Phosphor Based Temperature Indicating Paints

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PHOSPHOR BASED TEMPERATURE INDICATING PAINTS

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ABSTRACT

The ability to measure temperature in extreme environments such as the hot sections of gas turbines is critically important. Several on-line techniques exist but it is often not possible to measure in real-time the temperature of all surfaces of interest. Indeed, some surfaces are so inaccessible as to require complex, costly and intrusive instrumentation for on-line temperature measurement. Here, off-line sensors, also called thermal history sensors, can be used to record the temperatures to which they are exposed, in such a way that they can be extracted later off-line, at room temperature.

Probably the best-known types of thermal history sensor are the colour changing thermal paints, that are widely used in gas turbine development. These have been valuable tools of engine developers for many years, but their use presents a number of challenges so that alternatives would be welcome.

This paper reports the latest developments of a thermal history sensor based on phosphors that undergo permanent changes in their luminescence properties when exposed to high temperatures. Such thermal history sensors have several advantages over and address many of the shortcomings of existing sensors. The paper contains details of the application of a phosphor-based temperature indicating paint based on $Y_2SiO_5{:}Tb$ suspended in a chemical binder. The binder was found to influence the optical properties of the phosphor but despite this, a viable sensor paint for temperatures in the range 400°C to 900°C was formed.

A thermal history coating was installed using a thermal barrier coating architecture, applied on various components of a *Royce-Rolls Viper 201* engine owned by *STS* and operated for a number of hours at *Cranfield University*. Post-operation analysis revealed a temperature distribution on the surfaces/components and enabled hotspots to be identified. Overall the results suggest that phosphor-based temperature indicating paints have the potential to surpass the capability of existing paints.

INTRODUCTION

Designing, operating and maintaining engineering components for, or in, high-temperature environments is a common engineering challenge due primarily to the ubiquity of heat engines for energy conversion and the link between efficiency and temperature. There are probably no better examples than the components in the hot sections of gas turbine. These are made to complex designs from exotic materials by ingenious processes. Nevertheless, there is a limit to the temperature that they can withstand whilst continuing to operate as specified. Furthermore, the processes by which they degrade all have rates that are temperature-dependent. It is therefore vital that the designer be assured that cooling strategies employed and insulating layers incorporated work as expected throughout component life. Simulation is a valuable tool for the designer but there is still a critically important place for the measurement of temperature and heat flux on or in gas turbine components as there is in other prime movers and engineering processes.

Temperature measurement in such environments is very challenging. Sensors need to survive just as the components themselves need to do and access for sensor installation and signal transmission is often very difficult. Recognising the need for new and improved sensor/measurement technology, the gas turbine industry has established two user groups: The *Propulsion Instrumentation Working Group (PIWG)* and the *European Virtual Institute for Gas Turbine Instrumentation*

(EVI-GTI) to highlight sensor development priorities and to promote research and development to meet them. Both organisations have identified priority areas where new sensors are needed and both identify better temperature measurement capability as one of those priorities.

The authors have developed a new type of temperature indicating paint based on the spectroscopic emission properties of ceramic phosphors. These have the potential to show significant advantages over previous generations of temperature indicating paints in terms of measurement accuracy, cost of use and other aspects of their implementation. In the current paper the latest steps in the development of phosphor-based temperature indicating paints are reported, including the first implementation of them as a plasma-sprayed coating on engine components.

TEMPERATURE MEASUREMENT

On-Line

On-line refers to the measurement of a component's temperature whilst it is in operation – and at temperature. Contact and non-contact techniques are available. One contact technique involves the use of thermocouples. They are generally cheap, robust and accurate. They also have a wide dynamic range, -270^{o}C – 3000^{o}C at least. The main problem with thermocouples is associated with installation. Reading them requires leading wires out – possibly from rotating components, and attaching them to components is intrusive and in some cases even damaging.

Infra-red pyrometry is a non-contact technique that overcomes issues of intrusiveness. It can be precise but accuracy is harder to achieve. It requires optical access to the components being considered which is one of the more challenging aspects of its implementation. Ideally the surface emissivity should be known but this can change with ageing and surface deposition. Fouling of optics is also a factor and the technique is difficult to use with thermal-barrier-coated components, since the ceramic part of these coatings is translucent at wavelengths one would wish to observe. Nevertheless, pyrometers are quite widely used and indeed are a production-installed sensor on some jet engines such as the *RB199* and *GE90*.

Thermographic phosphor thermometry is a relatively new technique that should probably be characterized as semi-contact. The component in question is coated with a thin layer of ceramic phosphor, illuminated with ultra-violet light and the resulting emission observed. Changes in temperature cause distinct changes in the spectral and temporal emission that can be used to determine temperature with excellent precision and accuracy. Although, again, optical access is required, the technique is quite robust with respect to the cleanliness of the optical system and to the surface deposits. Feist *et al.* [1] have developed phosphorescent thermal barrier coatings (TBC) that allow temperature measurement in a truly non-contact/non-intrusive manner but, even here, optical access to components is required during operation.

Off-Line

The requirement for access to components *in-situ* and/or the ability to transmit data during operation are common problems for all on-line temperature measurement techniques. They are particularly acute in gas turbines and for this application a number of off-line temperature measurements have been developed. Here, the sensor is such that it undergoes permanent changes as a result of the temperature to which it is exposed and usually the duration of the exposure. The changes can be studied later off-line, quantified and hence the temperature of exposure deduced. In a sense such sensors have *memory* and as a result they are sometimes referred as *thermal history sensors*. The sensitivity to the duration of exposure is an important factor and, if temperature is the desired measurand, ways of decoupling its effect from that of temperature must be found. There are a number of sensors of this type available to the measurement engineer and some examples are given below.

Metallurgical sensors comprise a metallic plug that is inserted into the component of interest by, for example, drilling and tapping a hole in it and screwing in a plug of the sensor material. The materials are carefully chosen to undergo changes in hardness, magnetic properties or phase composition at prescribed temperatures. Temperature measurements in the range 400-900°C are possible but the required exposure times are hundreds or thousands of hours. An obvious drawback of this technique is the requirement to embed the sensor in the component with the attendant risk that doing so will compromise its structural integrity.

Nikolaenko *et al* [2] have developed *crystal* temperature sensors that comprise a ceramic chip irradiated to produce defects and vacancies in its crystal lattice. High-temperature exposure destroys the defects/vacancies and this can be quantitatively measured using X-ray diffraction (XRD) and the temperature determined. The range of temperatures that can be measured is quite wide: 150°C to 1450°C, with a claimed measurement uncertainty of 15°C. As before though, the chips need to be embedded in the object/surface of interest so that installation is destructive. In addition, sensor interrogation cannot be done *in-situ* as the chips need to be interrogated in a laboratory using XRD. This adds to the cost since, in the case of a gas turbine, it would require the engine to be stripped down to access the instrumented component.

Fair *et al* [3] suggested a thermal history sensor based on crystallization in glass-ceramics. The process results in changes to the material transmittance as a result of the level and duration of exposure and measurements of temperature between 500°C and 1300°C are possible. Calibration and interrogation, however, appear to be complex and the measurement resolutions, around 50°C, is relatively low.

Yokata *et al* [4] patented another form of thermal history sensor that works by virtue of changes in the electrical resistance of a sensor caused by thermally driven diffusion of a metal into a previously insulating porous diffusion layer that forms part of it. The sensor was developed for the automotive sector and is reported to have a dynamic range from 600°C to 900°C. Such sensors would provide only point measurements and are more intrusive than some of the other methods surveyed. Reading them *in-situ* also requires wires to be fed out of the engine, just as is the case for thermocouples.

Probably the best-known type of thermal history sensors, certainly in the context of gas turbine applications, are temperature indicating paints, Watson and Hodgkinson [5]. These comprise thermally reactive metallic components suspended in a binder or resin. The metallic components cause the paint to permanently change colour as a result of exposure to elevated temperatures. Paints are usually applied as a thin layer and so are relatively non-intrusive. The engine is run for a set duration (generally 5 to 10 min) at a fixed operating point in an attempt to ensure steady temperatures. After exposure, the painted component is removed and interrogated at room temperature and with the help of calibration colour maps, the temperature is determined. Although widely used, temperature indicating paints have a number of drawbacks: interpreting colour changes is subjective and labour intensive having not yet been successfully automated. The colour changes are often subtle so that only a few discrete temperature values can be discerned and the resolution is around 10°C at best. Most paints have large temperature ranges over which no colour change can be observed.

Some temperature indicating paints contain components that are hazardous, such as chromium, lead and nickel cobalt. The European Commission introduced REACH (Registration, Evaluation, Authorisation and Restriction of Chemical substances) legislation in 2007 that requires companies to seek for alternatives to hazardous materials. Other thermal paints contain expensive noble metals such as gold, silver, bismuth and platinum, adding significantly to the cost of their use.

Of the off-line temperature sensors reviewed, temperature indicating paints probably remain the best suited to routine use in gas turbine applications and certainly there is a wealth of accumulated experience with them. Nevertheless, they are flawed and a better sensor would be low cost, non-toxic, have a wide dynamic range and continuous variation in the measurement, a good temperature resolution and would permit automated reading via electronic imaging with the possibility of doing so *in-situ*, using a borescope for example.

PHOSPHOR TEMPERATURE INDICATING PAINTS

The concept of a phosphorescent thermal history sensor (proposed by Feist, Heyes and Nicholls [6]) is based on phosphors that undergo irreversible changes, when exposed to high temperatures, that are reflected in their emission properties. The changes are the result of both the temperature and duration of exposure and may be manifest in the temporal (lifetime decay) or the spectral (wavelength or relative intensity) emission properties. Each of these parameters may be observed to reveal the cumulated effect of temperature and exposure duration *i.e.* the thermal history of the phosphor. If the phosphors can be exposed to a constant temperature for a defined period (*i.e.* the engine run under steady state conditions for fixed duration) then by proper calibration the effect of duration can be decoupled from that of temperature and the latter can be determined. In short, phosphors may be used as the sensing element in a temperature indicating paint.

The optical properties of phosphors are such as to convey a number of advantages over the pigments used in existing temperature indicating paints. Thanks to intense and sharp emission lines in the spectra of phosphors, a sensitive photomultiplier tube (PMT) can be focused on a single wavelength peak to record both intensity and lifetime decay in a quantitative and objective way. The emission spectra of phosphors are brighter than the reflectance spectra from coloured surfaces, which promises a better signal-to-noise ratio under automated/machine reading conditions or where optical access is limited. The influence of lighting conditions, angle of observation and dirt deposition on the surface on the emission intensity can be removed, by incorporating into the paint a reference phosphor that is fully stable and does not change its emission properties during thermal exposure. The ratio of the emission from both components will cancel these effects, leaving only the influence of temperature. The lifetime decay on the other hand is automatically independent of these factors, and offers another robust measurement variable. These factors, taken together, suggest that phosphor-based temperature indicating paints would allow automated machine reading of temperature data, possibly *in-situ* via a borescope, and objective, software-based, signal processes for reliable determination of the temperature.

The authors have identified three physical processes that can lead to permanent changes in the emission properties of phosphors. These are described in detail elsewhere [7] but summarized here for the sake of completeness.

Amorphous to Crystalline Transformations

Phosphors in an amorphous state usually do not emit or have very weak and broadband emission. The excitation spectrum is also much broader than in the fully crystalline case, Zhou *et al* [8]. The emission intensity and the lifetime decay often increase during crystallisation. This is sometimes referred to as *activation* of the phosphor and results in increased emission but also sharpened emission lines.

Examples of amorphous-to-crystalline changes in phosphors are abundant in the literature. Zhang *et al* [9] calcined amorphous Y_2O_3:*Eu* particles and observed an increase of the emission intensity from 600°C to 1300°C. Zhou and Lin [10] crystallised YVO_4:*Eu* particles and reported an increase of the emission intensity from 500°C to 1100°C.

Phase Change

Some phosphors undergo post-crystallisation changes in their emission due to phase changes, and the emission spectra can change radically as a result. This is the case for oxysulfides (Poston *et al* [11], Feist and Heyes [12]). The thermal decomposition of such materials is a well-known and important metallurgical and chemical reaction. Sulphur evaporates at high temperature, and a sulphur-free phase appears in the material.

The ions within this sulphur-free phase are bound to the crystal differently and this influences the emission spectrum.

Diffusion

The diffusion of additive ions into the crystal lattice of phosphors is a time-dependent process that can affect emission in a number of ways. Activator ions and sensitizers can both lead to an increase in emission while quenching ions (sometimes known as *killers*) can lead to a decrease.

Each of the above processes proceeds at a rate that is temperature dependent so that, if the duration of exposure is known, the degree of completion of the respective reactions is a function of temperature, which can therefore, with appropriate calibration, be determined from the emission. Each process will occur over a prescribed temperature range but within that range will be continuous allowing continuous temperature measurement without discrete steps – unlike some other off-line temperature sensors discussed above.

Finally, the phosphors proposed by the authors for use in temperature indicating paints, are composed of a ceramic host doped with rare earth ions. They are highly stable (melting temperature in excess of 2000°C) and non-toxic. In the authors view therefore, they represent an excellent prospect for a generation of improved temperature indicating paints that are machine readable, offer a large and continuous dynamic range, improved accuracy and none of the issues associated with toxicity.

In the following sections the latest results in the development of phosphor temperature indicating paints will be presented. Then, some preliminary results from an experiment on a plasma-sprayed thermal history coating are also shown and discussed.

EXPERIMENTAL ASPECTS

The phosphor $Y_2SiO_5:Tb$ was previously studied as a potential sensor for temperature indicating paints (Rabhiou *et al* [7]). Kang et al [13] showed that the transition from an amorphous state to a crystalline state is accompanied by an increase in emission intensity for this phosphor. The authors synthesized this phosphor in its amorphous state using an alkoxy sol-gel preparation route (Rabhiou *et al* [7]). It was then exposed to temperatures from 600°C to 1400°C for 20 minutes in a box furnace. XRD was used to confirm the amorphous to crystalline transformation and compared to the evolving emission spectrum. The latter showed significant increases in emission intensity with increased temperature of exposure and a commensurate sharpening of the lines in the spectrum. However, when a single line was selected from the spectrum and its intensity plotted as a function of heat treatment temperature the behavior was not monotonic. The intensity initially increased for temperatures from 700°C to 900°C, then decreased and remained steady between 1000°C and 1200°C before finally increasing again between 1200°C and 1400°C. This behavior is consistent with that previously reported for $Y_2SiO_5:Tb$ which is known to be polymorphic and to undergo a phase change at around 1200°C (a change in the XRD pattern was also observed in this temperature range) but highlights a challenge in the use of phosphors for temperature indicating paints. A survey of the lifetime decay in phosphorescent emission for this phosphor showed a monotonic increase between 600°C and 1000°C and excellent repeatability and it was concluded that the phosphor could be used to form an effective temperature indicating paint for at least this temperature range and, with more sophisticated signal processing, perhaps beyond. Finally, a study was undertaken of the effect of exposure time and it was concluded that for a 40-minute exposure (far greater than that recommended for existing temperature indicating paints) the phosphor retained its temperature measuring capability. This is an important observation since longer exposure times promise greater accuracy because a greater proportion of the exposure period is spent on condition so that the effects of warm-up and cool-down are minimized.

Binder-based Coating Tests

Having identified a phosphor which, in powder form, has suitable properties, the next step in the development of phosphor-based temperature indicating paints is to apply the phosphor in paint form to a surface. Paints are formed by suspending the active ingredient in some form of binder. Important requirements are first that the binder allows a paint to be prepared that adheres to the surfaces of interest and can survive at the temperatures likely to be encountered and measured. Secondly, the binder must not react with the active ingredient or undermine its temperature response. There is a range of commercially available binders specifically designed for the preparation of paints intended to survive high temperatures. For the purposes of the current experiments a selection was made comprising a *Cotronics Resbond 792* binder, a *Zyp-Coating LRC* binder and an *Indestructible Paint (IP) 600* binder. In each case a paint was prepared using amorphous $Y_2SiO_5:Tb$ and sprayed onto stainless steel coupons. These were then heat-treated in the box furnace at temperatures between 500°C and 1000°C for periods of 20 and 40 minutes respectively.

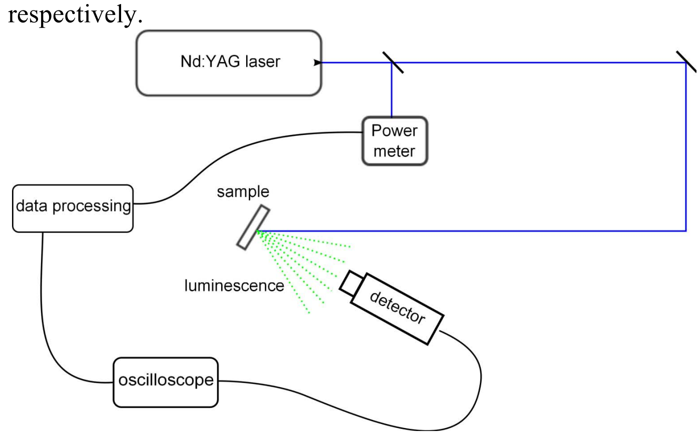

Figure 1: Experimental set-up

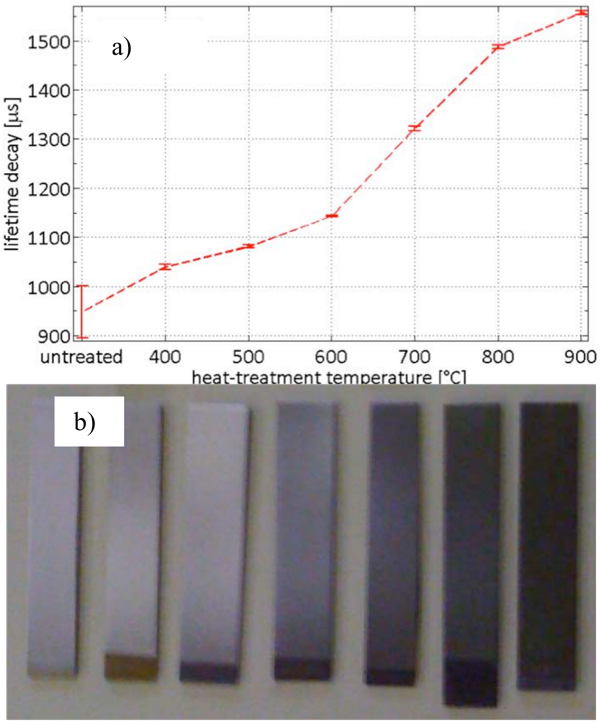

Figure 2: a) Calibration curve of Y_2SiO_5:Tb coatings sprayed using IP 600 binder. b) Photograph of the treated calibration samples (approx. 6cm long).

All three binders allowed a paint capable of surviving the tested temperature range to be made. Herein, for the sake of brevity, only the paint based on the IP 600 binder is reviewed. The samples were interrogated using the experimental set-up shown in Figure 1. Excitation was provided by a pulsed Nd:YAG laser (Spectra-Physics, Model Quanta-Ray Lab-150) operating in Q-switch mode at 255nm. Emission was recorded using a 50mm. *Nikon* lens to focus it onto the entrance slit (50µm) of a crossed Czerny-Turner spectrometer (*HoribaJobin Yvon MicroHR*, f=3.88). For lifetime decay measurements, the emission was captured with an optical probe with a high acceptance angle designed and provided by *Southside Thermal Sciences*. The collected light was coupled into a fibre bundle and delivered to a photomultiplier. For the initial survey of paint performance only the lifetime decay approach was used and a single exponential function was fitted to the emission decay following each laser pulse and characterized using the decay time constant.

Figure 2a shows a calibration curve for the painted samples. In Figure 2b is shown a photograph of the samples themselves. The first thing to note from the figure is that the samples blackened as a result of high temperature exposure. This is due to the binder and did result in some signal degradation. Nevertheless, it was possible to calibrate this paint for temperatures from 500°C to 900°C. Each point on the plot represents data from 30 laser pulses and the error-bars are composed of the standard deviation of the sample. Comparing this data to that obtained from the same phosphor in powdered form it can be noted that at each temperature the lifetime of the paint is consistently shorter than that of the powder. This indicates that the presence of the binder has affected the performance of the phosphor and indeed the effect is consistent with the binder having inhibited the crystallization process. Nevertheless, the paint still shows a monotonic variation in lifetime with temperature and good stability so that it appears to be an effective temperature indicating paint for the temperature range considered.

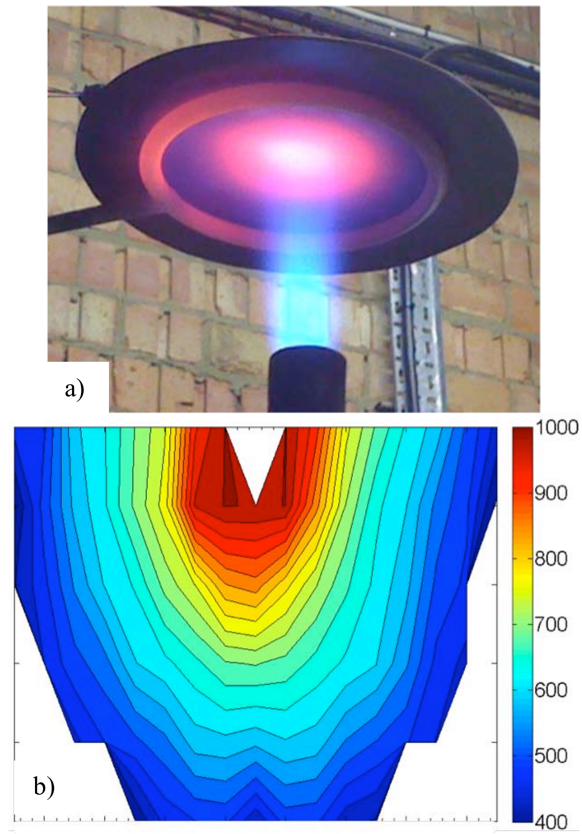

Figure 3: a) Application of Y_2SiO_5:Tb paint to a flame heated stainless steel disc. b) Map of the past temperatures experienced by the paint in °C.

To demonstrate the use of this combination (*Y_2SiO_5:Tb* suspended in IP 600 binder) a stainless steel disc was airbrushed with the paint and exposed by heating it from below using a propane flame – as shown in Figure 3a. Using the calibration data shown in Figure 2a the resulting temperature distribution was estimated and is also shown as a contour plot in the Figure 3b.

Binderless Coatings

Despite the initial success of the *Y_2SiO_5:Tb* / IP 600 paint, it was clear from the results that the binder does influence the performance of the phosphor to some extent. With proper calibration it should still be possible to make an effective temperature indicating paint based on the binder approach. However, it is also possible to make coatings without binders. Techniques such as air-plasma spraying (APS) and electron beam vapour deposition (EB-PVD) are routinely used to manufacture ceramic thermal barrier coatings in gas turbines that are capable of enduring the operating conditions within the engine for thousands of hours.

a)

b)

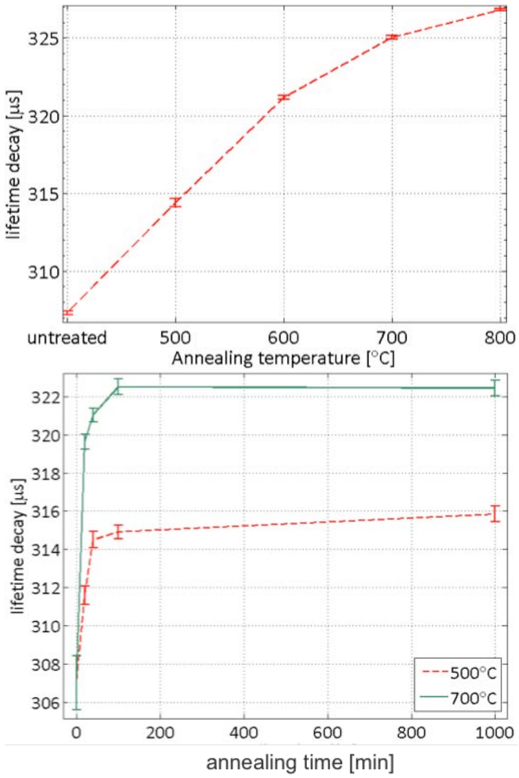

Figure 4: a) Calibration curve for the APS temperature indicating coating. b) The influence of the heat-treatment time on the lifetime decay.

A range of thermal barrier sensor coatings (TBSC) has been developed wherein the ceramic layer of a TBC system is made phosphorescent by the addition of rare earth ions into the crystal lattice. It is known that the manufacturing process for TBCs results in a coating that is not fully crystallized. It was therefore hypothesized that an as manufactured TBSC might undergo permanent changes in its emission properties upon heat treatment *i.e.* that it might behave as a thermal history sensor. The hypothesis was tested using APS coatings of *YAG:YSZ:Dy* supplied by *Southside Thermal Sciences*. These comprised calibration samples that were tested in the range from 500°C to 900°C. In addition, the same coating was applied to the combustion liner of a *Rolls Royce Viper* jet engine owned by *STS* and operated at *Cranfield University*. Some preliminary calibration results are shown in Figure 4a. It can be seen that the decay time constant increased monotonically with temperature exposure. Figure 4b also shows that there is very little change in the lifetime decay after the first 100 minutes and suggests that reliable temperature measurement could be made even after 1000 minutes of exposure. In addition Figure 5c shows a temperature map of the surface of the combustion liner (Figure 5a, 5b) derived from the TBSC after tens of hours of operation. These preliminary results suggest that TBSC-based temperature indicating coatings are technically feasible. Such coatings might offer significant advantages over current binder-based temperature indicating paints and further development is warranted.

a)

b)

c)

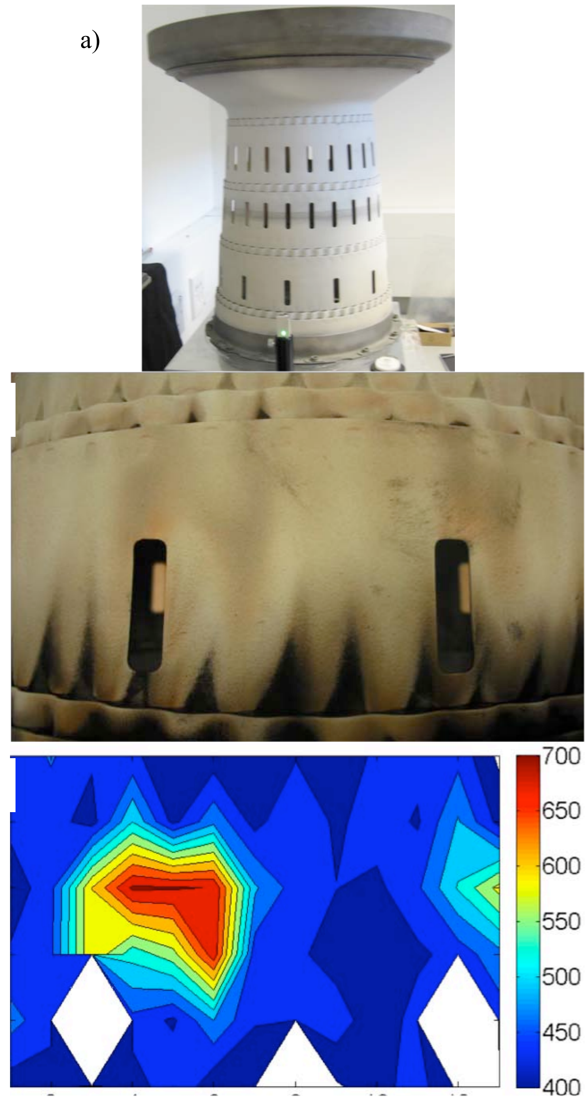

Figure 5: a) The untreated inner flame tube. b) A section of the inner flame tube after exposure in the engine. c) Preliminary result of the past peak temperature of that section in °C.

CONCLUSIONS

The results demonstrate that phosphor-based temperature indicating paints can be created using an amorphous phosphor powder suspended in a commercially available high temperature binder. Although the binder did influence the properties of the phosphor, a paint was prepared and shown to have a dynamic range extending from 400°C to 900°C. The result also show that it is possible to create a temperature indicating coating without a binder by techniques such as air plasma spraying. Both types of sensor have the potential to offer significant advantages over existing temperature indicating paints and further development of phosphor-based temperature indicating paints and coatings is warranted.

ACKNOWLEDGMENTS

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REFERENCES

1. Feist JP, Heyes AL, Nicholls J.R, "*Phosphor Thermometry In An EBPVD Produced TBC Doped With Dysprosium*" Proc. Instn. Mech. Engrs. Vol 215, Part G, (2001)pp. 333-341

2. Nikolaenko VA, Morozov VA, Kasianov NI, "*A crystal maximum temperature measure (JMTK) for special application"* Rev. Int. Hautes Temp. et Refractaires, vol. 13, 1976, pp. 17-20.

3. Fair GE, Kerans RJ, Parthasarathy TA, *"Thermal history sensor based on glass-ceramics"* Sensors and Actuators: A. Physical, 141(2): 245-255, 2008.

4. Yokata K, Kizaki Y, Sakamoto Y, Motohiro T, *"Method and sensor for detecting thermal history"* 1999, US Patent 5,975,758.

5. Watson HML, Hodgkinson EC, "*Temperature Indicating Paint"* , 2002, US Patent 10,229,002.

6. Feist JP, Nicholls J, Heyes AL, "*Determining thermal history of components"*, 2007, Patent WO/2009/083,729.

7. Rabhiou A, Feist J.P, Kempf A, Skinner S, Heyes A L, "*Rare Earth Ceramic Phosphorescent Thermal History Sensors*" Sensors and Actuators A: Physical, Vol. 169, 2011, pp 18-26

8. Zhou YH, Lin J, Wang SB, Zhang HJ, "*Preparation of $Y_3Al_5O_{12}$:Eu phosphors by citric-gel method and their luminescent properties"* Optical Material, 20(1):13-20, 2002.

9. Zhang J, Tang Z, Zhang Z, Fu W, Wang J, Lin Y, "*Synthesis of nanometer Y_2O_3:Eu and its luminescence properties"* Materials Science and Engineering A, 334(1-2):246-249, 2002.

10. Zhou YH, Lin J, "*Morphology control and luminescence properties of YVO_4:Eu phosphors prepared by spray pyrolysis"* Optical Materials, 27(8):1426-1432,2005.

11. Poston JA, Siriwardane RV, Fisher EP, Miltz AL, "*Thermal decomposition of rare earth sulphates of cerium (III), cerium (IV), lanthanum (III) and samarium (III)"* Applied Surface Science 214(1-4):83-102,2003.

12. Feist JP, Heyes AL, "*The characterization of Y_2O_2S:Sm powder as a thermographic phosphor for high temperature applications"* Measurement Science and Technology, 11(7):942-7, 2000.

13. Kang YC, Lenggoro IW, Okuyama K, "*Luminescence characteristics of Y_2SiO_5:Tb phosphor particles directly prepared by the spray pyrolysis method"* Journal of the Electrochemical Society, 146(3):1227-1230, 1999.

