31]. The tetragonal–monoclinic transformation is problematic since it occurs in the range of the operating temperatures in gas turbines.

The detrimental phase transformation can be avoided by stabilising the tetragonal phase. Various oxides, such as CaO, MgO, Y₂O₃, CeO₂, Sc₂O₃ and In₂O₃
Thermal expansion coefficient (µstrain/°C)

Thermal conductivity (W/m.°C)

Thermal expansion coefficient (µstrain/°C)

Thermal conductivity (W/m.°C)

Figure 10: Thermal conductivity and thermal expansion coefficient for zirconia compared to some other ceramics and Ni-alloys. Chart from CES EduPack 2012, Granta Design Limited, Cambridge, UK, 2012.

[13, 15, 30], can be added to stabilise the tetragonal phase, but yttria has become the most common. The optimum amount of 6–8 wt.% of yttria is based on the work of Stecura [32] who showed that TBCs with ~ 6 wt.% had the highest fatigue life in a thermal cycling test; see Fig. 11.

The phase being stabilised by the addition of 6–8 wt.% Y₂O₃ is the non-transformable tetragonal phase, t', which is stable from room temperature to approximately 1200 °C [4, 7, 30]. The t' phase is formed by rapid cooling during coating deposition and is a metastable phase [30]. At high-temperature exposure, the t' phase starts to transform to the equilibrium tetragonal and cubic phases. The t' → cubic + tetragonal transformation occurs as the Y-PSZ is only partially stabilised. The addition of > 11 wt.% Y₂O₃ would stabilise the cubic phase from room temperature to the melting temperature and thus enable higher operating temperatures, but, as shown by Fig. 11, that would give a shorter fatigue life. The high-temperature transformation of t' → cubic + tetragonal enables the undesired tetragonal → monoclinic transformation on cooling [33]. Hence, there exists an upper limit to the practical operating temperature of partially-stabilised zirconia.
Figure 11: The thermal fatigue life of yttria-stabilised zirconia as function of yttria content. Adapted from Stecura [32]

2.2.2 Bond coat materials

While the Y-PSZ top coat provides the necessary thermal insulation, it does not offer any protection against oxidation and corrosion. The Y-PSZ coating readily lets oxygen through and causes the underlying metal to oxidise [30]. To prevent the substrate from oxidising, an oxidation resistant bond coat is incorporated between the substrate and the top coat. The bond coat is chosen from alloys with excellent oxidation properties. Furthermore, the bond coat improves adhesion between the top coat and the substrate, particularly for plasma sprayed coatings.

While bond coats can be made from diffusion coatings [34], overlay coatings are probably the most used and most developed for use as bond coats. Overlay coatings enable elaborate alloy design as overlay coatings are independent in chemistry from the substrate on which they are deposited; therefore, numerous variations on the MCrAlY concept exist: Ni–(0–30 wt.% Co)–(10–30 wt.% Cr)–(5–20 wt.% Al)–(≤ 1 wt.% Y) covers the range of many bond coat compositions. Bond coat alloys contain the addition of one or several reactive elements. The purpose of the REs is often to improve oxide scale adhesion; even RE additions in the order of ~ 0.1 wt.% may increases adhesion of the Al oxide scale [35]. Y is the most widely used (typically ≤ 1 wt.%) [7, 9, 12, 17, 30, 36, 37], but other common additions include: Ce, Hf, Zr, Si, La, Re and Ta [13, 22, 30, 36].

MCrAlY coatings achieve oxidation and corrosion resistance through the
formation of a protective oxide scale in the bond coat/top coat interface. Such protective scales need to be: stable at high temperatures, dense, slow-growing and exhibit good adhesion to the coating [15]. Three oxides, alumina (Al$_2$O$_3$), chromia (Cr$_2$O$_3$) and silica (SiO$_2$), have the potential to fulfil these requirements [15, 38]. At temperatures common in gas turbines, a continuous layer of alumina is usually the most beneficial for TBC life [11, 12].

The necessary ability to form a layer of protective alumina influences the choice of chemistry for these alloys. The interfacial TGO is protective only as long as it consists of predominantly Al$_2$O$_3$, and as long as it is intact and adherent to the bond coat. The chemistry of the bond coat must be chosen to assure that: 1) aluminium is the preferred oxidising species, 2) the alumina has good adherence to the bond coat and 3) the alumina is reformed if it is damaged. A prediction of what kind of oxides an alloy will form can be obtained by an oxide map, such as the one showed in Fig. 12 for the Ni–Cr–Al system. There exists a critical Al content below which alumina cannot be formed. For example, Fig. 12 shows that \( \sim 20 \text{ wt.}\% \text{ Al} \), \( \sim 35 \text{ at.}\% \text{ Al} \), is needed to ensure Al$_2$O$_3$ growth in a Ni–Al system. However, the addition of Cr promotes the formation of a protective Al$_2$O$_3$ scale [15]; with the addition of 5 wt.\% Cr, \( \sim 5 \text{ at.}\% \), the alloy can form Al$_2$O$_3$ at an Al content as low as \( \sim 5 \text{ wt.}\% \), \( \sim 10 \text{ at.}\% \).

![Oxide map for the Ni–Cr–Al system at 1000 °C. Areas denoted Cr$_2$O$_3$ and NiO may also give internal oxidation of Al$_2$O$_3$. Based on Wallwork and Hed [39].](image)

Al and Cr are consequently added in amounts of \( \geq 5 \text{ wt.}\% \) to improve oxidation and corrosion resistance by assuring the formation of a protective alumina scale. The composition of the bond coat must also be chosen to account for the
depletion of aluminium during high temperature exposure by consumption of Al through oxidation and interdiffusion with the substrate; most bond coats are consequently quite rich in Al [30]. As the Al content in the coating drops, the $\beta$ and $\gamma'$ phases will dissolve [22]. Two possible decomposition routes are [11, 15, 26, 40]:

$$\beta \rightarrow \gamma \quad \text{(C)}$$

$$\beta \rightarrow \gamma + \gamma' \rightarrow \gamma \quad \text{(D)}$$

### 2.3 Manufacturing of TBCs

TBC systems are manufactured by methods belonging to process families such as thermal spraying, physical vapour deposition (PVD) and chemical vapour deposition (CVD). The group of manufacturing methods collectively referred to as thermal spraying includes processes such as plasma spraying and high-velocity oxy-fuel spraying, both commonly used for manufacturing of TBC systems [5, 7, 14, 19, 30]. Plasma spraying can be conducted in air or in vacuum and is, accordingly, referred to as atmospheric plasma spraying (APS) and vacuum plasma spraying (VPS) or, alternatively, low pressure plasma spraying (LPPS).

The raw materials for manufacturing of bond coats and top coats are typically in powder form. The plasma spray process uses a plasma jet to melt the feedstock powder into droplets which are sprayed onto the substrate: powder is introduced by a carrier gas into the plasma jet, melted and propelled towards the substrate [19]. The characteristics of plasma sprayed coatings are largely influenced by spraying conditions such as plasma jet velocity and the droplet dwell time in the plasma jet [19].

![Schematic drawing of a plasma gun. Based on Ref. [41.]](image)

A schematic drawing of a plasma gun is shown in Fig. 13. The plasma gas, for example argon, is brought into the plasma gun and led through an electric field...
that ionises the gas to produce plasma; the plasma may reach temperatures as high as 20,000 °C [19]. Due to the high temperature, the anode is water cooled and the cathode is typically made from tungsten which has a sufficiently high melting temperature and is a good thermionic emitter [19].

2.3.1 Microstructure of thermal spray coatings

The plasma spraying process gives rise to a very characteristic microstructure where droplets from the spraying process can be discerned as flat, so called, splats. As the molten droplets impact on the substrate, they form thin disc-shaped splats which cool on impact and solidify rapidly; for metal coatings, with a speed of up to $10^6$ K/s [19].

Atmospheric plasma sprayed metallic coatings have microstructures that include constituents such as splats, oxide inclusions/stringers, pores and unmelted or partially melted particles. The microstructural characteristics of an APS deposited bond coat are shown in Fig. 14 a) and can be contrasted to a VPS deposited bond coat, shown in Fig. 14 b), whose characteristic features are the absence of oxide stringers and lower porosity. The lower oxide fraction in VPS coatings are caused by the spraying being performed in vacuum. The HVOF process produces metallic coatings similar in appearance to the VPS coating.

For ceramic coatings, the rapid solidification typically causes a columnar grain structure within each splat [42, 43], shown in Fig. 15 a). The typical splat-on-splat structure is easily seen in Fig. 15 b) where it can also be seen that the splats segment by forming a cracked-mud-like pattern of microcracks. Such cracking is due to stresses caused by contraction during the rapid cooling of the splat [42]. Fig. 15 b) also shows interlamellar delaminations [30, 42, 44–46]. These crack-like voids are caused by the low area of contact between splats which may be as low as 20% [47]. Both the splat microcracks and interlamellar delaminations can be readily seen on cross-sections, as shown in Fig. 15 c). The APS process also gives rise to porosity, see Fig. 15 d). In the top coat, such porosity is desirable as it decreases the thermal conductivity of the coating [30]. Porosity levels in TBCs typically lie in the interval 5–20%.
Figure 14: Microstructure of plasma sprayed MCrAlY coatings. a) APS coating showing oxide inclusions/stringers, arrows, and partially melted particles, marked by $A$. b) VPS coating without oxide stringers and with lower porosity.

Figure 15: Microstructural characteristics of an APS top coat. a) Columnar grain structure in a splat. b) Fractured top coat showing the splat-on-splat structure, $C$; interlamellar delaminations, $B$; and cracking of the splats, $A$. c) Cross-section of a top coat showing interlamellar delaminations, $B$, and through-splat cracks, $A$. d) Cross-sectioned top coat showing porosity, $D$. 
Oxidation of coatings

The oxidation kinetics of high temperature alloys typically obey an Arrhenius-type equation [48]

$$k = k_0 e^{-\frac{Q}{RT}}$$  \hspace{1cm} (1)

where $k$ is the oxide growth rate constant, $Q$ is the activation energy, $T$ the temperature in K, $R = 8.314 \text{ J/(mol K)}$ is the gas constant and $k_0$ is a constant. Oxidation rate consequently increases exponentially with temperature and oxidation at high temperatures may be very fast. The formation of a protective layer of BC/TC interface TGOs is essential for oxidation resistance but is a sacrificial process during which the coating is consumed. Oxidation is a degrading mechanism that will eventually lead to the breakdown of the protective TGOs and might induce failure of TBCs.

The oxidation of the BC can be divided into three stages, shown in Fig. 16: 1) a *transient stage* of simultaneous oxidation of all oxide-forming species in the bond coat, 2) a *steady-state stage* of formation and growth of a protective oxide scale, and 3) a *breakaway stage* of rapid oxidation and spallation [38]. The second stage gives rise to a protective oxide scale whereas the third stage causes failure of the TBC system.

### 3.1 Formation of a protective oxide scale

The transient stage is the stage of oxidation before a continuous oxide layer has formed on the metal surface and during which all oxide-forming species in the alloy (Ni, Co, Cr, Al) might form oxides. The composition of the transient oxides is influenced by parameters such as: temperature, partial oxygen pressure,
coating composition and coating microstructure [49]; low partial oxygen pressure, for example, may promote the formation of alumina [50]. Each element’s affinity for oxygen will determine how it forms oxides. An Ellingham diagram, such as the one in Fig. 17, provides information at which oxygen partial pressure an oxide can form according to [51]:

$$P_{O_2}^{M/M_{ox}} = \exp\frac{\Delta G^o}{RT}$$

This is the dissociation pressure of the oxide; the partial pressure of oxygen must be higher than the dissociation pressure for the oxide to form. An Ellingham diagram can be used to rank the order in which the oxides will form; as seen in Fig. 17, Al will oxidise at lower oxygen partial pressure and thus oxidises more easily than, for example, Ni and Co.

The transient stage is usually quite short, typically $\lesssim 1$ h for Ni–Cr–Al systems oxidised at 1000–1200°C [52, 53]. Transient oxides include Cr$_2$O$_3$, NiO, CoO, spinel type (Ni, Co)(Cr, Al)$_2$O$_4$ and various forms of alumina: $\gamma$-, $\theta$-, $\alpha$-Al$_2$O$_3$ [40, 49, 52–55].

The transition from transient oxidation to the slower steady-state stage of growth occurs when a continuous oxide layer is formed and the oxidation rate becomes controlled by the diffusion rate of oxygen and metal ions through the oxide layer. Such diffusion controlled oxidation is typically described by a power-law expression:

$$h_{TGO} = h_0 + k t^{\frac{1}{2}}$$

where $h_{TGO}$ is the thickness, (or weight gain per area), of the formed oxide, $h_0$ is the thickness of the transient oxides, $k$ is the growth rate constant and $t$ is the...
high temperature exposure time. The classical oxidation law is parabolic \((n = 2)\) [56] but subparabolic models \((1/n < 0.5)\) are also in use [12, 57–59]; particularly the cubic law \((n = 3)\) has become common.

Protective oxide scales can be provided by Al, Cr and Si which form \(\text{Al}_2\text{O}_3\), \(\text{Cr}_2\text{O}_3\) and \(\text{SiO}_2\) [11, 12, 38]. At high temperature, \(\text{Al}_2\text{O}_3\) is usually the protective oxide. The use of \(\text{Cr}_2\text{O}_3\)-forming coatings is restricted to somewhat lower temperatures, \((\lesssim 950 °C)\) [11, 15], as \(\text{Cr}_2\text{O}_3\) may decompose to volatile \(\text{CrO}_3\) and evaporate according to [11, 12, 60]:

\[
\text{Cr}_2\text{O}_3\text{(solid)} + \frac{3}{2}\text{O}_2\text{(gas)} \rightleftharpoons 2\text{CrO}_3\text{(gas)} \quad (E)
\]

The use of \(\text{SiO}_2\)-forming coatings is also limited to lower temperatures as they may form low-melting or brittle phases [15].

A protective layer of interface \(\text{Al}_2\text{O}_3\) can be seen in Fig. 18; Fig. 18 a) shows a fracture surface produced by tearing off the top coat, thus exposing the underlying interface TGO, and Fig. 18 b) shows a polished cross-section of a layer of interfacial TGO.

Minor amounts of oxides other than \(\text{Al}_2\text{O}_3\) may also form in the BC/TC interface [61]. Such oxides may, for example, form as a chromium rich layer...
between the $\text{Al}_2\text{O}_3$ and TC or as bulky clusters containing a mixture of several types of oxides: $(\text{Al, Cr})_2\text{O}_3$, $\text{Ni(Al, Cr)}_2\text{O}_4$ and $\text{NiO}$ [61]. Such clusters of chromia–spinel–nickel oxide may form quite early during oxidation, and form in greater quantities with higher temperature, but may remain fairly constant once formed [61].

During oxidation, the oxide can form either internally, as a subscale, or as an external scale, explained in Fig. 19. In order for the oxide layer to be protective, it must be external; hence, in a Ni–Cr–Al system, the formation of an external $\text{Al}_2\text{O}_3$ scale must be promoted. There are several factors that influence the ability of the alloy to form external alumina: oxygen partial pressure, amount of solved O in the alloy, amount of aluminium in the alloy and the amount of other alloying elements, most importantly Cr.

The effect of Al content and O concentration in the alloy surface can be understood by the following equation which gives the thickness, $x$, of the subscale at time $t$ in s [11].

$$x = \left(\frac{2N_O D_O t}{\nu N_M}\right)^{\frac{1}{2}} \quad (4)$$

$N_O$ is the mole fraction of oxygen in the metal at the surface, $D_O$ is the diffusivity of oxygen in the alloy, $\nu$ is the ratio of oxygen to metal atoms of the formed oxide and $N_M$ is the mole fraction of the oxide forming element (Al in the Ni–Al system). Fig. 20 shows the internal oxidation depth at 1000 °C as function of Al content for different O concentrations at the alloy surface: max solubility of O in Ni, and 50%, 20% and 5% of full solubility [62]. As can be seen, the subscale thickness decreases with increasing Al and decreasing O in the alloy; eventually,
Figure 19: Two types of oxidation: a) Internal oxidation: formation of a non-protective subscale. b) External oxidation: formation of a protective oxide scale.

Figure 20: Subscale thickness as function of Al and O content. The hypothetical transition from internal to external oxidation is also marked.

A shift to external oxidation will occur. For Ni–Al, the amount of Al needed to cause a shift from internal to external oxidation is \( \gtrsim 17 \) wt.% [10] as evident from Fig. 12. The transition from internal to external oxidation may occur for \[ N_M > \sqrt{\frac{\pi g N_0 D_O V_{alloy}}{2v D_M V_{oxide}}} \]  

where \( g \) is the fraction of formed oxide at which the internal subscale becomes continuous and rate controlling, \( D_M \) is the diffusivity of the oxidising element.
and $V_{\text{alloy}}$ and $V_{\text{oxide}}$ are the molar volumes of the alloy and the oxide respectively. Fig. 20 shows hypothetical transitions from internal to external scales with $g$ arbitrary set to $g = 0.3$ and $D_M$ taken as a rule-of-mixture mean of the diffusivity in $\gamma$ with $30\% \beta$.

The addition of Cr to the Ni–Al system may also promote the formation of external $\text{Al}_2\text{O}_3$ through several mechanisms. As shown in Fig. 12, the addition of 5 wt.% Cr, ($\sim 5\text{ at.}\%$) enables the alloy to form $\text{Al}_2\text{O}_3$ at an Al content as low as $\sim 5\text{ wt.}\%$, ($\sim 10\text{ at.}\%$). Chromium may, for example, act as a getter for oxygen [63] which lowers the O concentration at the alloy surface. As evident from Eq. 5 and Fig. 20, lowering $N_O$ makes it possible to form external $\text{Al}_2\text{O}_3$ at lower Al contents. Another effect of Cr addition is its influence on Al activity. This is illustrated in Fig. 21 for a Ni–Cr–Al system with 5 wt.% Al at $1000^\circ\text{C}$. The Al activity has been calculated by Thermo-Calc as function of Cr content; it can be seen that the addition of Cr increases Al activity.

### 3.2 The reactive element effect

Bond coat alloys contain minor additions of reactive elements, such as Y, Hf, Zr, Ce or La [13, 22, 30, 36]. REs are generally considered to improve the oxide scale adhesion; several mechanisms have been suggested:

- REs tie up sulphur which would otherwise have segregated to the metal/oxide interface and lowered the metal/oxide adhesion [30]. Lowering the S content in the alloy can have the same effect [64].
• REs may slow down oxidation by segregating to Al₂O₃ grain boundaries and slow down Al grain boundary diffusion [65]. REs thus alter the oxide growth mechanism from an outward growing to an inward growing oxide scale [35]. This also decreases spalling of the oxide by decreasing lateral growth of the oxide, which could have happened if simultaneously inward diffusion of O and outward diffusion of Al had occurred [35].

• REs may form oxides in the metal/oxide interface and mechanically pin the oxide to the metal by so called pegging [49].

Y, which is the most common RE, readily forms oxides and may be found in the Al₂O₃ scale as: yttria Y₂O₃, yttrium aluminium perovskite (YAP) YAlO₃, and yttrium aluminium garnet (YAG) Y₃Al₅O₁₂ [49].

3.3 Breakdown of the protective oxide scale

The TGO will remain protective only as long as the bond coat contains enough Al to maintain a continuous alumina scale. During high-temperature exposure, aluminium will be depleted through oxidation and interdiffusion with the substrate [12, 37, 58]. An aluminium concentration of ≊3–5 wt.% is generally enough to maintain the Al₂O₃ scale [10, 11, 66, 67]; for low Al contents, non-protective oxides may start to form in the BC/TC interface and the oxidation rate increases; this marks the onset of breakaway oxidation, or chemical failure.

The chemical failure can be divided into two types: mechanically induced chemical failure (MICF) and intrinsic chemical failure (InCF) [68]. MICF typically occurs during thermal cycling where the protective oxide scale cracks on cooling and needs to be reformed; failure occurs when the Al content is too low to heal/reform the protective alumina layer.

InCF occurs when the Al content beneath the oxide layer drops to such a low level that the Al₂O₃ is no longer the thermodynamically preferred oxide. This occurs at considerably lower Al contents then MICF. This results in the formation of other oxides, either from the alloy or by decomposition of the alumina scale according to reactions such as [58]:

\[
\text{Al}_2\text{O}_3 + 2\text{Cr} \rightarrow \text{Cr}_2\text{O}_3 + 2\text{Al} \quad \text{(F)}
\]

or

\[
\text{Al}_2\text{O}_3 + \frac{1}{2}\text{O}_2 + \text{Ni} \rightarrow \text{NiAl}_2\text{O}_4 \quad \text{(G)}
\]

The Al₂O₃ scale is thus replaced, or partially replaced, by a layer of chromia (Cr,Al)₂O₃, spinel (Ni,Co)(Cr,Al)₂O₄, nickel oxide and cobalt oxide [40, 50, 53,
69–71]. Internal oxidation of the remaining aluminium may also occur [69]. These TGOs are not as protective as alumina and the layer of chromia and spinels has lower interfacial fracture resistance which may cause the top coat to spall on cooling [12, 40, 68, 69].
Thermal fatigue of coatings

In addition to applied mechanical load, there are two sources for stresses in an APS TBC system: 1) growth stresses in the interface TGO and 2) stresses that develop on heating or cooling due to the mismatch in coefficient of thermal expansion between the bond coat, interface TGO and top coat [30]. Both sources of stress act at the bond coat/top coat interface and failure of TBC systems consequently occurs by fracture in, or close to, the BC/TC interface [12].

Oxide growth stresses can partly be understood from the so called Pilling-Bedworth ratio, $PBR$, which is calculated as [72]

$$PBR = \frac{Wd}{wD}$$  \hspace{1cm} (6)

where $d$ and $D$ are the densities of the metal and the oxide respectively, and $w$ is the amount (weight) of metal necessary to produce the amount (weight) $W$ of oxide. A $PBR < 1$ gives tensile stresses in the oxide while a $PBR > 1$ gives compressive stresses (more so the higher the PBR). Table 2 shows the $PBR$ for some common oxides in coatings [51].

<table>
<thead>
<tr>
<th>oxide</th>
<th>$PBR$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Al_2O_3$</td>
<td>1.28</td>
</tr>
<tr>
<td>$Cr_2O_3$</td>
<td>2.07</td>
</tr>
<tr>
<td>$NiO$</td>
<td>1.65</td>
</tr>
<tr>
<td>$CoO$</td>
<td>1.86</td>
</tr>
</tbody>
</table>

Gas turbine starts and stops give cyclic variations in temperature and the resulting cyclic thermal stresses make the TBC system susceptible to fatigue.
The thermal mismatch stresses are often considered to be most harmful during cooling [70, 73] as, during heating, stress relaxation may occur. During cooling, however, there is little time for stress relaxation and stresses develop in the BC/TC interface that depend on the temperature drop [70, 73]; for large temperature drops, the thermal mismatch stresses during cooling may dominate over the TGO growth stresses [30].

The stresses that develop due to thermal mismatch depend, in addition to the temperature drop and the CTE mismatch, on BC/TC interface morphology and the thickness of the interface TGOs [74]. The TGO thickness and composition change as the TBC system is exposed to high temperature and thus affect the BC/TC interface stresses.

A simplified description of the stresses that arise during thermal cycling of a TBC system would be as follows [75]: When the TBC system is heated to high temperature, stresses are introduced in the BC/TC interface due to the differences in CTE between the bond coat and the top coat. These stresses are, partly or entirely, reduced due to stress relaxation at high temperature [73]. Long high-temperature exposure causes the interface TGO to grow, resulting in TGO growth stresses, which may also relax at high temperature. At cooling, stresses are again introduced due to differences in the CTE, only now there is little time for stress relaxation and stresses develop in the BC/TC interface.

In a rough BC/TC interface, with alternating peaks and valleys, thermal cycling would cause out-of-plane tensile stresses to form at the interface peaks and out-of-plane compressive stresses at interface valleys, as shown in Fig. 22 a). As the interface TGOs grow, the stress distribution will be affected as illustrated by Fig. 22 b) and c). A thicker layer of interface TGOs causes the compressive stresses at the valleys to shift to tensile stresses. Stresses formed through this mechanism will be able to propagate fatigue cracks in the vicinity of the BC/TC interface, and, consequently, cause the TBC system to fail by fatigue.

![Figure 22](image_url)

**Figure 22:** Out-of-plane (vertical) stresses in the BC/TC interface. The compressive stresses at the valleys shift to tensile stresses as the TGO grow. Based on Jinnestrand and Sjöström [75]
4.1 Crack nucleation mechanisms

The plasma spray process gives the top coat a very characteristic splat-on-splat structure. The degree of inter-splat bonding can be rather modest which gives rise to many crack-like defects in the top coat, see Fig. 15. These pre-existing interlamellar delaminations in the top coat may act as crack embryos. Several papers have attributed crack nucleation to these pre-existing interlamellar delaminations [50, 76–81].

Cracks have also been described to nucleate in the interfacial TGO during cycling. Crack initiation in the BC/TC interface is most commonly attributed to peak and off-peak positions in the BC/TC interface [48, 82, 83]. There are several suggested explanations for this, such as:

1. Out-of-plane tensile stresses prevail at peak and off-peak positions.

2. During cycling, in-plane compressive growth stresses may cause the layer of interfacial Al$_2$O$_3$ to buckle and delaminate at peak positions. The TGO will reform and the process is repeated. Such repeated delamination and regrowth will give rise to a layered TGO structure at peak positions, shown in Fig. 23 a), which may act as starting points for larger delamination cracks [36, 82, 84, 85].

3. Cracks may nucleate in the TGO due to large growth stresses in the voluminous clusters of chromia and spinels, shown in Fig. 23 b), that may form in addition to Al$_2$O$_3$ during high temperature exposure [50, 61, 80, 81].

![Figure 23: Crack formation in the interfacial TGO. a) Repeated cracking and regrowth giving a layered structure in the TGO. b) Cracking in a cluster of chromia, spinels and nickel oxide.](image-url)
4.2 Crack growth mechanisms

There are several micromechanic failure mechanisms described in literature; they differ in where the crack is assumed to have nucleated and the path of the growing crack, Fig. 24, 25 and 26 summarise some of these. Many of the suggested failure mechanisms from the literature assume that crack nucleation and growth mechanisms act on a microscale, typically the scale of an interface peak and valley. It is then assumed that crack growth, as that on a microscale, occurs simultaneously throughout the BC/TC interface such that failure eventually occurs by coalescence of microcracks causing the top coat to spall [12]. It hence becomes sufficient to study crack growth only in a least representative cell. The BC/TC interface is often idealised as some periodic function, often a sine wave, and the least representative cell typically includes a peak and a valley, similar to those shown in Fig. 24, 25 and 26.

The failure mode shown in Fig. 24 assumes crack initiation at peaks in a sinusoidal BC/TC interface, Fig. 24 a). The crack path will then either follow the BC/TC interface, Fig. 24 b), or kink out in the TC, Fig. 24 c) [73, 86]. Such crack growth is assumed to occur at every peak in the BC/TC interface and failure occurs when such microcracks meet and coalesce.

Fig. 25 shows a failure mode where crack nucleation occurs by opening of the pre-existing interlamellar delaminations in the top coat. Such crack embryos grow in the vicinity of BC/TC interface peaks and arrest as they encounter a BC peak, Fig. 25 a). Meanwhile, the growth of the interface TGO will increase the out-of-plane tensile stresses at off-peak positions, and when such stresses are high enough, cracks will nucleate in the TGO at peak positions, Fig. 25 b). The crack propagation then proceeds until several of these cracks coalesce and cause failure, Fig. 25 c) [76, 77].

Another mechanism, similarly, suggests that cracks initiate from pre-existing delaminations in the top coat, but above the bond coat peak positions, Fig. 26 a). Such cracks initiate while the out-of-plane stresses are tensile at peak positions but still compressive at valley positions, see Fig. 22 a). Since the cracks cannot grow through the areas of compressive stresses at flank and valley positions, the crack arrests until the growth of the TGO changes the compressive flank and valley stresses to tensile stresses as illustrated by Fig. 22 b) and c). Crack growth occurs in the top coat and the failure occurs as these cracks coalesce, Fig. 26 b) [78, 79].

In addition to failure by the growth and coalescence of microcracks, failure may also occur through growth of macrocracks from the edges of TBC coated specimens [87, 88]. Edge cracking occurs due to the stress concentration at the TBC edge where the coating ends. Sjöström and Brodin [87] investigated the influence of the chamfer angle on the edge cracking of TBCs and found...
Figure 24: Crack nucleation in the TGO, a), followed by either: b) crack growth in, or close to, the TGO, or c) crack growth by kinking out in the TC.

Figure 25: Crack nucleation in the top coat, a), followed by b) damage of TGO and c) crack growth.

Figure 26: Crack growth in the top coat: a) nucleation and b) growth.

Figure 27: Edge cracking of TBCs.
that any chamfer angle larger than 60° gave essentially the same risk of edge cracking whereas an angle < 60° gave a lower risk of edge cracking, see Fig. 27.

The crack growth paths suggested in literature is evidently quite divers, ranging from entirely in the BC/TC interface to mixed interface/TC fracture to entirely in the TC. Fracture that occurs in the TC is referred to as white fracture and fracture that occurs in the BC/TC interface is called black fracture as the fracture surfaces will appear white and black respectively when examined optically. Fracture by cracks that grow partly in the BC/TC interface and partly in the TC is referred to as mixed fracture.

Which failure mode, white, black or mixed, that results depends partly on the thermal cycle. Trunova et al. [89] compared the fracture mode of TBC systems subjected to thermal cycling with different dwell times. It was found that long dwell time gave mainly black fracture, intermediate dwell times gave mixed fracture and no dwell time gave white fracture. It was also noted that, as the dwell time decreases, the total number of cycles to failure increased and the cumulative high temperature exposure time decreased.

4.3 Coating life assessment

4.3.1 Microstructure-based life models

There are several microstructure- or composition-based life models for TBCs; they all rely on the tendency of TBC life to depend on TGO growth. Rabiei and Evans [77] showed, for example, that a TGO thickness in excess of ∼ 5.5µm could be critical for TBCs. TBC life can thus be predicted from oxide growth modelling.

Other models are in different way based on aluminium depletion of the bond coat. As the aluminium content reaches a critical value, the coating stop acting as an Al reservoir; the protective interface oxide layer can no longer be maintained and chemical failure occurs [12, 39, 49, 66, 90–93]. By modelling oxidation and interdiffusion with the substrate, TBC life models have been established [66, 90, 92–99].

It is necessary to have a criterion for when the aluminium content becomes too low. Since removal of Al from the coating causes dissolution of the β phase, the complete depletion of β phase, which can be observed from micrographs of cross-sectioned specimens, can be used as a life criterion [12, 91–93]. In other cases, a critical Al content may be a more suitable criterion; Renusch et al. [66] suggested ∼ 3 wt.% as a critical Al content.
4.3.2 The NASA model

The NASA model [100] takes its starting point in a Coffin-Manson type expression

\[ N = \left( \frac{\Delta \varepsilon_i}{\Delta \varepsilon_f} \right)^b \]  

(7)

where \( N \) is cycles to failure, \( \Delta \varepsilon_i \) is the inelastic strain range, \( \Delta \varepsilon_f \) is the inelastic strain range that causes failure in one cycle and \( b \) is a constant. The effect of high temperature exposure on life is included in \( \Delta \varepsilon_f \) which is a function of TGO growth and the adhesion strength of the unoxidised TBC. The growth of the TGO influences life through the expression

\[ \Delta \varepsilon_f = \Delta \varepsilon_{f0} \left( 1 - \frac{\delta}{\delta_c} \right)^c + \Delta \varepsilon_i \left( \frac{\delta}{\delta_c} \right)^d \]  

(8)

where \( \Delta \varepsilon_{f0} \) is the inelastic failure strain range for an unoxidised coating system, \( \delta_c \) is the critical oxide layer for which the coating would fail in a single cycle and \( c \) and \( d \) are constants which are \( c \approx d \approx 1 \). The oxide thickness, \( \delta \), can be obtained from a power-law equation, see equation 3.

4.3.3 Model suggested by Busso et al.

Busso et al. [76] have suggested the following life model for APS TBCs:

\[ dD = D^m \left( \frac{\sigma_{\text{max}}}{F} \right)^p \ dN \]  

(9)

where \( 0 \leq D \leq 1 \) is a fatigue damage parameter such that \( D = 1 \) at failure, \( \sigma_{\text{max}} \) is the maximum out-of-plane interfacial stress, \( N \) is number of cycles and \( m \) and \( F \) are given by

\[ m = 1 - C \left( \frac{\sigma_{\text{max}}}{\sigma_{c0}} \right)^{0.818p} \]  

(10)

and

\[ F = F_0 (1 - F_1 \sigma_{\text{max}}) \]  

(11)
where $\sigma_{c0}$ is the initial strength of the TBC and $p$, $C$, $F_0$ and $F_1$ are material parameters that need to be calibrated to experimental data.

The fatigue damage is driven by the maximum out-of-plane stress, $\sigma_{\text{max}}$, which is obtained from finite element analysis of a least representative cell of a TBC system. The $\sigma_{\text{max}}$ includes the combined stresses from the thermal cycle, oxide growth and sintering of the top coat according to [76, 101]

$$\sigma_{\text{max}} = \sigma_{\text{therm.}} + \sigma_{\text{ox.}} + \sigma_{\text{sintr.}}$$

(12)

where $\sigma_{\text{therm.}}$, $\sigma_{\text{ox.}}$ and $\sigma_{\text{sintr.}}$ are functions of temperature cycle, cumulative oxidation time and BC/TC interface morphology; they describe the out-of-plane stress contributions from thermo-elastic and visco-plastic deformation, oxidation and sintering.

### 4.3.4 Model suggested by Brodin, Jinnestrand and Sjöström

Brodin, Jinnestrand and Sjöström [70, 73, 102] have developed a fracture mechanics based life model using a Paris law type of equation:

$$\frac{dD}{dN} = C (\lambda \Delta G)^n$$

(13)

where $G$ is the energy release rate and $C$ and $n$ are constants. $D$ is a damage parameter which can contain contributions from cracks in the BC/TC interface, $I_{TGO}^I$, in the top coat, $I_{TC}^I$, and cracks running partly in the top coat and in the BC/TC interface, $I_{TC/TGO}^I$, according to

$$D = \frac{\sum_i I_{TGO}^I + \sum_j I_{TC}^I + \sum_k I_{TC/TGO}^I}{L}$$

(14)

where $L$ is the total analysed length.

The model involves cracks that partially, or completely, follow the BC/TC interface; such cracks will grow in a mixed mode [73]. To account for mixed mode crack growth, $G$ is multiplied by a mixed mode function, $\lambda$ [103]:

$$\lambda = 1 - (1 - \lambda_0) \left( \frac{2}{\pi} \tan^{-1} \left( \frac{\Delta K_{II}}{\Delta K_{I}} \right) \right)^m$$

(15)

where $\Delta K_I$ and $\Delta K_{II}$ are the stress intensity factors in mode I and II, and $\lambda_0$ and $m$ are constants.
The influence of thermal loads, surface morphology and interface TGO growth is included in the finite element calculation of $\Delta G$ and $\Delta K_{II}/\Delta K_{I}$ [73]. $\Delta G$ is calculated by a virtual crack extension method. $\Delta K_{II}/\Delta K_{I}$ is calculated from the crack flank displacements using the theory of interface cracks suggested by Hutchinson and Suo [103].
Experimental methods

5.1 Thermal fatigue

When a TBC system is cycled, the difference in coefficient of thermal expansion between the bond coat and the top coat causes thermal stresses close to the BC/TC interface. In the lab environment, two main types of thermal cycling tests exist: thermal cycling fatigue (TCF) (or furnace cycle test (FCT)) and burner rig test (BRT) (or thermal shock). Brodin [86] found, from literature, that TCF tests often had average heating and cooling rates in the order of 1–2 °C, whereas BRT tests often had average heating and cooling rates in the order of 6–12 °C. BRT does also, to a greater extent, give white fracture whereas TCF gives black fracture [86].

The burner rig test uses a flame to heat the specimen on the coated side. Burner rigs typically reach a maximum gas temperature of 1350–1750 °C [104]. During heating, the specimens are sometimes cooled on the uncoated side to introduce a larger temperature gradient during heating. After heating, the specimens are rapidly cooled by compressed air, typically with no, or very short, hold time at high temperature. Fig. 28 shows a schematic drawing of a burner rig and Fig. 29 a) gives an example of a BRT temperature curve. In addition to thermal shock testing, burner rigs can also be used for oxidation tests with long dwell times and hot corrosion tests, the latter typically performed at temperatures around 900 °C [104].

In a furnace cycle test, the specimens are thermally cycled by moving in and out of a furnace. Such testing is associated with lower heating rates than the burner rig test and the temperature gradients in the specimens are lower [86]. Furthermore, the high-temperature dwell time is usually very long compared to BRT. During cooling, the specimens can be cooled by compressed air.
Fig. 30 shows a schematic drawing of furnace cycling and Fig. 29 b) shows a temperature curve.

Figure 28: Schematic drawing of a burner rig. a) Heating by a flame on the coated side while cooling the uncoated side. b) The specimen is moved out of the flame and cooled by air.

Figure 29: Two thermal cycles. a) A burner rig cycle, based on Liu et al. [88]. b) A furnace cycle with forced air cooling.

Figure 30: Schematic drawing of a cyclic furnace. a) Dwelling in furnace during the hot part of the cycle. b) Cooling with air during the cold part of the cycle.
5.2 Corrosion test

Corrosion resistance evaluation of coatings may be conducted in many ways. Often, salt mixtures containing Na$_2$SO$_4$ are deposited onto the specimens in amounts of 0.075–5 mg/cm$^2$ and in intervals of 20–100 h. Salt deposition can occur with or without the addition of gaseous SO$_2$ in the temperature interval 700–1000 °C [105–111]. Table 3 summarises some of the corrosion conditions encountered in literature for coatings [105–107, 110–112]. Water vapour has also shown to influence the corrosion rate. Testing conditions including 5–15% water vapour at 800–1100 °C can be found in literature [64, 113–117].

A cyclic corrosion rig was built during the duration of the project to evaluate the corrosion properties of coatings. Fig. 31 shows the cyclic corrosion rig which operates by moving the furnace up and down. When in the lower position, the furnace covers the specimens; when in the upper position, the specimens are allowed to cool slowly in air; no forced airflow was used for cooling.

![Cyclic corrosion rig](image)

Figure 31: Cyclic corrosion rig.
Table 3: Some test parameters for corrosion, from literature [105–107, 110–112].

<table>
<thead>
<tr>
<th>Salt</th>
<th>Amount salt, mg/cm²</th>
<th>Interval of salt deposition, h</th>
<th>Total test duration, h</th>
<th>Temp., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄–20 mol% K₂SO₄</td>
<td>0.075–0.75</td>
<td>50</td>
<td>500</td>
<td>700–900</td>
</tr>
<tr>
<td>Na₂SO₄–0–5 wt.% NaCl</td>
<td>2.5</td>
<td>24</td>
<td>168–312</td>
<td>900</td>
</tr>
<tr>
<td>Na₂SO₄–50 wt.% V₂O₅</td>
<td>3–5</td>
<td>51</td>
<td>51</td>
<td>800</td>
</tr>
<tr>
<td>Na₂SO₄–25 wt.% NaCl</td>
<td>2</td>
<td>20</td>
<td>100</td>
<td>900</td>
</tr>
<tr>
<td>Na₂SO₄–K₂SO₄</td>
<td>1</td>
<td>100</td>
<td>300–500</td>
<td>950</td>
</tr>
<tr>
<td>Na₂SO₄–10 wt.% NaCl</td>
<td>0.1</td>
<td>20</td>
<td>100–430</td>
<td>1000</td>
</tr>
</tbody>
</table>

Figure 32: A temperature cycle during cyclic corrosion; the sudden drop in temperature at the end of the cooling is due to salt-solution deposition.

in this rig. When the furnace is in its upper position, a lid closes to reduce heat loss in the furnace; attached to the lid are also a number of nozzles which sprays the specimens with a corrosive substance. During the hot part of the cycle, the option exists to spray water into the furnace which instantaneously evaporates. Fig. 32 shows the temperature curve measured on a specimen during a corrosion cycle.

5.3 Adhesion test

A commonly used adhesion test procedure is to attach the coated and uncoated sides of a button specimen to two bars, that can be mounted in a tensile test machine, and load the coating until fracture. The set-up is schematically shown in Fig. 33. The tensile test machine must be equipped with universal joints to ensure moment free mounting. The specimen is fastened to the bars by a suitable adhesive, most commonly by epoxy which is cured at moderate temper-
atures (120–175 °C [19]). During curing, a slight compressive load is applied to the bar/specimen/bar system to ensure good adhesion between fixture and specimen. The method is described in ASTM C633 Standard test method for adhesion or cohesion strength of thermal spray coatings [118] as well as EN 582 Thermal spraying – determination of tensile adhesive strength [119].

Figure 33: Set-up for adhesion testing of TBCs. Based on Davis [19].

To ensure good results, the specimens need to be flat and the surfaces need to be clean and free from loose material; the coating may therefore have to be ground or grit blasted. Furthermore, any coating overspray onto the sides of the button specimen, as well as beads of excessive adhesive at the joint, must be removed before testing. Even if great care is taken, some critical comments to the method are [19]:

- Bending moments introduced by mounting in the tensile test machine will give erroneous results. This is avoided by the use of a self-aligning fixture, as shown in Fig. 33, and by ensuring that the specimens are ground flat before bonding to the fixture.

- The type of adhesive will influence the result, as will the thickness of the adhesive film. In a porous coating, the penetration depth of the adhesive will affect the results. These effects stress the importance of a consistent and repeatable curing procedure.
• The strength of the adhesive sets the upper limit for how strong coatings can be tested.
• The tensile test is unsuitable for evaluation of very thin and very porous coatings.
• Variation in coating thickness, distribution and size of defects in the coating and residual stresses may give scattered data.

5.4 Microscopy

5.4.1 Specimen preparation
TBC systems are challenging to prepare for microscopy since the ceramic top coat and TGOs may crack during polishing. Care must be taken not damage the ceramic parts during specimen preparation since [19]:

1. Ceramic particles that come loose during polishing, *pull-outs*, may scratch the specimen.
2. Pull-outs in the top coat will make the top coat appear more porous, so that the porosity of the top coat will be overestimated.
3. Cracking of the top coat and TGO during polishing makes it impossible to determine the amount of damage that was caused by thermal cycling of the TBC system.

To avoid damaging the TBC during specimen preparation, the TBC system is infiltrated with epoxy in vacuum. The specimen is placed in vacuum and epoxy is poured over the specimen. The epoxy will penetrate the pores and cracks of the top coat and reduce the amount of damage introduced during the subsequent cutting, mounting and polishing. Would the top coat be damaged during the polishing, it is still possible to distinguish damage introduced by the thermal cycling as those cracks would be filled with epoxy and cracks introduced during polishing would not.

5.4.2 Scanning electron microscopy
Scanning electron microscopy (SEM) offers, in addition to imaging, micro-analysis tools such as energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS), as well as electron backscatter diffraction (EBSD), a tool for studying crystallographic structure and orientation.
EDS and WDS provide compositional information of the specimen. WDS can better resolve different elements in the collected X-ray spectrum, but is more time consuming than EDS. The spatial resolution of both techniques depends on the electron beam energy and the studied element according to [120]

\[ R_{KO} = \frac{0.0276A}{Z^{0.89} \rho^{1.67}} \]  (16)

where \( R_{KO} \) is the electron range (the X-ray generating volume) in µm, \( A \) is the atomic weight in g/mole, \( Z \) is the atomic number, \( \rho \) is the density in g/cm\(^3\) and \( E_0 \) is the electron beam energy in keV. With \( E_0 = 20 \text{ keV} \), EDS/WDS on Ni would give a spatial resolution of \( \sim 1.4 \mu m \) and Al would give \( \sim 4.2 \mu m \). Poor spatial resolution of these techniques may sometimes be problematic.

A problem with SEM on TBC systems is that the top coat and the TGOs do not conduct electricity which causes the specimen to charge. This can be solved by applying a thin carbon film onto the surface of the polished specimen.

### 5.5 Interface roughness measurement

The BC/TC interface roughness can be measured on cross-sectioned specimens by image analysis. A Matlab script was written for the purpose. The interface roughness profile is acquired from greyscale light-optic micrographs. The steps of the acquisition process are outlined in Fig. 34 and involves:

1. Thresholding of the grayscale image to obtain a binary image, see Fig. 34 a) and b).
2. Acquisition of the interface roughness profile by simulating a profilometer stylus tip, see Fig. 34 c).
3. Filtering of the profile and establishing the mean line, see Fig. 34 d).
4. Cropping the profile to a suitable sampling length, see Fig. 34 e).

The interface roughness profile is then used for calculation of various surface roughness parameters, the most well-known probably being the profile arithmetic mean deviation, \( Ra \):

\[ Ra = \frac{1}{l} \int_0^l |z(x)| \, dx \]  (17)
where $l$ is the analysed length and $z$ and $x$ are explained by Fig. 34 e). A comparison of $Ra$ values, for some different surfaces, showed that the $Ra$ values obtained by image analysis were in good agreement with those obtained by a profilometer.

Figure 34: Roughness profile acquisition procedure: a) greyscale image, b) binary image, c) stylus tip simulation, d) filtering and establishing mean line, and e) the obtained roughness profile.
Discussion of appended papers

Paper I: Influence of isothermal and cyclic heat treatments on the adhesion of plasma sprayed thermal barrier coatings

The influence of different heat treatments on the adhesion properties of APS TBCs was studied with the aim of relating the adhesion strength of the TBC to high-temperature exposure and to the test method used. The studied TBC system consisted of a Hastelloy X substrate coated with an APS NiCoCrAlY bond coat and APS Y-PSZ as top coat. The specimens were subjected to three different thermal treatments: isothermal oxidation, furnace cycling and burner rig test; all at a temperature of \( \sim 1100 \, ^\circ\text{C} \). The adhesion of the coatings after thermal treatment was evaluated by the ASTM C633 method.

The differences between the thermal exposure conditions affected the microstructure. Specimens subjected to the burner rig test developed a very thin TGO and were never depleted of the Al-rich \( \beta \)-phase. Furnace cycling and isothermal oxidation developed thicker TGO and were depleted of \( \beta \)-phase after \( \sim 100 \) h. Furnace cycling and isothermal oxidation also gave more pronounced interdiffusion with the substrate.

The adhesion of the isothermally heat treated specimens increased about 50\% compared to specimens tested in the as-sprayed condition. Isothermally oxidised specimens were also found to retain their adhesion strength with oxidation time whereas the cyclic tests both decreased the adhesion with number of cycles. The adhesion decrease of the two cyclic heat treatments was attributed to the fatigue damage introduced in the specimens during cycling.

The paper provides valuable information on how different test methods influence the degradation of TBCs. If the decrease in adhesion is taken as an
indication of damage introduced in the TBC, then the tests, in increasing order of severity, can be ranked as 1) isothermal oxidation, 2) furnace cycling and 3) burner rig test, for the same exposure time. However, the burner rig test gave a slower decrease of adhesion per cycle: \( \sim 1.54 \cdot 10^{-3} \text{MPa/cycle} \), compared with \( \sim 20.44 \cdot 10^{-3} \text{MPa/cycle} \) for furnace cycling. Hence, if the life is measured in number of cycles, as opposed to time, the burner rig test gives longer lives than furnace cycling. This is consistent with the tendency for longer high temperature dwell times to reduce the number of cycles to failure.

Paper II: Fractographic and microstructural study of isothermally and cyclically heat treated thermal barrier coatings

A fractographic study was performed on fracture surfaces from adhesion tested TBC systems exposed to different heat treatments. The studied TBC system consisted of a Hastelloy X substrate coated with APS NiCoCrAlY and APS Y-PSZ. The coated specimens were heat treated at a temperature of \( \sim 1100 \degree \text{C} \) by isothermal oxidation, furnace cycling and burner rig test. The top coats were pulled off the specimens in a tensile test machine and the resulting fracture surfaces were studied.

The fracture occurred either almost entirely in the top coat or both in the top coat and the BC/TC interface (mixed fracture); no specimen fractured entirely in the BC/TC interface. Isothermal oxidation gave fracture almost entirely in the top coat while the two cyclic heat treatments gave mixed fracture. However, even for cyclic heat treatment, \( > 80\% \) of the fracture occurred in the top coat. The amount of BC/TC interface fracture did increase with number of cycles.

Regions where the fracture occurred in the top coat showed essentially the same characteristics regardless of heat treatment; the fracture occurred mainly between the splats in the splat-on-splat structure typical for APS coatings. Through-splat fracture occurred sparingly and was often associated with discontinuities in the microstructure such as partially melted particles.

If the amount of interface fracture from the adhesion test is taken as an indication of the amount of interface damage in the specimen, isothermally oxidised specimens were essentially undamaged at \( \sim 300 \text{h} \) of exposure whereas the furnace cycling test had developed some interface damage. The furnace cycle test had a larger increase in interface damage per cycle; it takes the burner rig test \( \sim 1000 \text{cycles} \) to reach the same damage as the furnace cycle test reaches in \( \sim 300 \text{cycles} \). Both cyclic tests reached the same amount of damage roughly
at the same fraction of their total lives; from experience, ~ 300 cycles and ~ 1000 cycles for TCF and BRT respectively corresponds to 30–50 % of the total life. A microstructural study of the top coat also show that the short hold times associated with burner rig tests gave considerable less sintering of the top coat. The study illuminates several of the degrading mechanisms of TBCs during isothermal and cyclic high-temperature exposure: fatigue damage, interface TGO growth and sintering of the top coat. In particular, the study showed the difference between isothermal and cyclic heat treatment. While the isothermal oxidation gave fracture entirely in the top coat, cyclic heat treatments gave increasing fractions of BC/TC fracture with number of cycles.

Paper III: Influence of substrate material on the life of atmospheric plasma sprayed thermal barrier coatings

The substrate material on which the coating is deposited may influence the life of the TBC. Therefore, a study on the influence of substrate material on the life of APS TBCs was conducted. The specimens consisted of Hastelloy X (HX) and Haynes 230 (H230) substrates with an APS NiCoCrAlYSiTa bond coat and an APS zirconia top coat. The specimens were exposed to both isothermal oxidation and thermal cycling at 1100 °C. The specimens were tested until failure and the resulting fracture surfaces were studied. Cross-sections were also prepared and used for measurements of the interdiffusion between substrate and bond coat by EDS, as well as to measure the Young’s moduli of the bond coat and the substrate by nanoindentation.

The H230 specimen had a thermal cycling life almost twice as long as the HX specimen, 1070 cycles compared to ~ 600 cycles. Investigation of the fracture surface revealed that both the HX and H230 specimens had failed roughly at the same fraction of black fracture, ~ 40 %. The black fracture was also shown to have occurred mainly in the TGO/TC interface rather than within the TGO. During the isothermal oxidation test, the specimens were removed from the furnace at regular intervals and the test was interrupted when the TBC spalled during removal from the furnace. The HX specimen, again, had a shorter life, 1000 h compared to 1650 h for H230.

EDS line scans on cross-sectioned specimens provided through-coating compositional profiles; it was found that Fe, Mn, Mo and W from the substrate diffused into the bond coat; the interdiffusion was more pronounced for the HX specimen. EDS on the fracture surfaces revealed that Mn and Fe from the substrate could be found in the oxide; Fe was present in very small amounts, whereas Mn appeared to easily form oxides in the BC/TC interface. EDS results
also revealed that the H230 specimen retained an Al reservoir in the bond coat centre longer than the HX specimen.

TGO thickness measurements revealed that, while the growth rates of Al$_2$O$_3$ were similar for both the HX and H230 specimens, there existed a difference in the total TGO growth rate (the total TGO growth rate also included oxides such as Cr$_2$O$_3$, spinels and NiO). The HX specimen had a faster total TGO growth than the H230 specimen. At the time of failure, the total TGO thickness was rather similar for the two specimens: 16.5µm and 14.4µm for the HX and H230 specimens respectively.

The Young’s moduli, measured by nanoindentation, were used together with CTE estimations, made by Thermo-Calc, in a finite element analysis of crack growth in the BC/TC interface. It was found that the small differences in Young’s modulus and CTE, which arose due to interdiffusion, did not cause any significant differences in the crack driving force and could thus not explain the difference in life. The difference in thermal cycling life of the two TBC systems was considered to be due to differences in Al depletion and growth rate of non-Al$_2$O$_3$ oxides. The faster total TGO growth rate for the HX specimen was likely to have caused a shorter life due to higher stresses in the interface and the fact that non-Al$_2$O$_3$ oxides tend to crack and cause additional damage to the BC/TC interface. The study showed that the substrate material influences the life of the coating and that the growth kinetics of all oxides, not only Al$_2$O$_3$, may have to be taken into account in life prediction of TBCs.

**Paper IV: TBC bond coat-top coat interface roughness: influence on fatigue life and modelling aspects**

A large number of studies on TBC life prediction and TBC durability rely on finite element modelling of the stresses in the BC/TC interface. The influence of BC/TC interface roughness on the thermal fatigue life of TBCs was therefore studied. Four TBC systems, with varying BC/TC interface roughness, were thermally cycled to failure and their fatigue lives were correlated to their corresponding BC/TC interface roughness. Based on the results, a few different interface models for finite element analysis were developed. The specimens consisted of Haynes 230 coupons coated with VPS NiCrAlY and APS Y-PSZ which were thermally cycled until failure.

The results showed that a rougher interface increased the fatigue life of APS TBCs. It was found that a ~ 50% increase in $Ra$ gave a ~ 70% increase in TCF life. This increase in life was attributed to roughness, and not to oxidation effects, since no major differences in oxidation composition and kinetics were
observed.

A number of different roughness parameters were evaluated to establish which parameters that best captured the characteristics of the interface. It was found that an amplitude parameter together with a slope parameter accurately captured the main features of the interface. The two parameters chosen as basis for interface model formulation were $R_q$ and $R \Delta q$.

A number of interface models were created based on the selected interface roughness parameters. The interface models were evaluated by finite element analysis and by the life model suggested by Brodin, Jinnestrand and Sjöström, (described in section 4.3). The life model initially predicted the smoothest interface to have the longest life which contradicted experimental observations. It was concluded that the crack growth path must be adjusted for surface roughness effects; experimental observations suggested that higher roughness would shift the crack growth path so that the cracks to a greater extent grew in the top coat as opposed to in the BC/TC interface. When the finite element model was adjusted to agree with the observation, the life model was able to capture the experimentally observed results of high roughness promoting longer lives.

The study illustrated the large influence of BC/TC interface roughness on the fatigue life of TBCs, and stressed the importance of accurate interface models in life prediction of TBCs. It was found that a sinusoidal interface model based on an amplitude parameter and a slope parameter may be sufficient for modelling of stresses in the interface.

Paper V: Cyclic hot corrosion of thermal barrier coatings and overlay coatings

Coatings in gas turbines may degrade due to corrosion. Testing was performed with the aim of mapping the relative severity of: 1) oxidation in lab air, 2) oxidation in moist air, 3) corrosion with salt deposits in lab air, and 4) corrosion with salt deposits in moist air. Both NiCoCrAlYSiTa coated and NiCoCrAlYSiTa + TBC coated specimen were used. The testing was cyclic, including 48 h at 750 °C and 30 min cooling to a minimum of $\sim 100 °C$. For the moist air condition, water was injected in intervals of a few minutes during the hot part of the cycle; and for salt deposition, a salt–water solution was sprayed on the specimens automatically at the end of the cold part of the cycle. Prior to analysis, the specimens were cleaned to remove the residues from the salt deposition.

For NiCoCrAlYSiTa coated specimens, salt deposition gave notably thicker TGOs. The TGOs of the salt exposed specimens also contained an Y-rich oxide which was not observed for oxidation in lab air or moist air. EDS on the oxi-
dised/corroded surfaces revealed that the TGOs on all specimens consisted of predominately Al$_2$O$_3$. Very low amounts of S were found on the surfaces indicating that there was little or no sulfidation; the presence of Na in the TGOs was also low. The apparent influence of water was to change the TGO morphology.

For TBC coated specimens, the salt penetrated the top coat and sped up oxidation/corrosion at the BC/TC interface. The salt exposed specimens developed a, at least locally, thicker TGO and the metal–oxide front of attack was considerably more uneven than for oxidation in lab air and moist air.

The performed corrosion test gave an overview of the relative influence of water vapour and salt deposits on the corrosion resistance of coatings. It also showed that bond coat corrosion due to salt deposition may be present also for TBC coated specimens. While the performed corrosion test may be unsuitable for careful corrosion kinetics measurements, the present test parameters could be used for screening and ranking of coatings.

**Paper VI: Modeling of microstructural evolution and lifetime prediction of MCrAlY coatings on nickel based superalloys during high temperature oxidation**

Aluminium depletion based life models involve oxidation and interdiffusion modelling; thermodynamics software such as Thermo-Calc and DICTRA show promising results when used for such purposes. Therefore, DICTRA was used for the development of an Al depletion based life model for MCrAlY coatings. The modelling was based on HVOF CoNiCrAlYSi coatings deposited on substrates of Inconel 792. The specimens were subjected to isothermal oxidation at 900–1100 °C and thermal cycling at 1100 °C. The interdiffusion simulation was made in DICTRA and the oxidation simulation was made by a Matlab script written for the purpose. The DICTRA script and Matlab script were alternately run in an iterative process, the result of which was a coupled oxidation–interdiffusion model for prediction of Al depletion in the coating. The aim of the study was to model the depletion of the β-phase, i.e. the decrease in thickness of the β-containing zone in the middle of the coating. The end of the life of the coating was taken to occur when the β-phase had been completely depleted.

The diffusion in a multi-phase system in DICTRA requires the calculation of an effective diffusivity which depends on the geometrical phase distribution. Several geometrical phase distributions were tried, but a simple rule-of-mixture model was found appropriate. Included in the model was also a diffusion blocking effect. This occurred due to oxides, pores and grit residues at splat boundaries and at the substrate/coating interface. The diffusion blocking
was introduced by correction of the diffusion time.

The coating developed two $\beta$-depleted zones, an inner, due to interdiffusion with the substrate, and an outer, due to oxidation. The inner and outer $\beta$ phase depletion occurred faster for higher oxidation temperatures. For the outer zone, thermal cycling was found to give faster depletion than isothermal oxidation at the same temperature. This was due to the faster oxidation rate caused by oxide scale spalling associated with thermal cycling. The inner depletion zones were, however, similar for both thermal cycling and isothermal oxidation at 1100 °C. For the higher temperatures, $\geq$ 1000 °C, $\beta$ phase could be observed to form in the substrate due to interdiffusion.

The model was largely successful in predicting the main features of microstructural development with high-temperature exposure and showed acceptable agreement with experimentally established through-coating compositional profiles. The $\beta$-depletion life of the coating was predicted to be $\sim$ 220 h and $\sim$ 3000 h for 1100 °C and 1000 °C respectively. For 900 °C, the life was in excess of 10000 h, which was the maximum simulation time used.

The work provided an important complement to fatigue-based life prediction approaches. Whereas a fracture mechanics-based approach may be useful for thermal cycling, TGO growth and Al depletion based models may be more appropriate for isothermal high-temperature exposure or thermal cycling with very long hold times.

### Paper VII: Microstructure-based life prediction of thermal barrier coatings

The research presented in this paper expands upon the $\beta$-depletion based model described in the paper *Modeling of microstructural evolution and lifetime prediction of MCrAlY coatings on nickel based superalloys during high temperature oxidation*. The $\beta$-depletion based model was adapted to APS coatings which also meant that internal oxidation had to be considered due to the formation of oxide stringers in the bond coat. The studied specimens were TBC coated while the original model was developed for MCrAlY coated specimens. The studied TBC system consisted of APS NiCoCrAlY and APS zirconia. The specimens were isothermally oxidised up to 2500 h at 900 °C and 980 °C. The specimens had not failed at the stop of the test and were still in very good condition. It could therefore only be concluded that the isothermal life of the coating was $\gg$ 2500 h.

The TGO thickness was measured on cross-sections and used as input for the $\beta$-depletion based model. It was found that the amount of internal oxi-
dation, which was measured by image analysis, remained fairly constant once formed; the amount of internal oxidation was higher for higher temperatures. Both interface TGO growth and internal TGO growth were assumed to follow a power-law type equation (see Eq. 3) with \( n = 3 \) for interface TGO growth and \( n = 5 \) for internal oxidation.

EDS was performed on a cross-sectioned as-sprayed specimen to get compositional profiles for input into simulations. The DICTRA software was used to model the size of the inner and outer \( \beta \)-depletion zones. The model results agreed well with experimental observations for 980 °C but considerably worse for 900 °C. The poor agreement between experimental and simulated \( \beta \)-depletion zone size occurred since the specimens oxidised at 900 °C developed \( \gamma / \gamma' \) zones adjacent to the \( \gamma / \beta \) zone; DICTRA failed to predict this and, as a result, underestimated the size of the \( \beta \)-depletion zone.

A few life criteria were tested for the specimen oxidised at 980 °C; based on literature, the end of the life was considered to have been reached when 1) complete \( \beta \)-depletion had occurred, 2) the TGO thickness reached 5 \( \mu \)m, or 3) the Al content in the bond coat had dropped to 3 wt.%. \( \beta \)-depletion occurred at \( \sim 600 \) h, the TGO-based criterion gave a life of \( \sim 1450 \) h and the Al-depletion based gave \( \sim 2250 \) h based on simulation results and 3500–4200 h based on extrapolation from experimental data. The \( \beta \)-depletion based life criterion was obviously too conservative, as was the TGO-based criterion. The Al-depletion based life criterion appeared to give more reasonable results; however, the Al depletion simulation in DICTRA overpredicted the Al depletion rate somewhat and gave a more conservative life than the experimental Al-depletion indicated.

The study improved the previously developed \( \beta \)-depletion based model by also including internal oxidation; internal oxidation can be very pronounced in APS bond coats.
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