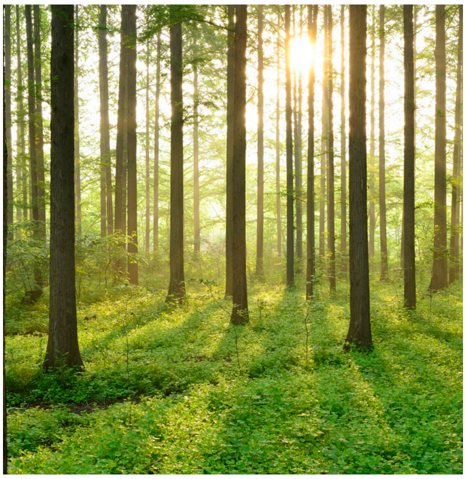
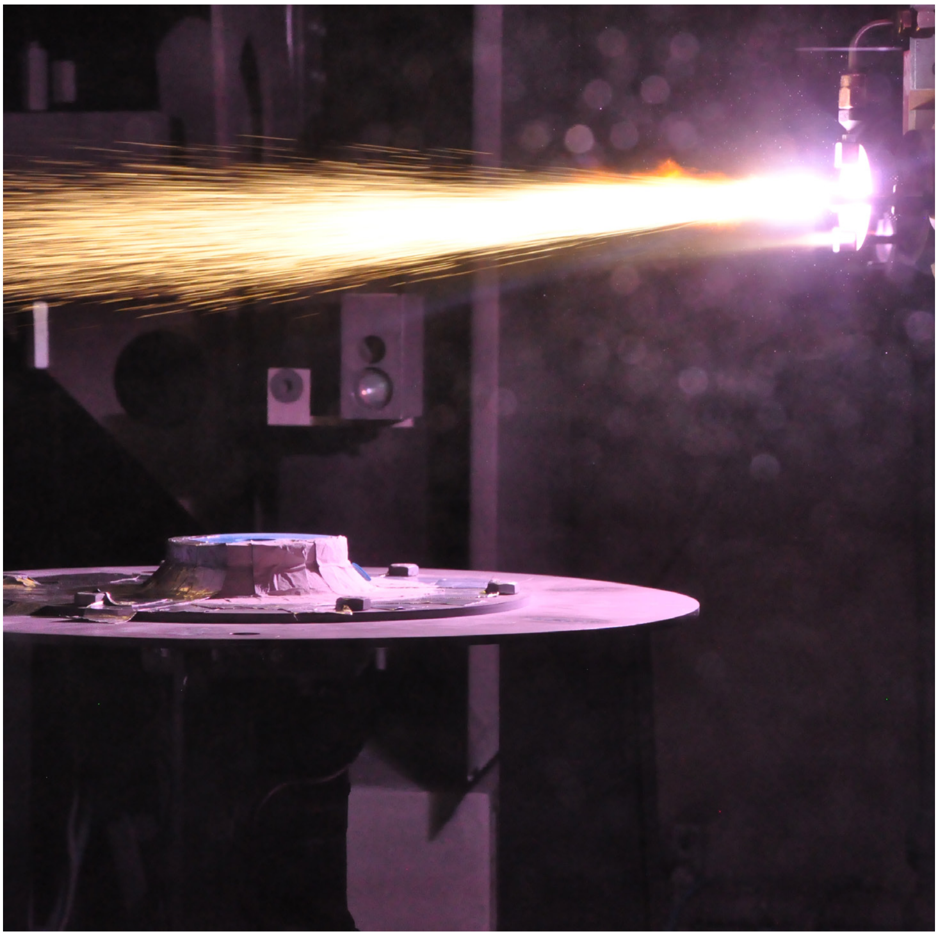
ADVANCED TEMPERATURE MEASUREMENTS ON/IN/BENEATH TBC COATINGS

RAPPORT 2015:213



BRÄNSLEBASERAD EL- OCH VÄRMEPRODUKTION



Energiforsk

Advanced Temperature Measurements on/in/beneath TBC coatings

Project: A38742

MATTIAS RICHTER (LU)

FAHED ABOU NADA (LU)

NICOLAIE MARKOCSAN (HV)

JENNY LARFELDT (SIT)

XIN-HAI LI (SIT)

ANDREAS LANTZ (SIT)

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Energiforsk AB | Phone: 08-677 25 30 | E-mail: kontakt@energiforsk.se | www.energiforsk.se

Förord

Denna rapport är slutrapportering av projekt A 38742 Avancerad temperaturmätning på/i/under ytbeläggningar syftande till optimering av förbränningssystem (Energimyndighetens projektnummer P 38742) som faller under teknikområde anläggnings- och förbränningsteknik inom SEBRA, samverkansprogrammet för bränslebaserad el- och värmeproduktion.

Projektet har följts av en referensgrupp bestående av:
Rikard Norling, Swerea KIMAB,
Anna Molker, WSP,
Kristian Huhtakangas, MH Engineering,
Martin Rokka, Göteborg Energi)

SEBRA, samverkansprogrammet för bränslebaserad el- och värmeproduktion, är efterföljaren till Värmeforsks Basprogram och startade som ett samarbetsprogram mellan Värmeforsk och Energimyndigheten 2013. All forskningsverksamhet som bedrevs inom Värmeforsk ingår sedan den 1 januari 2015 i Energiforsk. Därför ges denna rapport ut som en Energiforskrapport.
Programmets övergripande mål är att bidra till långsiktig utveckling av effektiva miljövänliga energisystemlösningar. Syftet är att medverka till framtagning av flexibla bränslebaserade anläggningar som kan anpassas till framtida behov och krav. Programmet är indelat i fyra teknikområden: anläggnings- och förbränningsteknik, processtyrning, material- och kemiteknik samt systemteknik.

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Helena Sellerholm
Områdesansvarig
Bränslebaserad el- och värmeproduktion, Energiforsk AB

Sammanfattning

Projektets huvudsyfte är att utveckla och tillämpa en teknik för att beröringsfritt mäta temperatur på ytan och under ytan av termiska barriärer så kallade TBC-skikt. TBC - Thermal Barrier Coatings. I gasturbiner skalar verkningsgraden med temperaturen på de förbrända gaserna från brännkammaren in till turbinen. De metalliska material som används i väggar och skovlar har redan idag smältpunkter som ligger under förbränningstemperaturen. Att detta överhuvudtaget är möjligt beror på att metallytorna kan skyddas av keramiska beläggningar som isolerar termiskt och på så sätt minskar värmelasten. För att kunna pressa upp verkningsgraden ytterligare i framtida gasturbiner så är det önskvärt att kunna använda ännu högre brännkammartemperaturer. För att detta skall vara realiserbart krävs det att man kan mäta och hålla koll på temperaturerna i TBC-skikten. Dels vill man beröringsfritt kunna mäta temperaturen på ytan och dels på ett givet djup under ytan.

För detta ändamål har projektet undersökt möjligheterna att utföra temperaturmätningar med hjälp av termografiska fosforer. I korthet bygger tekniken på att ytan beläggs med ett tunt skikt av den temperaturkänsliga fosforn. Därefter belyses fosforn med laserstrålning varefter ytan sänder ut ljus. Genom att utnyttja temperaturberoendet hos de spektrala och temporala egenskaperna för detta ljus, så kan man komma åt temperaturinformationen. Den approach som bedömdes ha bäst förutsättningar i denna applikation var temperaturbestämning genom mätning av ljusets avklingningstid. Initialt genomfördes tester i en högtemperaturugn för att identifiera lämpliga sensormaterial. För yttemperaturen blev lösningen mycket bra då det visade sig att en ny typ av TBC var stabiliserad med Dysprosium, ett ämne som ofta förekommer i termografiska fosforer. Det visade sig att DySZ kunde användas både som termisk barriär och som sensor i det förväntade temperaturområdet. För mätningar på ett sensorskikt beläget under TBC:n blev sökandet efter lämpliga kombinationer av fosfor och TBC betydligt mer komplicerat. Det största problemen orsakades av kraftig UV-absorption hos de kommersiella TBC-materialen, samt höga halter av störande föroreningar. I korthet identifierades slutligen en lovade lösning där Y_2O_3:Eu användes som sensor under en ”research grade” TBC, (Metco, 204B-NS). Genom detta val kunde excitationen ske med grön laserstrålning vilken uppvisade bättre penetrationsförmåga än den UV-strålning som vanligtvis används.

Som ett avslutande test av applicerbarheten utfördes ett fullskaligt försök i Siemens testrigg för brännare. Högskolan Väst belade brännaren med nämnda TBC/sensor-skikt varefter mätningar genomfördes på plats i Finspång. Resultaten visade, glädjande nog, att det var möjligt att beröringsfritt extrahera temperaturinformation från ytan och från positioner ända ner till 300μm under ytan. Av sekretesskäl har uppmätta temperaturer skalats om (normaliserats) i rapporten.

Summary

Introduction

This project is focused on remote probing of surface temperatures under conditions relevant for the gas turbine industry. More precisely the aim is to investigate the feasibility of applying phosphor thermometry for probing the surface temperature of Thermal Barrier Coatings (TBC) and of incorporating a thermal sensor layer into a functioning (TBC). The application of thermographic phosphors provides the ability to measure surface temperatures without being in physical contact with the surface of interest. In short the technique is based on utilization of the thermosensitive properties of the phosphorescent light that result from laser excitation. There are basically two methods to extract temperature information from the phosphorescence. One is based on the spectral shift of the light that occurs as the temperature is changed. The other utilizes the shortening of phosphorescence decay time that comes with increasing temperatures. In this study the decay time method was chosen for two main reasons. The temperature sensitivity, i.e. shift in properties for a given shift in temperature is greater for the decay time method. Typically the decay time can change three to four orders of magnitude when the temperature changes less than 1000 K. The other benefit associated with this method is a better robustness in noisy environments. The search for suitable sensor/TBC materials was far from trivial as should be evident after reading the full report.

Goal and objectives

It should be mentioned that the ambition level of the project was very high already from the start, including during the writing of the proposal. The task of probing the temperatures from within thermal barrier coatings through remote sensing is a research field on its own. However, some indications in published materials were positive enough for the involved partners to propose and perform the presented study. In short the aims can be summarized as:

- Develop a TBC with embedded sensor material that will function both as a heat shield and as a sensor.
- Gain knowledge about the feasibility of probing phosphor signal decays through different TCB thicknesses.
- Perform temperature measurements on the TBC surface to gain information on temperature gradients.
- Perform temperature measurements at different coating depths.
- Identify a suitable sensor material for the application in Siemens atmospheric combustion test rig.
- Incorporate the selected sensor material into a functional TBC.
- Perform a full scale feasibility test of this technique for remote sensing temperature in the combustion test facility at Siemens.

Discussions and analysis

The initial task was to identify suitable phosphor materials. There is a quite extensive amount of luminescent materials that possess temperature sensitivity. However, every material has a temperature range where the temperature sensitivity is sufficient. Also the material survivability has to be taken into account, especially under such extreme conditions such as those found in a gas turbine combustor. For measuring the TBC top surface the main challenge was to select a phosphor with suitable temperature range. The real challenge was the probing of temperature within the TBC layer. The basic idea of incorporating a sensor layer at a specific depth of the TBC requires that the laser excitation radiation as well as the phosphor signal can penetrate trough the TBC layer covering the sensor material.

Many thermographic phosphors comprises a ceramic host doped with a rare earth element. In principle they are similar to many of the TBC commonly used in the industry. For practicality and durability reasons it would be an additional benefit if a TBC material could also be utilized as temperature sensor. Since the expected peak temperatures where in the region of 800 Celsius, Dysprosium doped phosphors/TBC´s were investigated. The optical response to temperature was investigated for the TBC material "Dysprosium Stabilized Zirconia" (DySZ). Tests with 355 nm excitation and probing of the resulting decay times in high a temperature furnace indicated that DySZ could serve as both sensor and thermal barrier. For the embedded sensor material lower temperatures were expected. The first requirement was to identify a TBC that was translucent to both laser and signal. Furthermore it should be inert, i.e. it should not produce any temperature dependent signals. In short these two requirements were harder than expected to achieve. Published work indicated that the material itself should be transparent to UV radiation. However, in practice the porous nature of plasma sprayed TBC induced severe scattering and the transmission of excitation light was extremely poor. It also became evident that industrial grade "Yttrium Stabilized Zirconia (YSZ) contained impurities of commonly used phosphor dopants, such as Dysprosium and Erbium. This, of course, caused a non-acceptable disturbance. After many tests a sufficiently pure research grade TBC (. Metco, 204B-NS) was identified. The opacity to UV radiation was an issue also for the 204B-NS. Eventually a thermographic phosphor with a suitable temperature range and that could be excited in the green spectral region was found, Y_2O_3:Eu. The optical transmission for 204B-NS at 532 nm proved to be significantly better than in the UV region.

To test the ability to measure beneath a TBC, several test coupons were coated with the Europium based phosphor Y_2O_3:Eu which was then covered by 204B-NS of different thicknesses. These coupons were placed in the high temperature furnace, one by one, and the results reveal significant damping of the signal already at 50 µm, although it was possible to extract temperature information through a 200 µm TBC layer.

The final step was the feasibility test in the combustor test facility at Siemens in Finspång. Furnace tests provide high quality data on the phosphor´s thermal response but to investigate the overall robustness and ability to cope with noise and background luminosity, these on-site investigations on a real burner were necessary. For these tests a, full scale, third generation DLE burner from an industrial gas turbine was coated by Högskolan Väst. To maximize the output from this campaign the burner was divided into several sections, each with different coating thickness and sensor depth. Temperatures were probed on the top coat as well as from the embedded sensor layer. A very positive result was that it proved feasible to extract temperature information from a sensor layer positioned 300 µm beneath the TBC surface. This is very promising for the continuation and it is actually 200 µm deeper than in the published literature. From the applied measurements performed at Siemens two important aspects could be verified, one was that the phosphor technique proved capable of handling the background luminosity levels found in the real application and the other was that temperatures could be extracted both from the surface and from within the thermal barrier coating. So far the project must be considered a success. Having said that it should be mentioned that, as for every experimental investigation, new questions have appeared. For example the peak surface temperature seems to be higher than initially expected. This implies that a different phosphor material would be beneficial for the top layer. The burner was also equipped with some thermocouples embedded in the steel alloy beneath the TBC. Although the phosphors and the thermocouples are not probing in the same location, currently there seems to be a discrepancy between the newly generated results and the expectations from Siemens. To protect the intellectual property rights of the project partners, the exact details cannot not be given here.

Commercial perspectives

The gas turbine efficiency increase with increased temperature of the exhaust gases from the combustor into the turbine. The metallic materials used in combustor designs have a melting point lower than the combustion temperatures and already today they are protected by thermal barrier coating (TBC). For future gas turbines higher efficiency is targeted and therefore even higher combustor temperatures. Increasing the firing temperature the temperature distribution in the combustor needs to be optimized for all types of operation. For instance new types of fuels might change the flame shape and position, new ways of operation with flexible load (cycling) will alter the heat load on the combustor walls.

Predicting the TBC lifetime is of crucial importance for the industry since the component lifetime is heavily linked to the coating lifetime. If TBC spallation occurs the metallic design material may be exposed to the hot environment and partly melt, in worst case leading to interrupted operation. Being able to measure the temperature distribution on the walls of the combustor, as well as probing the thermal gradients in the TBC, would facilitate an optimized heat load for the critical components. This in turn would improve the life time expectancy while operating with low emissions and, at the same time, high temperatures.

Conclusions

The search for thermal barrier coating materials and thermographic phosphors that fulfilled all the requirements for this ambitious project became more demanding than initially expected. The two major hassles were severe attenuation of UV radiation caused by the TBC materials commonly used in industrial turbines and the level of impurities found in these coatings. However, all major obstacles could eventually be addressed and two suitable sensor materials were identified, one for the top surface (DySZ) and one for the embedded layer (Y_2O_3:Eu). After successful tests in a high temperature furnace, these two sensors were applied on a full scale burner and measurements were performed in Siemens combustor test facility in Finspång. The outcome is positive. All the aims mentioned above could be accomplished. Temperatures could be extracted through remote sensing from both the surface and from within the TBC also in this harsh environment. At present there are discrepancies between the measured temperatures and the temperatures expected/calculated by Siemens. The origin of this deviation is considered very interesting by the partners involved and further investigations will follow also after the end of this project.

For a continuation of this research it would be of great interest to explore new phosphor materials and to examine other means of excitation with the aim of reaching deeper into the TBC. Also tests were phosphors are used in parallel with e.g. thermosensitive paint would aid the understanding of temperature probing in porous media.

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1 Introduction

The ability to measure temperature is crucial for the development of efficient combustion devices such as reciprocating engines and gas turbines. Especially when the measurements are to be performed in high temperature environments or on moving parts, there is a distinct advantage if the measurements can be conducted through remote sensing. Pyrometry is one alternative but this approach suffers if there are unknown variations in emissivity over time or with temperature. Also if the object is not a perfect black or gray body, the emissivity will alter differently for different spectral regions. An alternative that has seen significant development over the last decade is phosphor thermometry. Pioneering work in this field has been performed by NASA and Rolls Royce to name a few. In this study phosphor thermometry has been applied for measurements of surface and sub-surface temperatures of thermal boundary coatings, with the aim of providing a new diagnostics tool for the gas turbine industry.

2 Thermal boundary coatings

2.1 INTRODUCTION

Thermal barrier coatings (TBC) have now been used extensively in the gas turbine industry for over 30 years. TBC's are used in hot section components of the engine; these include the combustor, turbine inlet guide vanes, turbine blades, turbine stator blades and afterburners. Areas coated with a TBC can be seen in figure 1:

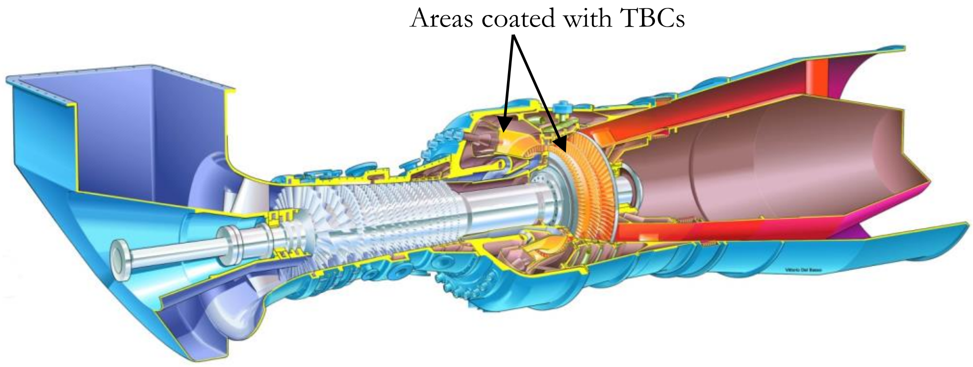


Figure 1. SGT-800 Industrial Gas Turbine, Courtesy of Siemens Industrial Turbomachinery.

The function of a TBC system is to allow higher temperature operating conditions than would be allowed by the metals used to make the engine [1].

Gas turbines operate under the Brayton cycle. The efficiency can be described by the following formula:

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \left(\frac{P_1}{P_2}\right)^{(\gamma-1)/\gamma}$$

Where η is the efficiency, T1 is the inlet temperature, T2 is the outlet temperature, P1 is the inlet pressure, P2 is outlet pressure and γ is the heat capacity ratio of the working fluid. Overall efficiency of the turbine will increase if the pressure ratio is increased.

However, a consequence of increasing the pressure ratio is a higher compressor outlet temperature, leading to higher turbine temperatures. It can be seen that higher turbine temperatures will also raise the efficiency of the process combined with an increased specific power output. The trend in both aero turbines and industrial power turbines is a need for greater efficiency and specific power. The main barrier to this upward trend has been the development of materials capable of withstanding the increased turbine inlet temperatures required. TBC's have allowed an increase in turbine inlet temperature to a level beyond the softening point of the metal alloys used to construct the engine. Components have developed from simple forged and wrought components in the 40's, to modern single crystal turbine blades [2]. Present developments of single crystal nickel alloy blades with film and internal cooling have reached the limit of capability. There are presently no immediate replacements for the nickel blades used in the high pressure turbine section.

TBC's were first used towards the end of the 50's as protection on duct work and rocket nozzles within experimental projects at NASA. By the 1970's, the first TBC with the familiar structure appeared on sheet metal components within gas turbines. TBC's began first in military service but progressed to civilian engines around the mid to late 70's. By the early 80's, companies were generating long term lifetime data for TBC's [6-7] under service conditions. By the 21st century, thermal barrier coatings have become integral to almost every modern aero turbine and stationary gas turbine produced.

TBC's consist of at least three component layers; a diagram of a TBC system is shown in figure 2. The first layer is the bond coat applied onto the base component. An intermediate layer is formed during operation called the thermally grown oxide (TGO). The final layer is the ceramic top coat that provides the operating temperature increase. The ceramic material chosen has a very low thermal conductivity allowing up to 200K temperature drop across the coating [1]. Thicknesses for a bond coat can be in the range 100-200µm with a ceramic top coat layer of between 200µm and 1.5mm.

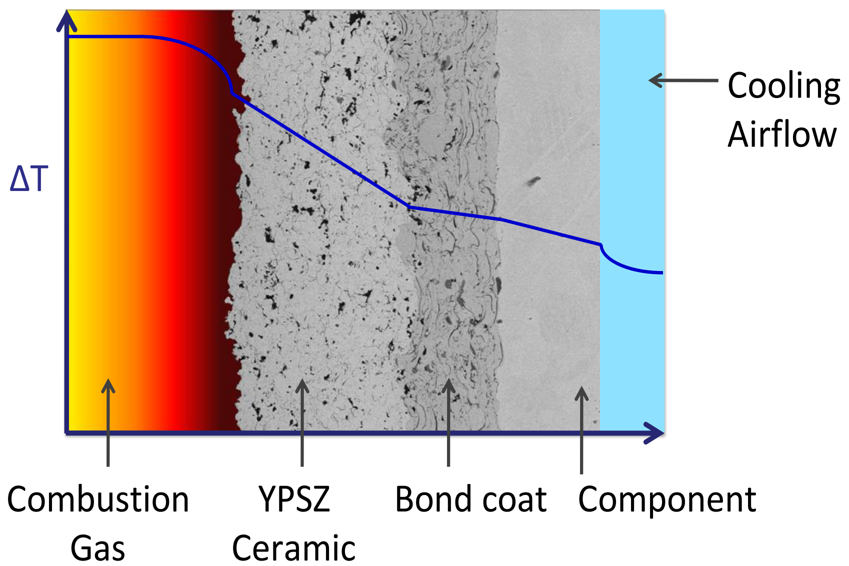


Figure 2. Diagram of a TBC system with temperature drop illustrated across the coating cross-section.

2.2 TBC MATERIALS

To operate effectively, a TBC needs a heat sink on the component side. This is commonly air cooling (at 400-600°C) from the compressor stage. Cooling is required to set up a thermal gradient in order to exploit the insulating effect of the system. At peak power a TBC may have a ceramic surface temperature around 1200°C with a bond coat temperature in the region 950-1050°C. Civilian aero-turbines are operated at peak power for short periods during take-off and landing. A military engine may experience higher temperatures during combat. An industrial gas turbine by comparison normally runs at slightly lower temperatures but for many months rather than hours [8].

A thermal barrier coating may be used in a number of different components within an engine. A combustor component will experience mainly thermal load whereas a coated turbine blade may experience centripetal loading from rotation as well as thermal load. The result of having different components within different types of engine mean there is no single TBC system suitable for all situations; it must be tailored to meet specific requirements in each case.

2.2.1 Bond coat

The bond coat provides a number of functions to the system:

- Improved adhesion between the top coat and the substrate
- Reduction in the interface stress due to the mismatch in thermal expansion coefficients between top coat and substrate component
- Protection of the substrate from oxidation and corrosion by the formation of a slow growing thermally grown oxide (TGO)

Bond coats are commonly of two types. Diffusion based aluminide coatings or MCrAlY (Metal-Chromium-Aluminum-Yttrium) overlay coatings [9]. The M can be Iron, Cobalt, nickel or a mixture of more than one element. Present standard coatings are mixtures of nickel and cobalt depending on the environmental requirements. High nickel content coatings are more suitable for oxidation resistance and high cobalt content suitable for high corrosion environments. The quality and rate of oxidation of the bond coat is arguably the limiting factor in the total TBC lifetime [10]. This will be discussed in more depth later.

2.2.2 Top coat

The ceramic top coat is the component which gives a TBC system its thermal insulation properties. The choice of material for the ceramic layer is determined by a number of factors:

- Low thermal conductivity to prevent heat transfer to the component from the combustion gas
- High thermal expansion coefficient to allow the ceramic to expand and contract with the component without cracking
- Phase stability at high temperatures to prevent any changes in volume that would cause failure

Over the course of development, 6-8 wt.% yttria partially stabilized zirconia (YSZ) has become the material of choice for this application [1]. The reason for the choice has been its combination of properties. This material is used due to its relatively high coefficient of thermal expansion and very low thermal conductivity of around 2.25 W m^{-1} K^{-1} in bulk form and the region of 1 W m^{-1} K^{-1} for a standard TBC coating. YSZ is also stable up to 1200°C [9, 11].

The addition of a rare earth element, yttrium, to the zirconium oxide is required to stabilize the tetragonal prime phase of zirconia [3]. If stabilization was not achieved there would be a high temperature (900°C) phase change of the zirconia on cooling with the appearance of increased monoclinic phase. The phase change is accompanied by a 4% volume change that would result in cracking and failure of the coating [11-12]. A content of 2 mol% yttria is the minimum required weight fraction in order to partially stabilize the tetragonal phase of zirconia.

The common usage of 3-5 mol% (6-8 wt%) yttria has come about as a product of lifecycle testing. While 2 mol% is the minimum required for stabilization as discussed earlier; higher fractions of yttria have been used in the past. Figure 3 illustrates the effect of yttria content on the stable phase present within the YSZ. If the mole fraction is pushed to 8% or above then the YSZ will be completely cubic at all temperature ranges. In fact such compositions were tried during the 1980's due to their lower thermal conductivity than 8 wt% YSZ. However, it was discovered that higher yttria content negatively impacted the cyclic lifetime of the coatings and that 6-8 wt% gave the best compromise in properties [1, 13].

YSZ was chosen as a TBC material due to its low conductivity. The addition of substitute cations to zirconia lowers the thermal conductivity of the resulting ceramic. Incorporation of cations leads to a great increase in the number of oxygen vacancies within the ceramic. These vacancies act as phonon scattering centers in the crystal lattice, lowering the thermal conductivity of the material [14]. This reduction is proportional to the amount of substitute cations added to the ceramic.

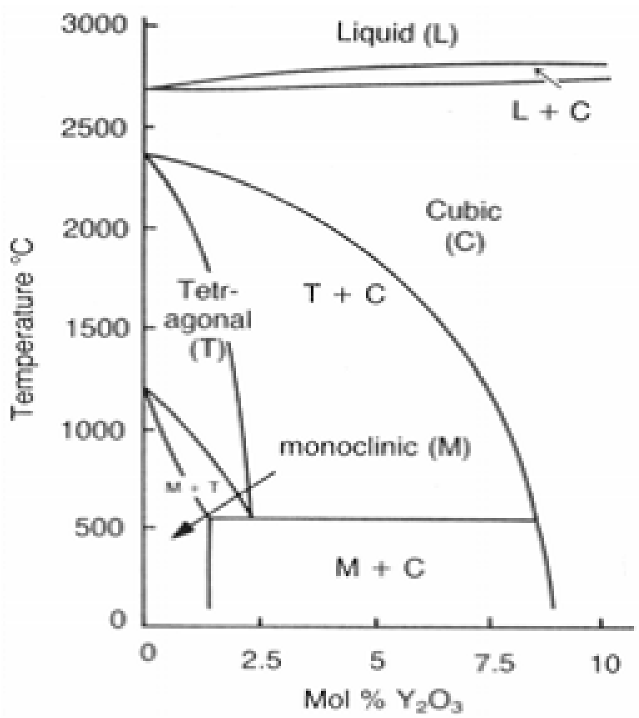


Figure 3. Yttria/Zirconia phase diagram.

It has also been discovered that the reduction in thermal conductivity is proportional to the difference in the ionic radius between the zirconium ions and the substitute ions. By adding cations with larger ionic radius, thermal conductivity is reduced [14]. Commonly this substitution is done using other rare earth elements. Coatings have been produced with zirconium doped with erbium, dysprosium, hafnium and gadolinium oxides amongst others [9].

Another characteristic of YSZ is that it is very efficient at transportation of oxygen at high temperatures due to the large number of oxygen vacancies. This transparency to oxygen in the environment is perhaps the greatest problem with the use of YSZ for TBC's. The zirconia top coat layer is unable to provide any barrier to the oxidation of the metal underneath [15]. While this weakness has been countered by the development of bond coats with higher and higher oxidation resistance; this fundamental problem means the YSZ layer often never achieves its maximum lifetime due to failure of the bond coat.

2.3 TBC COATING TECHNIQUES

Thermal spray comprises a number of methods used to deposit coatings onto various supporting structures. The coating feedstock material is fed into the spray 'gun' by a controlled feed system. The coating material may be metallic or nonmetallic and come in the form of a rod, wire, powder or solution. The guns energy source heats the injected coating material to a semi-molten or molten state. Droplets or particles of coating material are accelerated towards the substrate by exhaust gases from the energy process or by a separate gas jet. The particles solidify rapidly on contact with the substrate surface, forming a strong bond.

Further impact of droplets or 'splats' build up the coating to the required thickness. Any material can be used to produce a coating provided it does not decompose on heating in the gun [16]. A schematic of the type of structure built up by thermal spray is shown in figure 4.

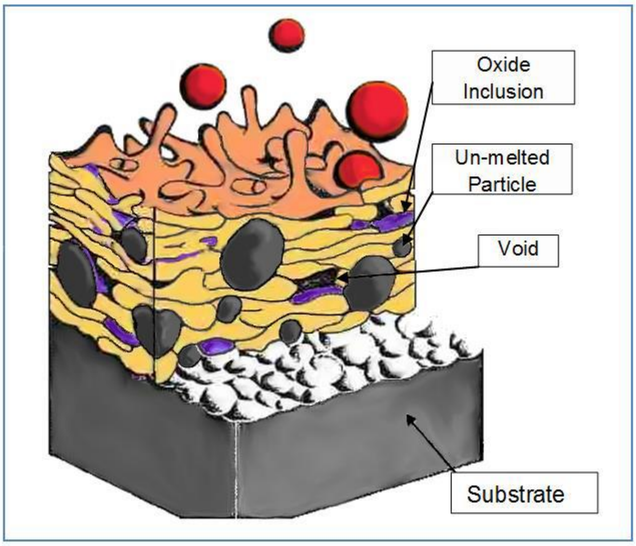


Figure 4. Schematic of a thermal Spray Coating.

Thermally sprayed coatings show common microstructural characteristics. The build-up of the coating through successive 'splat' impacts with the surface produces a lamellar structure, with individual splats forming the lamella as they cool. If the cooling rate is sufficiently high, columnar grains will grow within the splat. The process does not produce a perfect coating; oxides formed on the surface of a molten droplet will become inclusions in the coating along with unmelted particles. As a general rule the inclusion of oxides, unmelted particles and foreign objects is detrimental to coating properties.

The porosity present in a TBC topcoat provides the system with two important features. Firstly, the presence of pores acts to enhance the low thermal conductivity of the coating. Secondly, the network of pores acts to lower the stiffness of the layer, thus, allowing some compliance when the coating is exposed to cyclic heating. The primary function of the ceramic top coat is to provide thermal insulation; therefore the microstructure is created in order to maximize this property. However, the requirement to withstand thermal cycling stress will often result in a compromise in order to gain the best coating. Common features of a ceramic coating are shown in figure 5.

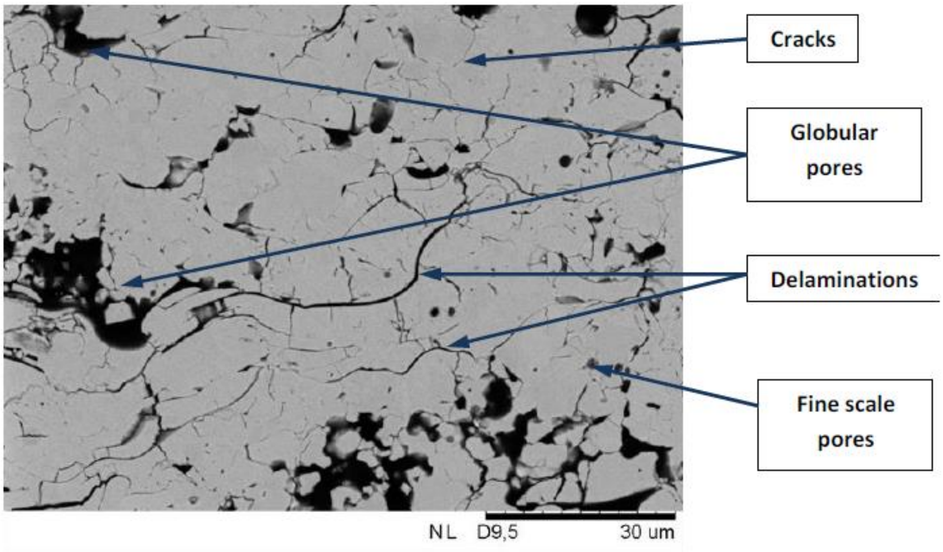


Figure 5. SEM micrograph of a ceramic coating with key features highlighted.

The thermal spray process can be used to produce coatings without significant heat transfer to the component. This avoids thermal distortion and possible damage to heat sensitive components. Coatings can be stripped if damaged and re-sprayed. The disadvantage of thermal spray is that it is a line-of-sight technique; certain component geometries will be difficult if not impossible to coat in a satisfactory manner.

Thermal spray comprises a number of possible methods for application. The methods vary in the source of heat and the method for accelerating the material to the surface. The principles for each are roughly the same.

2.3.1 Plasma Spraying

The plasma spray process derives its heat source and particle acceleration from a plasma jet. The jet is generated in a gas stream containing a mix of gasses (hydrogen, argon, nitrogen, helium) using a high frequency direct current. An electrical arc is struck between an anode and cathode within the gun. The plasma forming gas flowing past this arc is heated to the point where electrons are stripped from the gas atoms and plasma is formed. This plasma is accelerated out of the gun nozzle. Powder material for coating is injected into the plasma jet to form a coating on the substrate. The figure below shows a cross-section of a typical plasma spray gun.

Plasma spraying is the primary method in which thermal spray TBC's are produced. The temperature of the plasma can vary from 6000°C to 15000°C and the velocity of the particles can be up to 1500m/s, depending on the process parameters and gasses used [16]. The powder feedstock is injected into the plasma where it becomes molten; droplets of material are then accelerated towards the substrate by the plasma jet exiting the spray gun. This process can be carried out in a normal atmosphere, in which case the process is termed Atmospheric Plasma Spray (APS). The spray process can also be carried out in a controlled environment; in this case the process is termed Vacuum Plasma Spray (VPS) or Low Pressure Plasma Spray (LPPS). Carrying out the spray procedure under a controlled environment can improve coating quality by excluding oxygen. However, these processes add additional expense due to the environmental handling equipment and longer process times.

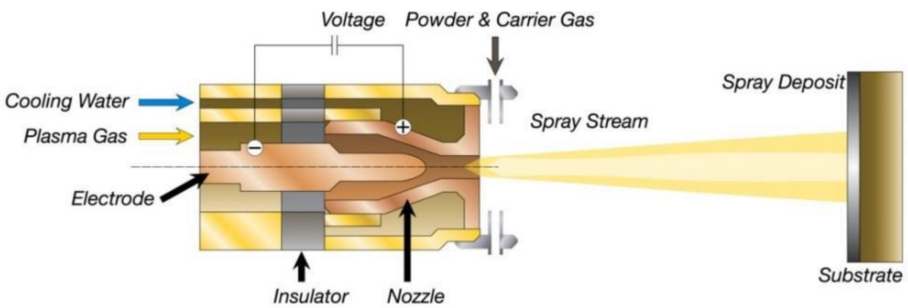


Figure 6. Schematic of a single anode/single cathode DC plasma torch, reproduced by permission of Sulzer Metco AG.

A scanning electron microscope (SEM) image of a typical thermal spray TBC system is shown in figure 7. It can be observed that a standard TBC contains a fair volume of open space or porosity (black regions within the coating). This porosity is characteristic to many thermal spray coatings and is beneficial to the performance of a TBC. Thermal spray TBC's commonly have a thermal conductivity around 1 W m-1 K-1 compared to more than double for the bulk material. The porosity created during spraying enhances the thermal insulation of the coating and also increases its strain tolerance [17].

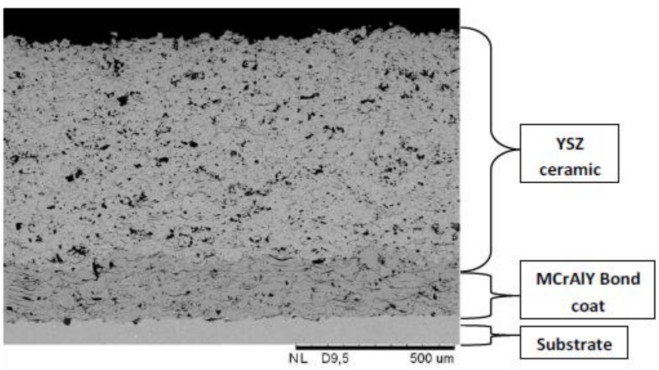


Figure 7. Micrograph of a plasma sprayed TBC system on Hastelloy X substrate.

2.3.2 Flame Spraying

The flame spray process uses the combustion of fuel to create a flame and thus the heat source and accelerating force for the deposition process. Flame temperature is controlled by the mix of fuel gasses and oxygen.

The most recent advance in flame spraying has been High Velocity Oxy-Fuel (HVOF) and High Velocity Air-Fuel spraying. In these processes a fuel (either liquid or gas) is mixed with oxygen (or air) in a combustion chamber. The mix is ignited and the combustion gasses are accelerated down a long convergent/divergent nozzle. The nozzle design creates a supersonic combustion jet into which powder can be injected.

The benefits of this process are that the process temperature is reasonable but the particle velocity on impact is very high. The resultant coatings are generally very dense, adherent and contain few oxides. These processes are suited to spraying high quality metallic coatings as well as cermets [16]. The quality of the coatings makes them very attractive as an application method for a bond coat within a TBC system.

3 Thermographic phosphors

3.1 INTRODUCTION

Thermographic phosphors (TP) are remote temperature sensing materials that have the capability of probing temperatures starting from cryogenic temperatures up to around 1800 K. Temperature probing applications using thermographic phosphors are extensive and include, but are not exclusive to, biological, electric, industrial and combustion research applications. The constituents of an thermographic phosphor are an inorganic host that is doped by an activator which can belong either to rare earth ions or transition metals. Thermographic phosphors react to the change of temperature by altering their phosphorescence emission characteristics. The changing characteristics could be a spectral change (e.g. a wavelength shift of the emission distribution or intensity variations of spectral components), or of temporal nature, phosphorescence decay-time reduction with increasing temperature. By computing phosphorescence spectral ratios of two of the phosphorescence emission lines using 2-D detectors, e.g., CCD or CMOS cameras, surface temperatures can be obtained by inverting the relation between the spectral peak ratios and temperature. Similarly, by implementing a detector to measure the phosphorescence decay-time, usually a photomultiplier tube, single-point temperature measurements can be done. It is important to point out that the method chosen for this project was the temperature measurement using the decay-time methods due to experimental limitations. These limitations will be discussed in details in a later section.

3.2 PHOSPHOR MATERIALS

Thermographic Phosphors are usually produced as fine powders with an average size distribution ranging between 1-5 μm. These doped ceramic substances are then mixed with a binder. By the use of an airbrush, this phosphor/binder mixture can be sprayed on the surface of interest. The binder used in this study is "HPC", a water-based liquid binder that is composed of water (98%) and magnesium silicate (2%). This binder is designed to withstand high temperatures up to 1800 K. TPs are usually excited with a UV-laser which effectively produce phosphorescence luminesce.

3.3 METHODS OF EXTRACTING TEMPERATURE INFORMATION

Temperature extraction from thermographic phosphor characteristic change of emitted luminescence is most often done by two methods. The first method utilized the change in the emission spectrum of the phosphor as function of temperature. While the second method implements the measurement of the rate of decay of the delayed luminescence. Each of the aforementioned methods have their pros and cons compared to the other.

3.3.1 Intensity ratio Method

The change of emission is usually displayed as an intensity variation where one band displays a relative increase in intensity while another band displays a counter behavior. Then, by simultaneous measurement of the intensity of both spectral bands, one can deduce a relation of their ratio as function of temperature.

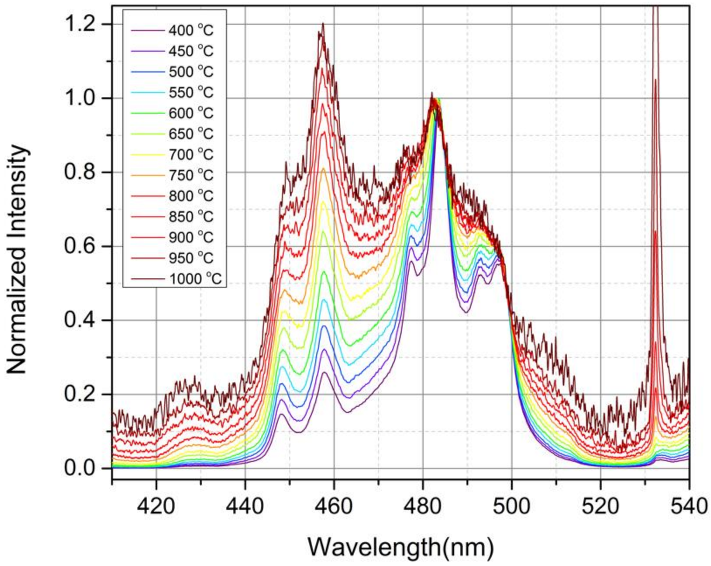


Figure 8. Emission spectrum of DySZ thermographic phosphor/TBC as function of temperature.

As seen in figure 8 above, the emission spectrum of the thermal barrier coating/ thermographic phosphor displays a strong dependence on the temperature, ranging between 400 to 1000 °C, especially the spectral band centered at 458 nm. By calculating the ratio of the intensity of the band centered around 458 nm over the intensity of the band centered at 483 nm, a calibration curve is obtained. Spectral selection is done using interference filters that selectively transmit luminescence within a certain band while suppressing luminescence from other spectral bands. A calibration curve is a function that relates the change of phosphor luminescence to temperature which can be later used to deduce the surface temperature. An example of intensity ratio calibration function is illustrated in figure 9.

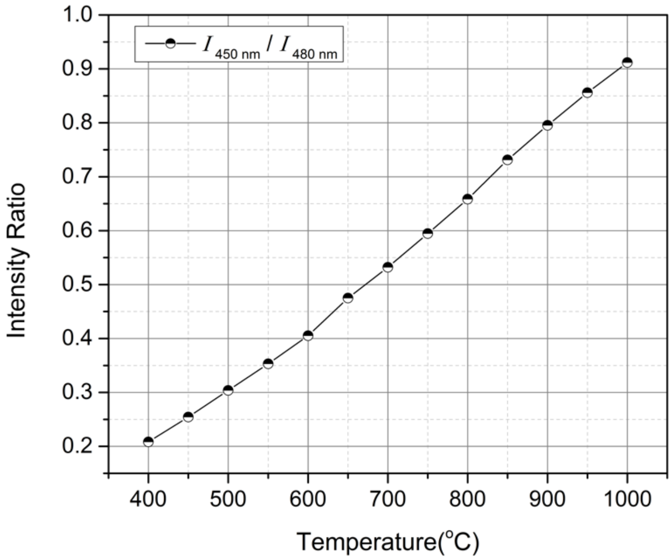


Figure 9. Calibration function of the intensity ratio deduced from the DySZ emission spectra as function of temperature.

At a specific temperature by using a scientific camera equipped with one interference filter, an intensity image (I_1) is recorded for the luminescence that only originates from one specific emission band. Then, by changing the interference filter to select the luminescence originating from another emission band, a second image is recorded (I_2). After background subtraction and signal averaging a ratio image is obtained by dividing I_1/ I_2. This ratio is then averaged over all of the pixels and corresponds to one point of the calibration curve (fig. 9). This process is then repeated over the full range of temperatures at which the phosphor is sensitive.

A calibration curve is a function that relates the change of phosphor luminescence to temperature which can be later used to deduce the surface temperature. An example of intensity ratio calibration function is illustrated in figure 9.

The ratio method is advantageous in the manner that a two-dimensional temperature information can be obtained with high spatial and temporal resolution. However, temperatures attained by this method are more prone to errors originating from detector alignment and detector distortions. In addition, this method has a higher experimental cost and complexity compared to the decay-time method.

3.3.2 Decay time Method

This method alternatively utilizes the sensitivity of the temporal decay rate of the emitted luminescence to temperature. After an excitation by a short pulse (nanosecond), most often from a UV laser, the thermographic phosphor emits luminescence (phosphorescence) that is shifted to longer wavelengths compared to the excitation wavelength. Temporally the emission has a much longer duration (ms-μs) than the excitation pulse duration (ns). The emission intensity decays with time and this decay can be described by an exponential function as that presented below.

$$I(t) = I_0 e^{-t/\tau} + C$$

$I(t)$ and I_0 are the intensity of the emitted signal at any given time t and at t = 0, respectively. τ is associated with the decay-time and C is a constant signal offset. The luminescence emitted by the thermographic phosphor is usually detected using a photomultiplier tube.

As seen in the fig. 10 the sensitivity of the decay-time method is better in terms of sensitivity to the ratio method. The decay-time exhibits a change in the measured decay-time that spreads over three orders of magnitude within the phosphor temperature sensitivity range that typically spans over few hundred of degrees.

This method has a high temporal resolution. The spatial resolution is governed by the local beam size of the exciting laser. As in the case of the intensity ratio method, the decay-time method requires the acquisition of a calibration curve that is used to convert the measured decay-times to temperatures. A calibration is built by simultaneously acquiring the temperature, of a substrate where the phosphor being calibrated is sprayed upon, and the decay waveform of the phosphorescence. An example of a calibration curve can be found in fig. 11 displayed below.

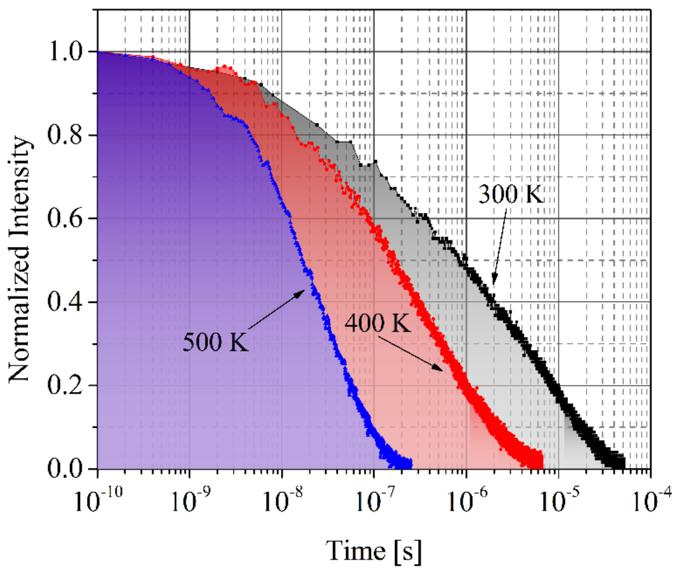


Figure 10. Phosphorescence decay curves of $CdWO_4$ phosphor at 300, 400 and 500 K.

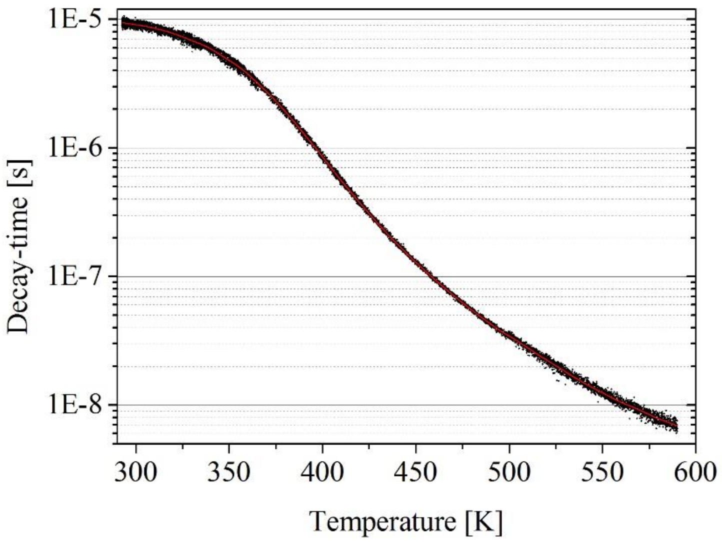


Figure 11. Temperature Calibration curve of $CdWO_4$.

The decay-time method has many advantages compared to the intensity ratio method. One of which is that the required optical access can be much smaller and optical fibers can be utilized to deliver the excitation radiation and the emitted phosphorescence. Since photomultiplier tubes have a higher gain combined with the fact that the collected signal is focused to a spot using a lens, much lower phosphorescence signal levels can be detected. This is important since thermographic phosphor luminescence intensity decreases as the temperature increases due to different quenching mechanisms. Another advantage can be seen in the higher sensitivity of the decay-time method compared to the later method which reflects as significant increase in the precision of the temperature measurements established. Using the decay-time method a precision around and even better than ±5 K degrees is attainable.

3.4 ADVANTAGES AND DISADVANTAGES OF USING THERMOGRAPHIC PHOSPHORS

Temperature distribution in any combustion system is vital for the development and understanding of the combustor behavior. In the case of turbine engines, knowing the temperature distribution of the different components such as, combustor wall, burner tip, flame holder, just to name a few, can provide an insight on the performance and longevity of these components.

The use of thermal barrier coatings (TBCs) in such engines made the achievement of higher efficiency possible due to the thermal shielding they provide to the different components they are applied to. The performance and durability of TBC coatings are heavily affected by the temperature at which they are exposed to and thus having a precise measurement of temperature is essential to the development of these coatings.

Due to the insulating nature of the TBC, steep thermal gradients are present within the coating. Attaining temperatures of the surface of the top coat and the temperatures of the interface between the top coat and the thermally grown oxide (TGO) offers a clear idea about the thermal load the coating is subjected to and facilitates the optimization of these coatings.

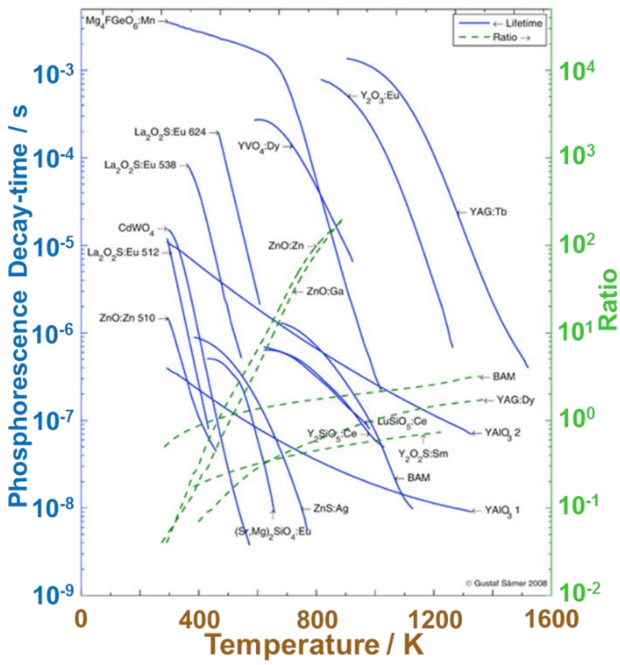


Figure 12. Temperature sensitivity range of different thermographic phosphors for both the decay-time and intensity ratio measured as function of temperature.

Measuring the temperature in devices like a turbine engine is far from trivial and thermocouples can’t be used due to the fact that the sensor need to be placed on the surface of the coating and deep within. Thermographic phosphors on the other hand provides a suitable substitute that can provide accurate and precise measurement of temperatures on and in/beneath the surface at different depths within the TBC. Thermographic phosphors are usually composed of ceramic material that is doped by a rare-earth element so they are capable of surviving operating in harsh environments present in the turbine engine. Another aspect of TPs is the remoteness where they can be excited and their signal collected from a remote location. TPs have a high sensitivity, see fig. 12, especially when the decay-time method is employed that provides a high precision temperature measurement. It is important to point out that the sensitivity range is individual to a specific thermographic phosphor. Moreover, TPs display fast response to temperature changes and are able to resolve quick thermal changes like those present in an internal combustion engine. One of the most important benefits is its minimal intrusiveness due to the reason that only a very thin layer (≈20µm) is deposited on the surface of interest.

TP also have some drawbacks, one of which is the requirement of optical access for the delivery of the excitation radiation and the collection the emitted phosphorescence luminescence. The size of the optical access depends on the measurement method used and the detector employed for signal detection. The utilization of TPs for temperature measurement necessitates an experienced user to be able to operate them without falling into error or disturbances that can lead to erroneous temperature values.

4 Develop a TBC with embedded sensor material

4.1 INTRODUCTION

Monitoring the performance of high temperature components in advanced gas turbine engines is more and more required in order to accelerate the insertion of advanced materials, coatings, fuels and novel designs. Collecting continuously the component temperature, one can provide feedback on the efficiency and performance of the engine as well as the health of engineering components. For example, the growth rate of the thermally grown oxide layer (TGO), an alumina scale that forms at the interface between the bond coat and the top coat and which can destabilize the coating leading to one of the primary failure mechanisms, is strongly temperature dependent. Indeed, an increase of the temperature at the bond coat of approx. 50 °C from 1010 °C to 1060 °C can approximately triple the growth rate of the TGO and lead to premature failure. No method for measuring temperature inside a TBC in an operating turbine currently exists. Hence, the temperatures in key regions are not known and lifetime prediction models cannot be applied with certainty. As a result, TBCs have, to date, been used conservatively, to extend the life of turbine components rather than to realize increases in operating temperature and efficiency. The current generation of TBC's could be used more effectively if closer control of temperature were enabled by a reliable on-line temperature measuring technique. Traditional techniques for measuring temperature such as those relying on thermocouples or pyrometry suffer from certain serious limitations. Thermocouples in combustion applications are not only intrusive but prone to a multitude of possible errors, including those of radiation, conduction along the wires, catalytic effects and the slow response. Pyrometry is a non-contact sensing method based on measuring the naturally emitted electromagnetic radiation by all objects. In combustion applications, temperature dependent emissivity variations from surfaces and flames, as well as absorption by gases and soot, become inevitable making the results questionable. Measurement techniques based on the use of temperature sensitive phosphors known as (thermographic phosphors has become an important tool) for temperature measurements in various combustion environments but also in related phase-changing processes, e.g. droplets, sprays and pyrolysis.

For TBC applications the most reliable method is to embed a sensor coating i.e. a coating that contains a photoluminescent element into TBC system. However, the incorporation of sensors coatings in TBC working in harsh turbine environments represents a challenging task. Issues concerning sensor location and integration, sensor performance, robustness and reproducibility must be addressed. In addition, the extraction of signals in harsh environments requires advanced and accurate measurements. One goal of this project was to develop sensor coatings within TBC systems. The sensors need to be robust and reproducible and applicable for harsh environments.

Measuring thermal gradient across the TBC layer requires temperature information from at least two locations on and beneath the top coat surface. The utilization of thermographic phosphor for such a task involves extensive investigations to determine which TP is most suitable for such a measurement. Probing the top coat surface temperature involves a lower level of complexity compared to the probing of sub-surface temperature. The highly scattering nature of atmospheric plasma sprayed (APS) TBCs and the fact that yttria stabilized zirconia (YSZ) are opaque for UV radiation, presents a large challenge for sub-surface temperature measurements.

4.2 IDENTIFYING SUITABLE PHOSPHOR AND TBC MATERIALS

4.2.1 Requirements on temperature range and optical properties

To determine which thermographic phosphors that can be utilized for such a task a rough knowledge on the expected temperatures is needed for both probe locations. It is important to indicate that the temperature measurements will be performed on the TBC coated burner tip of a Siemens SGT-800 gas turbine. The temperatures at the burner tip is expected to range from 500 up to 900 °C. Such a TBC system is of composite nature and its structure and properties can vary depending on the thermal load it experiences (see fig. 13). Most of the changes occur in the top coat, where phase transformation of the sprayed porous oxide may occur, and the TGO layer, which is growing due to prolonged exposure to high temperatures. The rate of phase transformation of the YSZ TBC and the growth rate of the TGO are dependent on the temperatures both layers experience, thus precise knowledge of their temperatures is crucial.

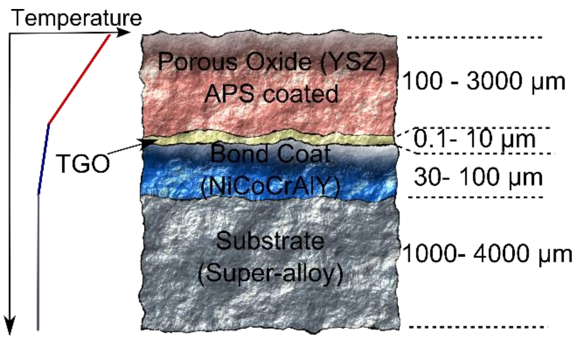


Figure 13. Schematic of a typical thermal barrier coating system.

There are several requirements that are deemed necessary for the success of this project listed as the following:

- At least two sensing materials are needed for probing temperatures at the surface of the top coat and at the interface between the top coat and the TGO.
- The selected thermographic phosphors should have a temperature sensitivity range that covers the expected temperatures (from 500 up to 900 °C).
- The selected thermographic phosphors should not have any interference in the emission wavelengths selected for experimentation to prevent the possibility of crosstalk.
- TPs should maintain a good luminescence intensity at high temperatures.
- TBCs used as a top coat should have the lowest content of contaminants that may luminesce and interfere with the luminescence emitted by the TPs.
- The top coat TBC should be translucent to the excitation radiation used to excite the sensor layer deposited beneath the TBC surface.

All of these requirements need to be met otherwise temperature probing is unachievable. In the next section, several optical investigations on a couple of selected thermographic phosphors and an array of YSZ TBC materials are reported to investigate the feasibly of such measurements.

4.2.2 Investigations on YSZ optical properties and Impurity content

High level of porosity is a common and desired feature of the plasma sprayed thermal barrier coatings due to their improved reduction in thermal conductivity compared to other coatings obtained by the use of electron-beam physics vapor deposition (EB-PVD). However, this high level of porosity is detrimental to optical experiments due to the increased scattering coefficient that means less excitation radiation is able to reach the sub-surface temperature sensing layer. The attenuation due to scattering influence the emitted phosphoresce as well as the exciting laser radiation. The inherent nature of this issue means that little to none can be done to improve such a problem. The level of porosity is the highest for as-sprayed condition before subjecting the coating to any thermal load. It has been noticed signs of coating sintering after exposing the TBC to a thermal load which in return lead to the reduction of porosity. Keep in mind that the TBC porosity variation due to possible sintering has not been investigated in this project.

The main issue this project faced was the inability for UV radiation to penetrate through the top-coat and excite the thermographic phosphor layer located at a certain depth beneath the surface, see figure 14. The UV opaqueness of the YSZ material cannot be changed and the only possibility of sub-surface temperature depend on the selection of an excitation source whose wavelength can be partially transmitted to the phosphor sublayer. Nd:YAG lasers are usually used as an excitation source producing UV radiation at 266 nm and 355 nm. Moreover, Nd:YAG lasers also produce radiation at 532 nm, at this wavelength the APS YSZ material has a transmission of around 5%. Other coating techniques (EB-PVD for example) that produce YSZ coating in a columnar structure result in a better transmission characteristics of the YSZ coating. However, such coating techniques are expensive and the product coating suffer from a higher head conductivity compared to APS coatings.

Laser radiation at 532 nm is the only alternative to UV radiation that can penetrate the top coat and successfully excite the sub-surface sensing layer. Laser radiation at 355 nm is suitable for TP excitation at the surface of the YSZ top coat.

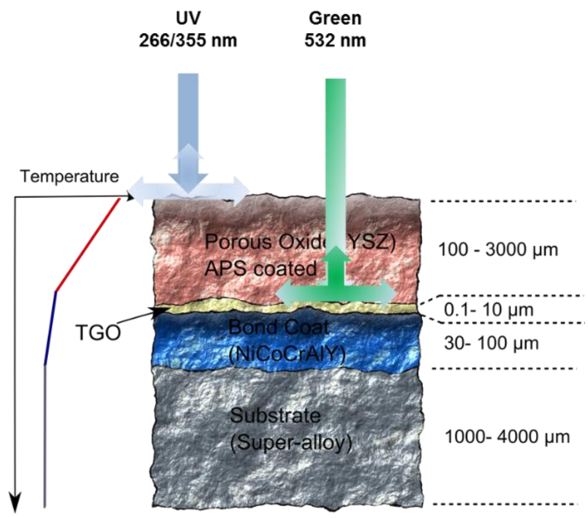


Figure 14. Illustration of the APS YSZ transmission for different laser radiation wavelengths.

Another major issue faced in this project was the existence of impurities in the supposedly inert YSZ material chosen as a top-coat material. The first choice of YSZ was the Amperit 827 from H.C. Starck, which is a standard TBC available from the suppliers. Optical investigation showed that the Amperit 827 has a high level of impurities that interfered significantly with the chosen TPs which rendered this material unusable for the current project. An array of higher purity YSZ materials produced by Metco were tested. A list of the tested YSZ samples along with information about the source and composition is provided in table 1. The test were conducted as the following, a UV-laser radiation at 355 nm was used to excite each of the different materials at room temperature and an emission spectrum was recorded. After which the signature emission lines of some contaminants were identified in addition to the broadband emission from ZrO_2. The measured emission spectra are presented in fig. 15.

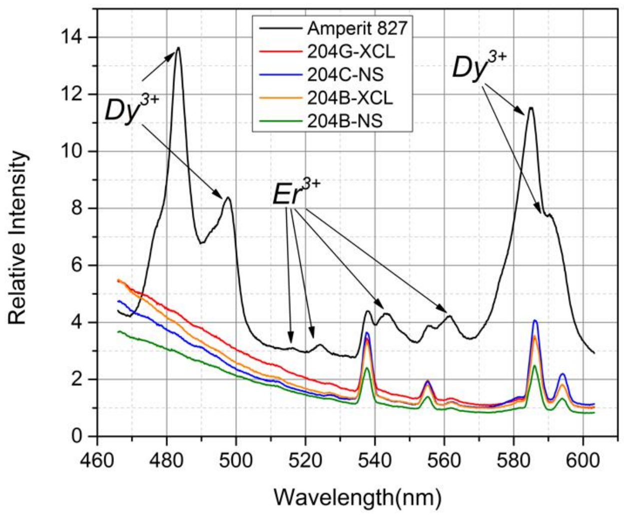


Figure 15. Emission spectra of several YSZ materials under excitation by laser radiation at 355nm.

Table 1. List of investigated YSZ materials

Sample #	Manufacturer	Name	Composition	Manufacture method
1	H.C. Starck	Amperit 827	ZrO_2-$7Y_2O_3$	Agglomerated & sintered
2	Metco	204B-NS	ZrO_2-$8Y_2O_3$	Agglomerated & HOSP
3	Metco	204B-XCL	ZrO_2-$8Y_2O_3$	Agglomerated & HOSP
4	Metco	204C-NS	ZrO_2-$8Y_2O_3$	Agglomerated & HOSP
5	Metco	204G-XCL	ZrO_2-$8Y_2O_3$	Agglomerated & HOSP

It can be seen in figure 15 that high contamination levels by dysprosium and erbium in the case of the Amperit 827. On the other hand, YSZ material produced by Metco display lower levels of contamination. Metco sample 204B-NS was selected as the most suitable YSZ powder to be employed as a top coat material for optical testing purposes.

4.2.3 Investigations on the optical properties of selected thermographic phosphors

As stated earlier, the process of selecting the suitable thermographic phosphors is constrained by requirements set by the range of temperatures expected to be measured and the excitation wavelength chosen to excite each phosphor. These requirements are not the same for the two locations at which the temperature is to be measured. The requirements for each of the locations, listed below, are based on estimations made by Siemens for the application in the atmospheric test rig.

- For temperature measurement at the top coat surface:
  - TP with temperature sensitivity range 500-800 °C
  - Excitation possible with UV laser radiation
  - Strong luminescence intensity
- For temperature measurement at the top coat/TGO interface:
  - TP with temperature sensitivity range 400-800 °C
  - Excitation possible with 532 nm laser radiation
  - Strong luminescence intensity

The most suitable TPs that meet these criteria are the following:

- For temperature measurement at the top coat surface:
  - Dysprosium stabilized Zirconia (10% by wt. DySZ)
- For temperature measurement at the top coat/TGO interface:
  - Europium/Yttria mixture (Y_2O_3:Eu) 75 mol% Eu concentration

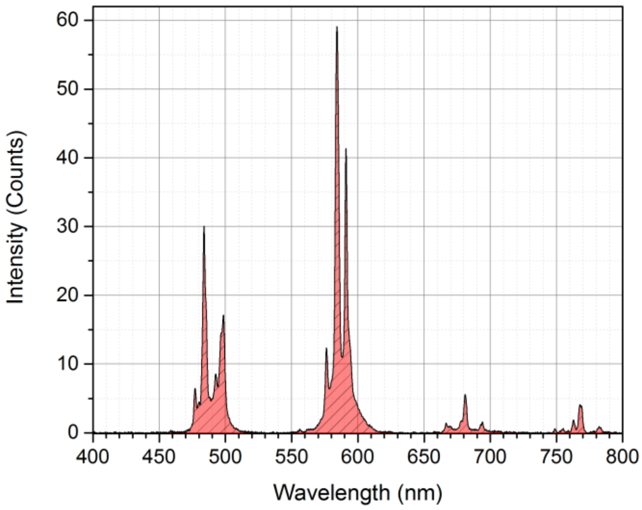


Figure 16. 10% DySZ emission spectrum at room temperature after excitation by 355 nm laser radiation.

The emission spectrum of DySZ at room temperature is acquired and illustrated in figure 16. The emission spectrum exhibit four emission bands, the stronger two located around 485 nm and the other at 585 nm are most suitable for the planed temperature measurements. These emission bands are mainly emitted by the Dysprosium present in the zirconia host. These bands have a temperature sensitivity and the high temperature tests results will be reported in a later section

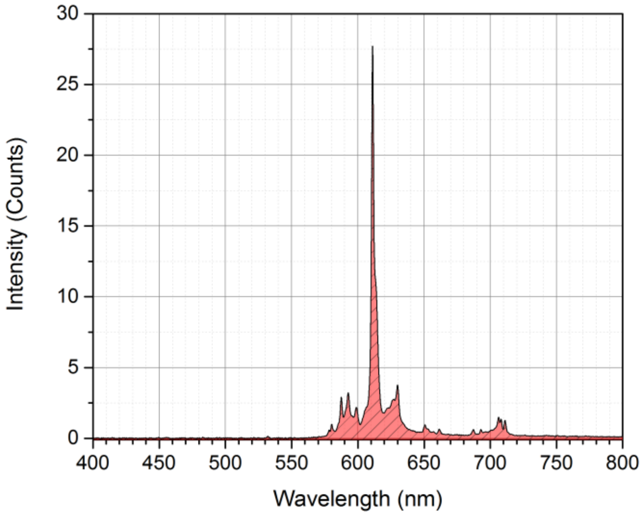


Figure 17. Y_2O_3:Eu (75 m/o) emission spectrum at room temperature after excitation by 532 nm laser radiation.

Y_2O_3:Eu after excitation by 532 nm radiation has an emission spectrum that is dominated by a single band centered around 611 nm, figure 17. This band will later be used for temperature measurement and its luminescence intensity as function of temperature will be investigated. The emission originates from the europium dopant, while the host has a minor influence on the emission spectrum. It is important to note that since DySZ doesn't display any significant emission when excited by the 532 nm radiation, there would be no interference from the two sensor materials when they are excited simultaneously using the appropriate laser radiation wavelength.

4.2.4 TBC system with embedded temperature sensor material

After the selection process of the sensor material was completed, the final design of the TBC system with the embedded sensor materials took a final shape. In fig. 18, it can be seen that the DySZ will be coated on the surface of the burner tip while the Y_2O_3:Eu material will be coated at the interface between the TGO and the top coat as indicated.

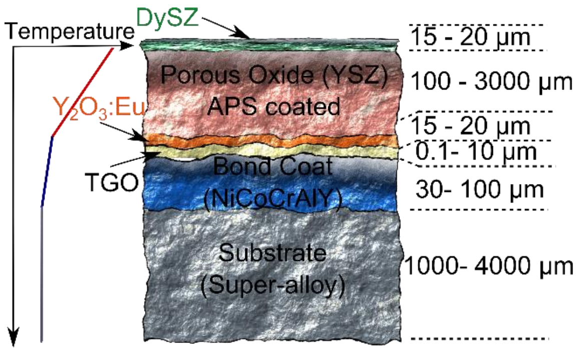


Figure 18. TBC system with embedded temperature sensing materials.

4.3 PREPARATION OF TEST COUPONS

In order to develop TBCs with integrated photoluminescent coatings several alternatives of composition and coating configurations have been tried. The sensor coating should consist of high temperature materials (similar to those used for top coats) and phosphorescent material(s) which may give information regarding the temperatures inside the coating. It was decided that the best location for the sensor coating is at the interface between the ceramic top coat and the metallic bond coat as presented in figure 19. There are basically two reasons why the coating was placed at the bond coat/top coat interface. One is that most of the failures of the TBC originates from this region. Under oxidizing conditions at high temperatures the TGO (thermally grown oxide), consisting mostly of alumina, starts to grow. The growth of the alumina layer generates some level of stress (growth stress). This is thermal mismatch stress caused by the difference in coefficient of thermal expansion (CTE) between the ceramic TGO and metallic bond coat. At some critical thickness for the TGO the strain developed will be sufficient to drive crack formation at the interface; this is known as critical strain energy. In practice much of the strain developed in an oxidizing TBC system is dissipated by creep in the bond coat due to its high ductility at operating temperatures. The second reason was from design perspectives. A continuous demand on designing next generation components for hot part of a gas turbine, is to allow higher inlet temperatures, so that better engine efficiency can be reached. The temperature levels in the turbines should however not exceed the temperatures at which the metallic structure of the engine loses its mechanical properties but should be as close as possible. For that accurate temperature information is needed from the metallic structure under thermal cyclic tests. On the other hand new top coat materials, various thicknesses and different level of porosity have a direct influence on the heat transfer through the top coat that ultimately will reach the metallic substrate. Having direct temperature measurement from the metallic interface may avoid laborious calculations/modeling which most of the cases are not exact due to the complexity of the TBC’s microstructure.

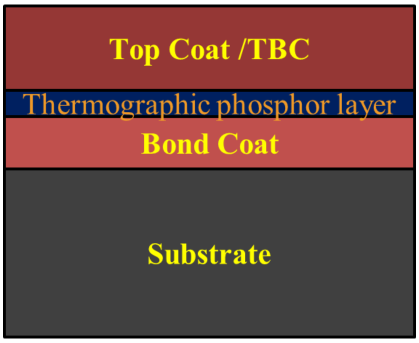


Figure 19. TBC configuration containing a sensor layer

One purpose of the experimental work performed in the project was to figure out the appropriate volume content of the phosphor material that gives the best signal from thermal sprayed coating, as well as if the thickness of the coating can have any influence on the signal intensity.

All coatings investigated in this study were deposited by atmospheric plasma spraying. Sulzer Metco F4 atmospheric plasma gun was used for this purpose. The substrates used for spray trials were coupons of 25.4 mm in diameter and 6 mm thick, made of the nickel based superalloy (Hastelloy-X). Prior spraying the bond coat the substrates were grit blasted with Al_2O_3-60 mesh. The bond coat material used was NiCoCrAlY (AMDRY 365-2). The spray conditions for bond coat were the same for all the samples and the spray parameters used were standard (given by the spray equipment manufacturer). The thickness of bond coats was approximately 150 µm. The substrate and bond coat were kept the same through the whole project while several iterations were done with different top coats. Same spray parameters were used for spraying the top coats in order to minimize the changes in the top coat microstructure. A sprayed TBC sample is presented in figure 20.

Figure 20. TBC coated sample

The different iterations for spraying the top coat are presented below:

4.3.1 Spray trial 1

Spraying top coats of ZrO_2 stabilized with 10 wt.% Dy_2O_3 (10DySZ). The powder was produced by Oerlikon Metco (AE9773AS Agglomerated and sintered). Coating thickness 500 µm. This top coat was developed by Univ. West and Siemens in a previous projects and it is planned that Siemens will implement it industrially in the near future.

4.3.2 Spray trial 2

Top coats of 8 wt.% yttria stabilized zirconia (8YSZ) (Oerlikon Metco 204B-NS, HOSP) mixed (mechanically) with 10DySZ (Oerlikon Metco, AE 9556 HOSP) in ratios so that the Dy_2O_3 weight content in the top coat was 0.3%. This coating is labeled 0.3DySZ-YSZ. Both zirconia powders used in this trial were high purity TBC i.e. the impurity contend is lower than 0.1 wt.%.

Three set of samples with three different thickness of the ceramic layers were sprayed i.e. 40 µm, 60 µm and 80 µm respectively.

4.3.3 Spray trial 3

The top coat material used in this spray trial was agglomerated and sintered 7 wt.% YSZ (HC Starck, AMPERIT 827). AMPERIT 827 is common TBC powder used for industrial applications. It has a higher level of impurities (<1%) so that is a cost effective solution.

Same substrate and bond coats were used as in the previous trials. The thickness of the sensor coating is 50 µm. The samples sprayed with this powder are presented in the table below.

Sensor coating	Top coat	Top coat thickness, µm
0,3DySZ-YSZ	No top coat	-
0,3DySZ-YSZ	AMPERIT 827	50
0,3DySZ-YSZ	AMPERIT 827	150
0,3DySZ-YSZ	AMPERIT 827	250
0,3DySZ-YSZ	AMPERIT 827	350
10DySZ	No top coat	-
10DySZ	AMPERIT 827	50
10DySZ	AMPERIT 827	150
10DySZ	AMPERIT 827	250
10DySZ	AMPERIT 827	350
YAG Dy	AMPERIT 827	50
YAG Dy	AMPERIT 827	150
YAG Dy	AMPERIT 827	250
YAG Dy	AMPERIT 827	350
YAG Tb	AMPERIT 827	50
YAG Tb	AMPERIT 827	150
YAG Tb	AMPERIT 827	250
YAG Tb	AMPERIT 827	350

4.3.4 Spray trial 4

As the higher impurity top coats had influenced negatively the signal from the sensor coating it was decided that high purity top coats to be used further i.e. 8YSZ - Metco 204B-NS. Two sensor coatings were selected also for next measurements. The samples sprayed in this spray run are presented in the table below:

Sensor coating	Top coat	Top coat thickness, µm
10DySZ	No top coat	-
10DySZ	Metco 204 B-NS	100
10DySZ	Metco 204 B-NS	200
10DySZ	Metco 204 B-NS	300
10DySZ	Metco 204 B-NS	400
YAG Tb	Metco 204 B-NS	100
YAG Tb	Metco 204 B-NS	200
YAG Tb	Metco 204 B-NS	300
YAG Tb	Metco 204 B-NS	400

4.3.5 Spray trial 5

New phosphor layers are to be used for further experiments as the signal from the previous sprayed coatings was not satisfactory. The phosphor layer used in this spray trial was Europium doped yttria (Y_2O_3:Eu) and it was sprayed by air brushing.

The samples sprayed in this run are listed in the table below.

Sensor coating	Top coat	Top coat thickness, µm
Y_2O_3:Eu	No top coat	-
Y_2O_3:Eu	Metco 204 B-NS	50
Y_2O_3:Eu	Metco 204 B-NS	100
Y_2O_3:Eu	Metco 204 B-NS	200

The conducted tests revealed that a good signal can be obtained from the Y_2O_3:Eu sensor coatings through all tested thicknesses of the 8YSZ top coats.

4.4 HIGH TEMPERATURE FURNACE TESTS

After determining the suitable sensor materials for temperature probing at the two different locations on and within the top coat, high temperature investigation is the natural next step to determine the behavior and temperature sensitivity range of each of them. The sprayed test coupons were coated either with DySZ or a layer of Y_2O_3:Eu with a layer of Metco 204B-NS top coat of different thickness. These samples were then inserted into a tubular ceramic furnace and the characteristics of the emitted phosphorescence as function of temperature were studied.

4.4.1 DySZ

Starting with DySZ, this material is in reality a TBC and the dysprosium dopant emits phosphorescence that is sensitive to change in temperature. DySZ sample was placed in the furnace and the temperature was increased from 400 °C in steps of 50 degrees up to 1000 °C. At every attained temperature an emission spectrum and a series of 100 decay curves are acquired and later processed to extract the spectral information and the decay-time values. This information was then used to build a calibration curve for DySZ sensor material.

DySZ was excited using 355 nm laser radiation, the spectrum was measured using a spectrometer while the decay-time was detected using a photomultiplier tube. The photomultiplier tube was equipped with an interference filter centered at 586 nm and with a bandwidth of 20 nm to select the luminescence originating from DySZ and suppressing the any spurious radiation. The spectral information obtained is presented in figures 21 and 22 below.

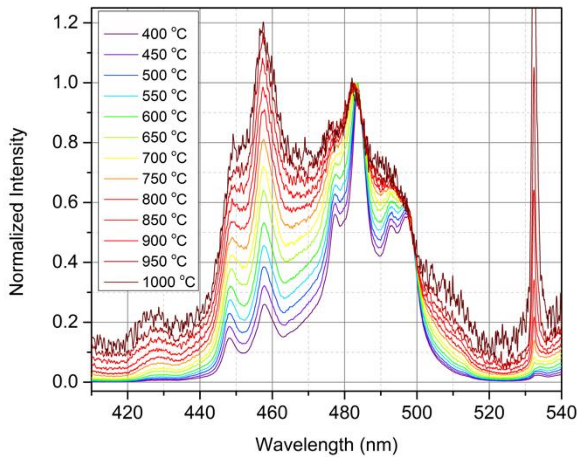


Figure 21. Dysprosium-stabilized Zirconia (DySZ) emission spectra as function of temperature. Laser excitation radiation at 355 nm was used.

The emission spectra of DySZ exhibit high sensitivity as function of temperature. It can be clearly seen that at temperatures higher than the room temperature another emission band around 458 nm starts to appear. Its intensity increases as function of temperature relative to the band centered at 485 nm.

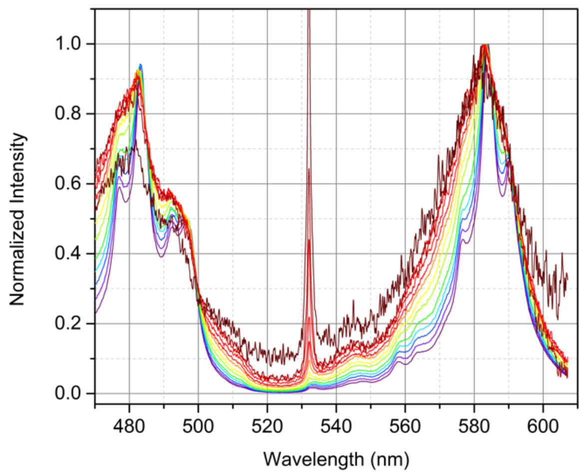


Figure 22. Dysprosium-stabilized Zirconia (DySZ) emission spectra as function of temperature. Laser excitation radiation at 355 nm was used.

The decay time of the DySZ sensor was calculated as function of temperature and plotted in figure 23. DySZ display a decay-time that has a temperature sensitivity up to 1000 °C. The sensitivity of the DySZ thermographic phosphor is high within the tested temperature range as the decay-time changes more than two orders of magnitude. It is important to note that the sensitivity range is also affected by the DySZ luminescence intensity levels due to the fact that these tests were performed under laboratory conditions at which the intensity levels are better than those found when experimenting on the Siemens burner. Thus no signal amplifiers were needed. For the tests performed at Siemens test rig, the attained maximum temperature range was around 900 °C due to the usage of an electronic amplifier after the detector to amplify the signal, which limits the temporal response range of the detection system. These tests verify that DySZ can be used as a thermographic phosphor for temperatures ranging between 400 and 900 °C under engine test conditions.

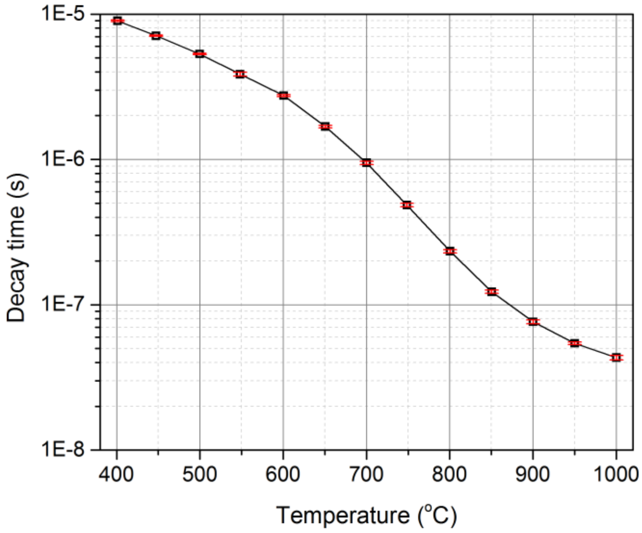


Figure 23. Calibration function of the decay-time deduced from the DySZ as function of temperature.

4.4.2 Y_2O_3:Eu

Y_2O_3:Eu phosphor was selected to be the temperature sensor for the boundary between the thermally grown oxide and the YSZ top coat. Similar to the case of the DySZ, high temperature tests on YSZ were performed and the temperature was increased from 400 °C insteps of 50 degrees up to 800 °C. Using the small absorption peak of Y_2O_3:Eu that is located at 532 nm and matches the wavelength of the radiation produced by an Nd:YAG laser, Y_2O_3:Eu was effectively excited. Emission spectra were acquired at a temperature intervals of 50 °C. Y_2O_3:Eu spectrum doesn't show any dependence of the profile of the emission spectrum as function of temperature, but as expected, the emitted luminescence intensity of Y_2O_3:Eu drops as temperature increases due to thermal quenching of the thermographic phosphor (see fig. 24).

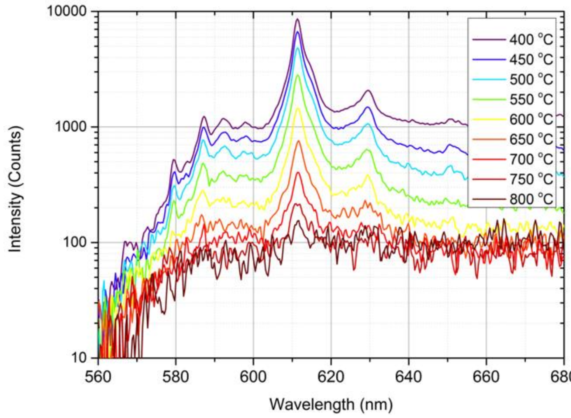


Figure 24. Y_2O_3:Eu emission spectra as function of temperature under 532 nm laser radiation excitation Beneath 50µm of 204B-NS YSZ top coat layer.

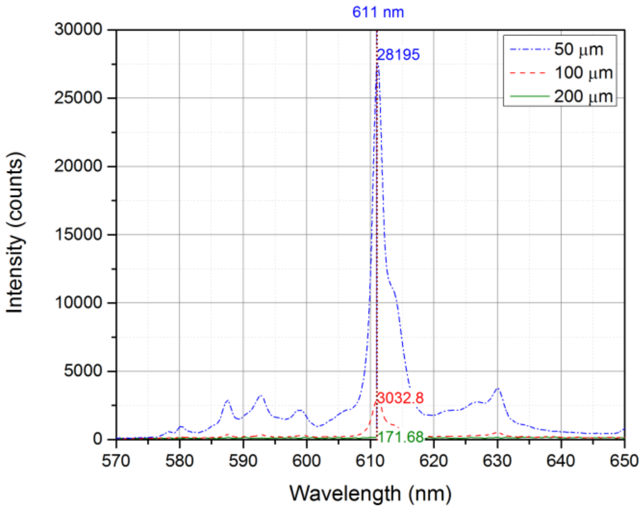


Figure 25. Y_2O_3:Eu emission as function of 204B-NS YSZ top coat thickness.

An important aspect to test for in the case of the Y_2O_3:Eu TP is the emission strength as function of top coat thickness sprayed above this sensing layer. The emission spectrum of Y_2O_3:Eu at room temperature was acquired from three different samples that were coated with three different thicknesses, 50, 100 and 200 µm of atmospheric plasma sprayed 204B-NS YSZ. The wavelength of the excitation laser was 532 nm and the emission spectrum was recorded using a spectrometer. The peak located at 611 nm displays a significant attenuation as the top coat thickness was increased from 50 to 100 and then to 200 µm. The intensity of the Y_2O_3:Eu luminescence was attenuated by a factor of 10 as the thickness of the top coat was increased from 50 to 100 µm. Increasing the top-coat thickness to 200 µm decreased the signal by a factor of almost 164 times the intensity emitted from beneath a 50 µm YSZ top coat, see fig. 25. It is clear that temperature probing of the interface between the TGO and the top coat might be challenging with top coat thicknesses greater than 50 µm. Moreover the sensitivity of the decay time of Y_2O_3:Eu TP covers the temperature ranges from 400 up to 900 °C, see figure 26.

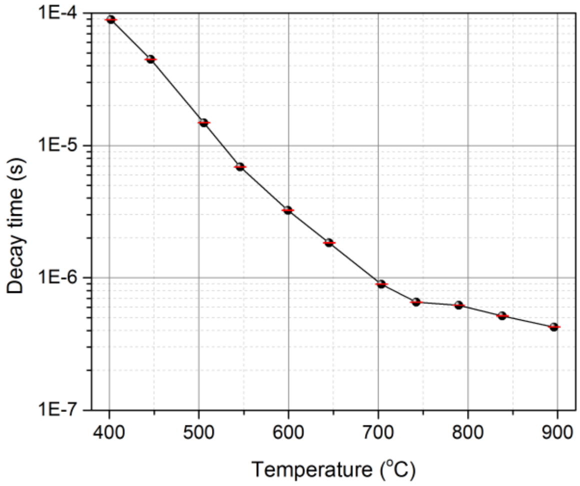


Figure 26. Calibration function of Y_2O_3:Eu thermographic phosphor after excitation by 532 nm laser.

5 Feasibility test at Siemens

5.1 THE SIEMENS BURNER

The burner used in the measurements is a low swirl standard third generation DLE burner used in industrial gas turbines. The main parts of the DLE burner are shown in fig. 27. The air flow enters a swirl generator, basically a four quarter-cones, which are shifted with respect to each other to create a swirling flow. The swirl cone is connected to a circular mixing tube with a secondary air inlet by means of film air rows. The swirling air/fuel mixture passes through the mixing tube and enters the combustion chamber, where it expands in a radial direction and ignites as it mixes with hot recirculated combustion gasses. Additional fuel can be injected through the pilot flames, which are equally distributed circumferentially around the burner tip, or through the central gas nozzle.

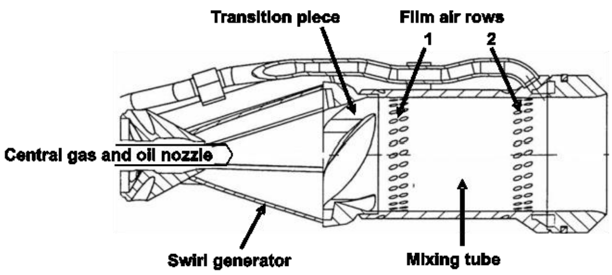


Figure 27. Siemens SGT-800 burner.

5.2 PREPARATION OF THE SIEMENS BURNER

In order to spray the burner a special fixture was built up so that it can be kept fast during spraying the layers. The burner placed in the fixture is shown in figure 28.

Figure 28. Burner and fixture prepared for spraying

Spraying the coatings on the burner was done in several steps. The structure of the multilayered TBC with sensor coatings is presented on figure 29.

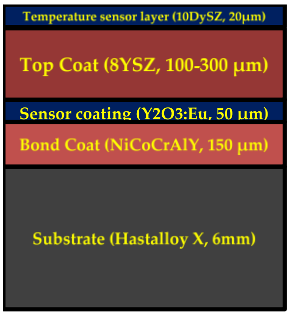
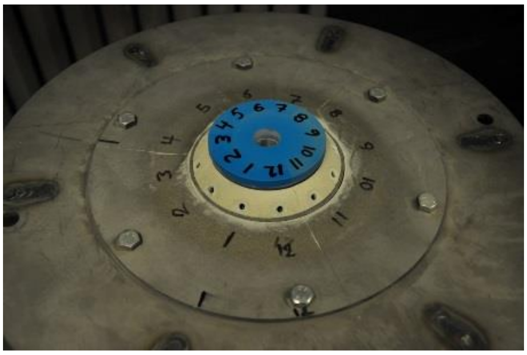


Figure 29. Multilayered TBC system for temperature measurements on the burner

As presented above the purpose for spraying the sensor coating at the bond coat / top coat interface was to measure the temperature of the metallic sublayer and substrate. The role of the sensor layer on the top of the TBC system was to measure the temperature from the ambient. Therefore the top sensor layer was not sprayed on the whole coated surface but only in the areas where the temperature is highest. The configuration of the coatings as well as the spraying sequences on the burner is presented below.

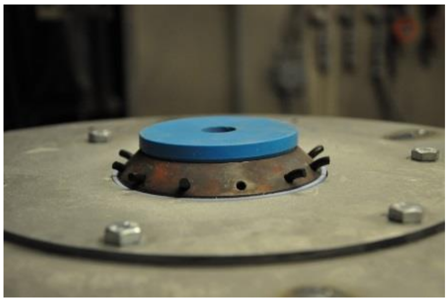
a. Dividing the burner's area to be sprayed in specific zones



b. Preparing the substrate for bond coat spraying

Cleaning (shot-blasting followed by ethanol)

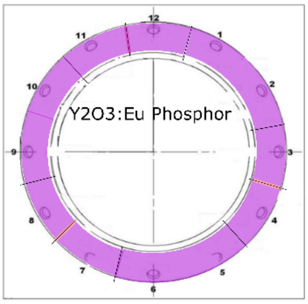
Masking



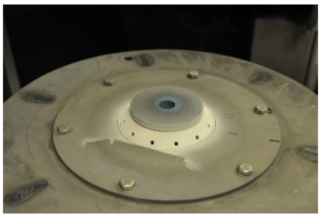
c. Spraying the NiCoCrAlY bond coat, 150 µm thick.

APS spraying

d. Airbrush deposition of the Y_2O_3:Eu phosphor layer, 50 µm thick



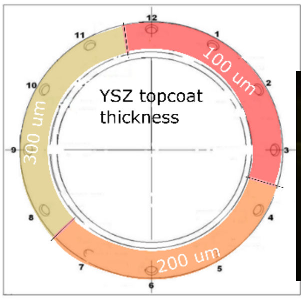
Area to be coated with Y_2O_3:Eu



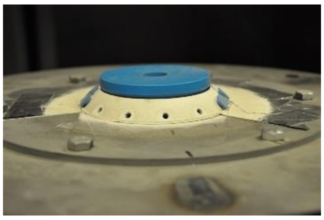
Air brushing

Y_2O_3:Eu coating

e. Spraying the 8YSZ top coat, 100 µm, 200µm and 300µm thick. Various thicknesses were sprayed in order to assess how the thickness of the top coat can affect the signal from the phosphor layer.



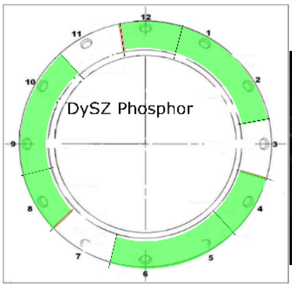
Areas to be coated with 8YSZ



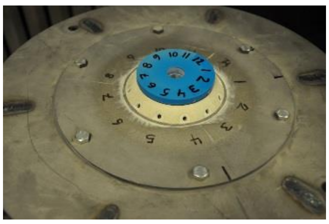
Plasma spraying of 8YSZ

8YSZ coating

f. Spraying the top sensor layer, 10DySZ, 50 µm thick as specified on the picture



Areas to be coated with 10DySZ

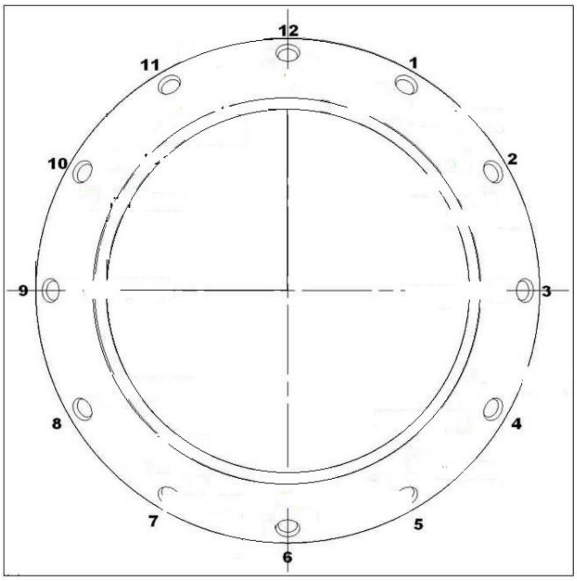


Plasma spraying of 10DySZ

10DySZ coating

g. Burner after completed spraying ready for temperature measurements

h. Numbering of the positions



5.3 MEASUREMENT OBJECT AND SETUP

5.3.1 Siemens Atmospheric Rig

In all experiments, the DLE burner was mounted in an atmospheric combustion test rig. The combustion chamber consists of a casing and a liner that is cooled convectively and has a single can configuration, see Fig. 31. The circular cross section has a similar expansion ratio as the Siemens SGT-800 annular combustor; however, the section closest to the burner exit has square cross section with smoothed corners to allow for improved measurement quality. The combustion air and cooling air is separated in order to control the liner wall temperature; thus, it is possible to provide the liner wall with either a constant or a variable temperature. The combustion air can be preheated up to 820 K prior to entering the plenum, where it is evenly distributed to the burner. Optical access to the flame region is possible through quartz windows, according to Fig. 30, on three sides of the liner (two opposed on each side and the other perpendicular below) allowing application of optical and laser diagnostic techniques. Emission probes, pressure transducers, and thermocouples is used for monitoring and measuring emissions, the dynamic pressure and temperatures at different positions in the combustion chamber.

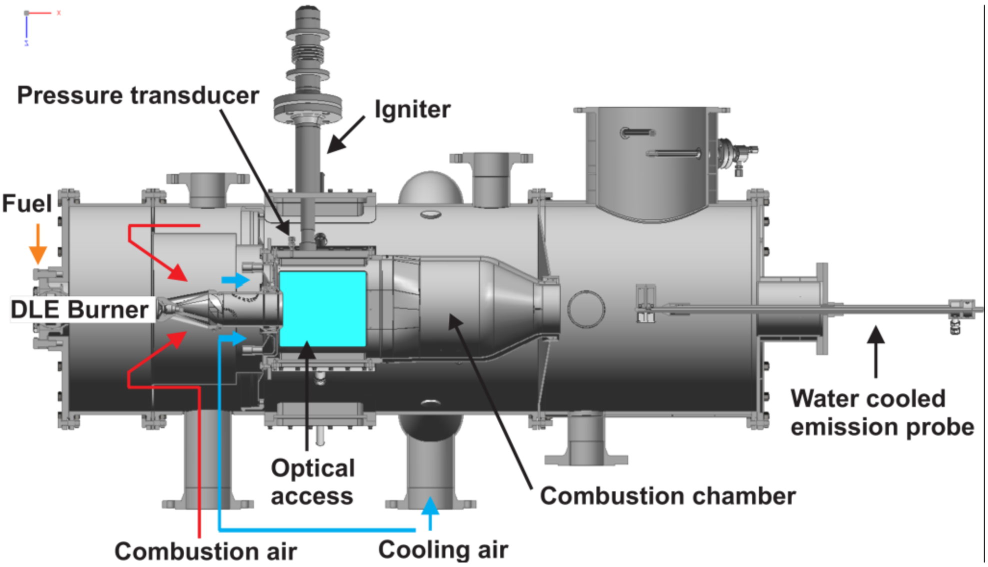


Figure 30. Siemens atmospheric combustion test rig

5.3.2 Experimental Setup

The experimental setup to perform temperature measurements on and beneath the TBC top coat is illustrated in the figure below. Two Nd:YAG lasers were used to produce laser pulses at the wavelengths 355 nm and 532 nm to selectively excite DySZ and Y_2O_3:Eu thermographic phosphors respectively. The emitted phosphorescence was then collected by a lens and the collected luminescence was directed onto a photomultiplier tube and the output signal was registered using a digital oscilloscope. Band-pass filters along with long pass filters were used to select the luminescence emitted from each of the excited sensors individually. Interference filters used were centered at 586 and 607 nm for DySZ and Y_2O_3:Eu thermographic phosphors respectively. An illustration of the experimental setup built at the test facility in Siemens atmospheric test rig is shown in fig. 31.

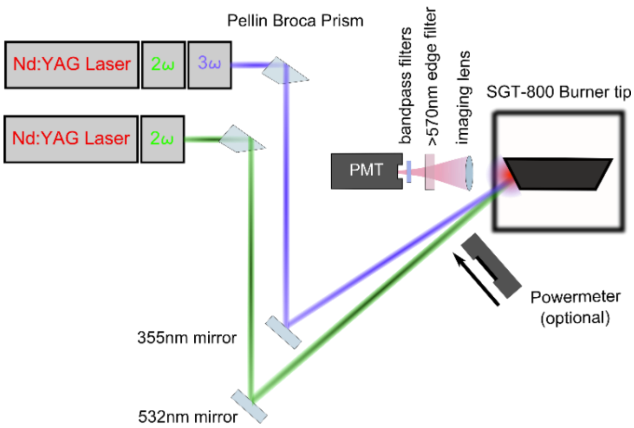


Figure 31. Sketch of the experimental setup to measure the temperature on the surface and beneath the TBC top coat.

The collected decay-time signal were afterwards post-processed and fitted with a single exponential function using a least-squares nonlinear solver available in MATLAB. The evaluated decay-times were then plugged into the calibration polynomial obtained for each of the sensors used, and temperatures could be extracted. At each of the measurement locations two series of 200 single shot measurements were acquired for both DySZ and Y_2O_3:Eu.

5.3.3 Burner measurement locations and running conditions

Six different measurements points were designated at the burner tip for which temperature measurements at the surface of the YSZ top coat and at the TGO/top coat boundary layer to be done. These locations were selected based on rough temperature estimations that were obtained from thermocouples placed couple of mm beneath the surface of the substrate. These locations were selected to cover all the regions of the different top coat thicknesses applied on the burner tip, see fig. 32.

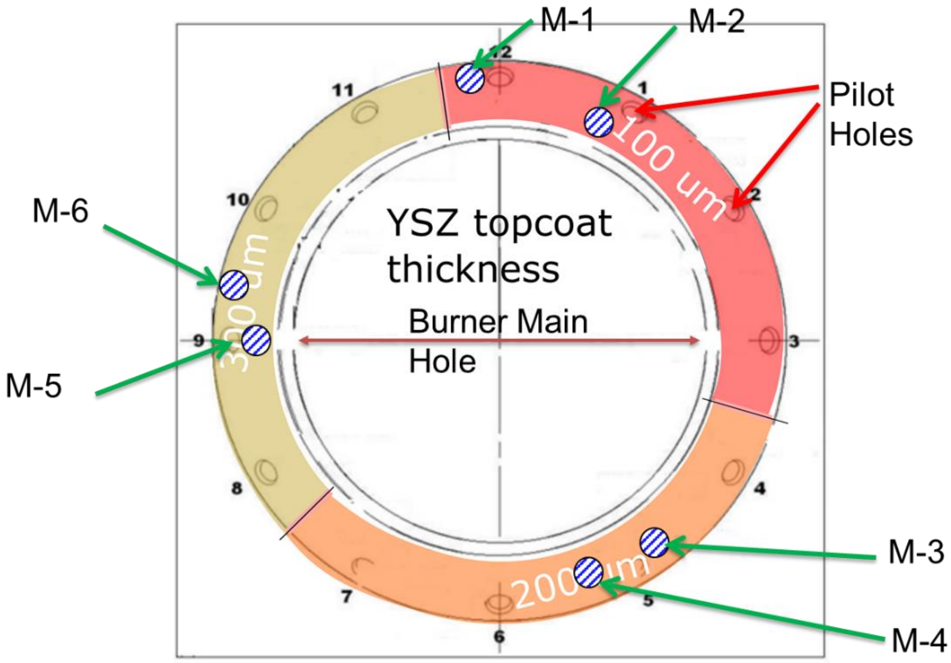


Figure 32. Siemens SGT-800 burner tip with the designated measurement locations.

Also, six different running conditions were selected as test running conditions to investigate the effect of factors such as the estimated flame temperature and pilot fuel percentage, see table 2. The condition no. 1 is considered as the reference operating condition for the Siemens SGT-800 burner. It is important to note that the fuel used for these experiments was natural gas.

Table 2: Selected engine running conditions for each of the measurement locations.

Running Condition #	Pilot (%)	Preheated Air Temp. (K)	Flame Temp.
1	0	820	T_{ref}
2	3	820	T_{ref}
3	6	820	T_{ref}
4	12	820	T_{ref}
5	0	820	T_{ref} +100
6	0	820	T_{ref} +200

5.4 RESULTS AND DISCUSSION

The temperature of each of the predetermined locations was measured at all of the different test conditions. At a single location phosphorescence from both sensors was detected by the photomultiplier tube. Luminescence from each sensor was detected separately and then the interference filters were changed to match the emission spectrum of the other sensor. It is important to note that the measured temperatures presented in this sub-section are normalized by dividing with the reference flame temperature (T_f).

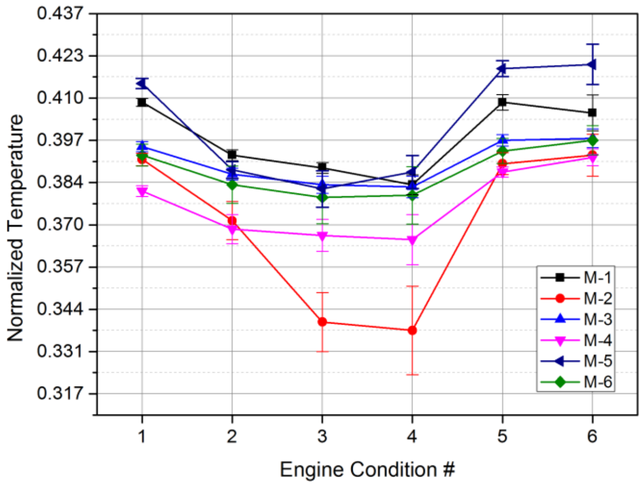


Figure 33. Normalized temperatures experienced by the Y_2O_3:Eu TP as function of position and selected test condition. The error bars represent the 96% confidence interval.

Starting with the TGO/top coat boundary layer, the sensing material for this layer is the Y_2O_3:Eu thermographic phosphor. The decay curves were evaluated and the temperatures deduced and plotted in figure 33. Every single point in the figure represents the average phosphor temperature from 200 single shots with the error bars representing the corresponding standard deviation (2σ). The majority of the deviations are from temporal variations of the sensor coatings. This illustrates the high temporal resolution of the presented measurement technique.

The first noticeable behavior is that all of the measurement point show a decrees in their temperatures as the pilot fuel percentage was increased from nil to about 12 %. This behavior is monotonic and the minimum temperatures are found with the running condition with the highest pilot fuel percentage. The temperature profiles then shows an increase back to almost the same temperature values obtained by the reference running condition (#1). Even with the increased flame temperatures the Y_2O_3:Eu shows only a slight increase in temperature in comparison to the first test condition.

It is important to point out that the paramount finding of this campaign is the feasibility to probe temperatures beneath the atmospheric plasma sprayed YSZ top coat. This challenge has been overcome by extensive research on the material properties which resulted in the ability to extract temperature information from beneath 300 µm of APS YSZ top coat. The largest thickness ever to be reported in literature for subsurface temperature probing of APS top coatings was around 100 µm. The investigations were reported by Eldridge et al. [18] and were performed in a laboratory environment where the emitted luminescence intensity is better than in an engine test condition. In other words, the ability to measure temperatures from 300 µm beneath a TBC layer is the main and most important achievement of this project.

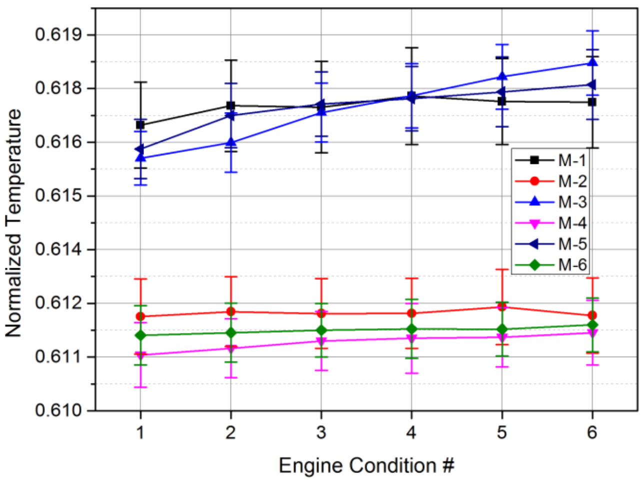


Figure 34. Normalized temperatures experienced by the DySZ TP as function of position and selected test condition.

For the surface temperatures, the measured values exhibit almost a constant temperature regardless of the engine operating condition. This behavior was not expected. M-1, M-3 and M-5 are slightly hotter than the other three positions, figure 34. However, the difference is negligible. One plausible explanation could be that in reality the temperature was higher than expected during the phosphor selection. Since the DySZ is sensitive up to 900 °C, it would not be able to provide proper response if the actual TBC surface temperatures are higher than 900 °C. Another thermographic phosphor is needed to probe such high temperatures. There are several candidates to be investigated. Then the most suitable one should be applied to attain accurate measurement of the TBC surface temperature.

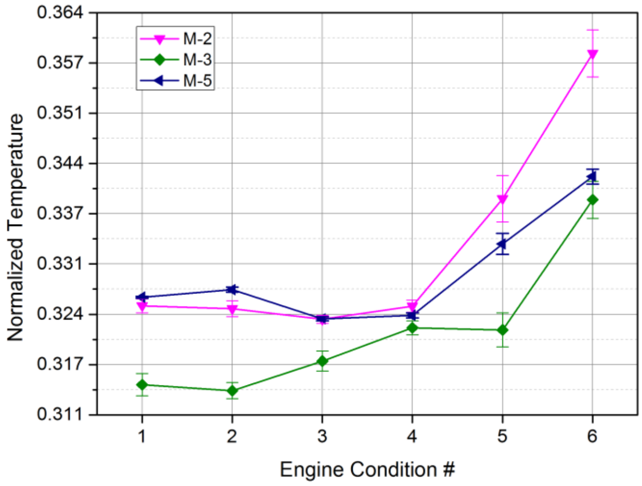


Figure 35. Normalized temperature data from thermocouples embedded few millimeters beneath three of the measured positions.

Thermocouples embedded within the burner tip at a close proximity from three of the measurement locations at a depth of few millimeters provided temperature readings (see figure 35). At first glance, the thermocouples located at M-2 and M-3 display a similar behavior to that seen from the sublayer temperatures displayed in figure 33 but with a much lower degree of change. The temperatures at conditions # 5 and #6 seem to have a much larger increase in reference to condition #1 than that shown by the sensing sublayer. There is no clear indication to why such behavior occurs and the complex flows within the combustion chamber might have a contribution to this observed difference.

These results establish the feasibility of conducting temperature sensing experiments that permits the measurement of temperature well beneath an optically thick material such as a TBC. The measurement campaign confirmed the experimental results obtained from the investigations and even showed that a temperature probing through a 300 μm of TBC is indeed successful and surpassed the previously laboratory investigations that indicated a maximum thickness of 200 μm.

Although some locations on the tip of the Siemens burner were instrumented with thermocouples, a direct comparison with the temperatures retrieved from the thermographic phosphors is not relevant. There are several reasons for this. First, the thermographic phosphor particles share one inherent property with thermocouples, i.e their output correspond to the temperature of themselves. High quality thermocouples with well specified precision and accuracy can be purchased. However, these numbers only relates to the thermocouple´s ability to probe its own temperature, something they do very well. In a real application the challenge is to either make sure that the thermocouple adopts to the temperature of the gas or substrate of interest, or to find means of compensating for the deviations. Both conductive and radiative energy transfer can induce significant measurement errors, especially at elevated temperatures such as in combustion applications. The signal intensity decay time from a thermographic phosphor is linked to a specific temperature. This implies that, just as for the thermocouple, the temperature of the phosphor particles can be extracted with high precision. (The absolute precision is established in the calibration measurements where four thermocouples are used as reference.) However, it can always be argued how well this phosphor particle represents the temperature of the measurements object. For this specific application it is obvious that there is no other temperature data from the top surface to compare with.

For the embedded sensor coating it might be tempting to just perform a direct comparison with the thermocouples mounted on/in the burner tip. This comparison was performed and this is where the discrepancies were mentioned to be significant. Having said that, it should also be mentioned that the thermocouples are not directly sensing the temperature of the bond coat. Instead they are placed at a certain depth beneath the bond coat. Furthermore, the mechanical coupling between the thermocouple tip and the measurements object is here unclear. In short, the temperatures obtained from phosphor thermometry in this test cannot be directly compared with thermocouple data. The phosphor technique provides a new possibility to probe temperature in porous materials like TBC´s and the findings have already initiated new research questions that will be addressed outside this SEBRA project.

6 Conclusions

6.1 BACKGROUND AND AIM

The burner delivers about 4 MW thermal power when it is in operation in the gas turbine combustor at 20 bars pressure. In the test performed here the burner is fired in an atmospheric test rig in which the thermal power is about 300 kW. The heat load on the burner tip and its coating is therefore much less and the surface temperature will differ between rig conditions and the full engine.

In this project the focus was to test the temperature measurement method and therefore a phosphor chosen believed to be suitable. There will in both cases be a heat transfer from the hot flame zone in the combustor through the burner tip (the coating layer) that is cooled by the preheated air. This is actually the heat load of the burner tip that Siemens desires to get more knowledge about since it is related to the life of the hot component – in this case the burner tip but it could as well be the combustor wall.

6.2 CHALLENGES

The UV opaqueness of plasma sprayed YSZ top coat was a challenge to overcome since earlier publications falsely indicated that plasma sprayed YSZ TBC are translucent to UV radiation. This claim however was found to be incorrect and a solution was needed to circumvent such a problem which could have brought this project to a halt especially for the part that is concerned with sub-surface temperature measurement.

It is also important to point out that there was no experience existing prior to this project on conducting temperature measurement upon and beneath the TBC layer. Given the short project duration an array of issues had to be solved before the next step of the project could proceed. This required the input from all of the project partners which was time consuming.

A difficulty that was not foreseen in its full dimension and that caused delays in the progress of the project came from the fact that the experimental work couldn't be done in parallel by the research groups at Lund University, University West and Siemens but had a chain structure so that the samples had to be circulated from one partner to another during its preparation and investigation.

Another difficulty come from the specific morphology of a TBC. A thermal spray coating is a highly heterogeneous and full of defects (cracks, pores, and delamination) structure. Structural phase alteration, residual stress and impurities in coating can even more contribute to its heterogeneity. All these "characteristics" introduced a need for repeated trials and several iterations (more than planned) of the photoluminescent measurements before a final composition and structure could be established and used for in-situ measurements.

6.3 MAJOR STRENGTHS/ACHIEVEMENTS

Despite the difficulties mentioned above the final results are remarkable. In quite a short time (and with limited budget) the results obtained are comparable with those obtained in several years by other research groups. It is the first time in Sweden (a country with long experience in gas turbines for both aerospace and power generation) a multilayered TBC with incorporated sensor coatings is realized and tested in-situ. The ability to extract temperature information from a sensor coating covered by 300 μm TBC is above expectations. (Comparable results presented by NASA are limited to 100 μm.)The results obtained can now be adopted to other applications.

6.4 COMMERCIAL BENEFIT

Industry spends substantial effort in measuring and modelling heat load on thermally loaded designs such as combustors. For future gas turbines higher efficiency is an important driver for development towards even higher combustor temperatures which will lead to higher heat loads. Also gas turbines operating on varying fuel may experience changes in temperature distribution as flame shape and position change. In future gas turbine cycles with exhaust gas recirculation the more radiating CO_2 gas can influence the heat load situation.

Measuring the actual wall temperatures for varying operational conditions is important in order to optimize coating design and guarantee the lifetime of the combustor. The lifetime of the combustor is linked to the coating lifetime since a coating failure/spallation/crack will expose metallic design material to temperatures that potentially supersedes the melting point which risks fatal damage to the gas turbine.

Detailed and accurate measurements are also important for model validation and further understanding of the heat load contribution from convection and radiation as well as conduction respectively.

In the development of new TBCs with higher durability and lower conductivity the coating performance can be evaluated in the true environment on-site.

6.5 RECOMMENDATIONS

After the assessment of the project outcomes the following recommendations can be implemented in a future project to further improve the TBC temperature probing capability developed here within this project. The first is further investigations on the optical properties of different TBC coating techniques to search for the feasibility of using UV laser excitation instead of green for sub-surface temperature probing. The ability to use the UV excitation is very advantageous since it greatly increases the number of phosphors that could be potential sensor that may provide a better temperature sensitivity. Second, search for an alternative thermographic phosphor that has a temperature sensitivity range that is higher than the one provided by DySZ.

7 Acknowledgements

The project participants would like to thank Energiforsk, Energimyndigheten and Siemens for the financial support, crucial for making this development work possible.

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ADVANCED TEMPERATURE MEASUREMENTS ON/IN/BENEATH TBC COATINGS

Metalliska material i gasturbiner är belagda med skikt som isolerar termiskt. Ju högre temperaturen är i förbränningsgaserna desto högre blir verkningsgraden. Det finns alltså ett intresse att öka temperaturen, men då behöver också temperaturen på ytan och under ytan av de termiska barriärerna, så kallade TBC-skikt, kontrolleras så att inte metallen smälter.

Här har en mätmetod utvecklats där man använder fosforer som sensormaterial och temperaturmätningen kan på så sätt ske beröringsfritt genom att analysera ljusets spektrum och avklingningstid. Mätning kan ske både av yttemperatur och temperaturer ned till 300µm under ytan.

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