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Improvements in Plasma Sprayed Thermal Barrier Coatings for Use in Advanced Gas Turbines

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Summary

This project was focussed on the development of improved thermal barrier coatings (TBCs), produced by plasma spraying. Such coatings are in extensive industrial use for aeroengine and industrial power plant gas turbines. They commonly fail by spallation, exposing the underlying metallic substrates to high temperatures and leading to component failure. The project involved upgrading the vacuum plasma spray facility used for coating production. The project provided one post-doctoral position, which was filled consecutively by three research workers, partial support for a technician post and some support for one PhD studentship.

The following technical conclusions can be drawn from the work.

- Sintering of the top coat at temperatures commonly encountered during service has been shown to result in substantial increases in stiffness, and hence in the driving forces for spallation generated during thermal cycling. Modelling of the associated residual stress levels has indicated that the changes induced might well be sufficient to cause spallation in practice.
- Study of the associated microstructural changes has highlighted the importance of microcrack healing and improved inter-splat bonding. These are promoted by diffusion at high temperature, but are inhibited by the presence of in-plane tensile stresses from differential thermal expansion.
- The sintering has been shown by dilatometry studies to be quite significantly anisotropic. Contraction (shrinkage) in the through-thickness direction is greater than in the in-plane directions. This technique is much more sensitive to the microstructural changes induced during sintering than is the porosity level, which does not change very dramatically. Dilatometry data are currently being used in the development of a model for the sintering process in plasma sprayed top coats.
- The toughness (fracture energy) of the top coat – bond coat interface has been found to be dependent on the interfacial roughness. It increases as the roughness is raised, but there are clear indications that the value reaches a plateau, so there is little point in generating very rough surfaces. The reason for this appears to be that the interfacial fracture path switches to being within the top coat, just above the interface, when the roughness becomes high.
- Over the (relatively narrow) range of improved purity (notably lower silica content) which can be achieved without serious economic penalty, it was found that this had very little effect on the sintering characteristics
- A model has been developed for in-flight heat and momentum transfer during spraying. This model has been used to simulate co-spraying, and to explore how porous microstructures could be formed which might be resistant to sintering
- The in-flight model has also been used to explain how hollow particles can be produced by melting and re-solidification, and the material properties which favour this happening.
- Work has been done on the laser drilling of TBCs (which is carried out to create cooling channels). The effect of laser drilling on the likelihood of top coat spallation has been investigated, and the nature of the damage resulting from this operation has been studied. The formation of overhanging top coat material was found to inhibit melt ejection from the substrate. A numerical process model was developed (in a parallel EPSRC project), which explained this effect.

Fourteen publications have already arisen from the project, with several more likely to appear shortly. There has been extensive and fruitful collaboration between Cambridge and both Sulzer Metco and Rolls Royce (partly via the UTC based in the Materials Science Department). DSTL have also been strongly involved, via Prof. Richard Jones.

1. Objectives and Background

1.1 Overview

The original objectives of this project are listed below.

- To improve current understanding of the mechanisms by which sprayed thermal barrier coatings on turbine components degrade and fail.
- To explore the efficacy of proposed modifications to the production of thermal barrier coating systems on their mechanical stability under service conditions.

These objectives have both been achieved. Several contributions have been made to the current state of knowledge about TBC failure and progress has been made in evaluating the promise of several different approaches to the problem of obtaining improved performance.

1.2 Research Personnel

Several researchers contributed to the project, which ran from October 1999 until October 2002. Joe Thompson was employed as the post-doctoral research associate position for 12 months, starting in October 1999. He then left to become a management consultant. Colin Creighton then worked on the project for about 4 months, before being offered an attractive industrial post in Cambridge. Both Dr.Thompson and Dr.Creighton had previously completed their PhDs within the Gordon Laboratory.) Finally, Dr. Igor Golosnoy was recruited from the Russian Academy of Sciences and he held the post-doctoral position from January 2001 until the end of the project. (He is currently supported within an EPSRC platform grant.) Thomas Klocker started his PhD in October 1999 and finished in October 2002. He received a small top-up bursary from the project. Sofia Tsipas started her PhD in October 2001 and will finish in autumn 2004. Her studentship is partly supported by Sulzer, one of the industrial partners in the project. These arrangements are broadly in line with the initial projections, although obviously the changes in the post-doctoral appointment did cause some disruption. One enforced change was that Dr.Reed, one of the original co-Investigators, left the Department in Dec. 2001 to take up a chair in Vancouver. However, this did not affect the progress of the project and he continued to take an interest in the work after his move.

1.3 Resource Utilisation

Expenditure under different headings broadly followed the original plan. A major overhaul and upgrade of the vacuum plasma spray (VPS) facility was undertaken at the start of the project. This was carried out by Sulzer Metco. The total cost was about £150k, of which about £55k was contributed by Sulzer Metco as an agreed industrial contribution to the project and £95k was paid from the project. Costs under the other headings were approximately in line with projections.

1.4 Industrial Collaboration

This project has been carried out in close cooperation with industrial partners throughout. There have been regular (quarterly) meetings, all attended by personnel from Sulzer and many attended by people from Rolls Royce as well. Substantial cash contributions to the project were made by both firms, along the lines outlined in the proposal. The value of Sulzer Metco’s cash contribution was about £80k, mainly made up of the cost of the VPS upgrade and support for a PhD studentship, while that from Rolls Royce was in the form of purchase of a dilatometer, which cost about £50k. There were also substantial in-kind contributions from both firms. The total value of these cash and in-kind contributions to the project was around £170k, which is actually somewhat higher than anticipated in the proposal. In addition, Prof. Richard Jones, from the Defence Science and Technology Laboratory (DSTL), previously from DERA, has kept in close contact with the work throughout. Links have also been established during the project with Alstom, who are industrial partners in a recently-submitted proposal taking this work forward.

2. Project Areas

In the proposal, the planned work was itemised under the headings listed below as §2.1-§2.7. An eighth project area emerged during the course of the work – namely laser drilling of TBC systems.

This was the result of synergy between this project and a concurrent EPSRC project, concerned with laser drilling.

2.1 Plasma Spray Deposition and Interfacial Toughness Measurement

The VPS upgrade included uprating of the control system of vacuum plasma spray rig, which allowed improved process control and facilitated the *in situ* measurement of interfacial toughness (by over-spraying until spontaneous debonding occurs). This technique is now used routinely in the group and has been widely recognised as a useful tool for studies in this area. The work described here was mostly obtained using standard Yttria-Stabilised Zirconia (YSZ) top coats, deposited by atmospheric plasma spraying, and bond coats of NiCRAlY or CoNiCrAlY deposited by vacuum plasma spraying. Specific results obtained concerning the factors that affect interfacial toughness are reported below under various headings.

2.2 Residual Stresses and Sintering Characteristics

Extensive work[1-5] has been done within the project on the development of residual stresses in TBC systems, the influence of top coat sintering (and associated stiffness increases) on these stresses and the role of residual stresses in promoting top coat spallation. It is now clear that top coat sintering is often a key factor in determining whether and when spallation occurs and the work at Cambridge is becoming recognised as having had a pioneering role in highlighting this issue.

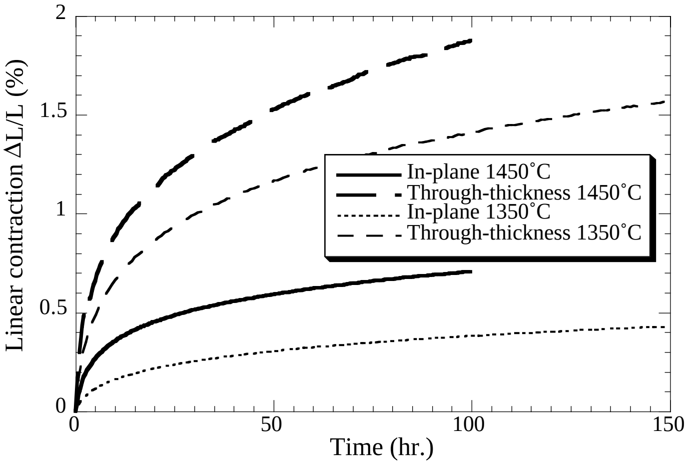
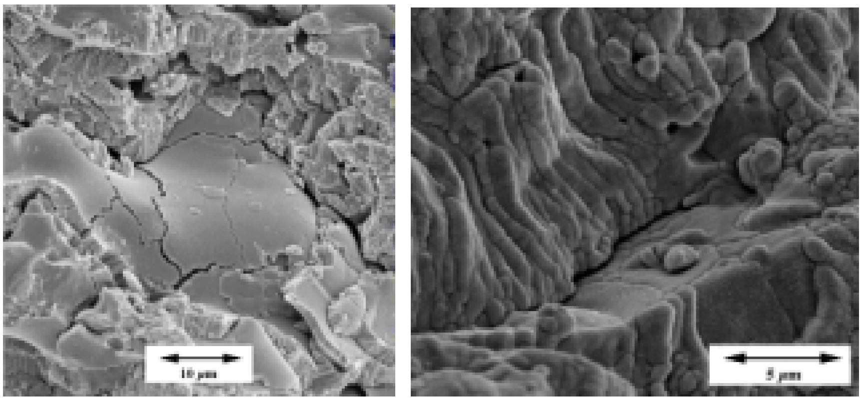


Fig.1 Dilatometer plots obtained during heat treatment of detached YSZ top coats.

The dilatometer acquired within the project proved to be very useful for study of top coat sintering[6], particularly in revealing that the associated volume contraction is anisotropic - see Fig.1. This information is being incorporated into a model currently being developed for sintering of sprayed top coats[7]. A recent development is the commissioning of an experimental rig in which a high thermal gradient is generated, similar to those typically created under service conditions. Study is currently under way of the top coat sintering behaviour under these conditions and forms part of the planned programme for a further joint EPSRC/industry project. The fact that the stress state in the top coat differs from that in an isothermal system is expected to affect the sintering behaviour[6].

2.3 Study of TGO Growth Kinetics and Microstructural Studies

Some work has been done on the growth rate of the Thermally Grown Oxide (TGO), with and without the top coat present. It has been confirmed[8, 9] that the top coat is virtually transparent to oxygen, and that this is at least partly due to permeation of gas through the top coat. Much of the microstructural work has been focussed on changes occurring within the top coat. Some of the changes responsible for the stiffness increases are illustrated in Fig.2, where it can be seen that the microcracks and poor inter-splat cohesion present in as-sprayed top coats become modified or eliminated by diffusional processes and grain growth at high temperature.



(a) (b)

Fig.2 Typical plasma sprayed YSZ top coat microstructures (a) as-sprayed and (b) heat treated (100 hours at 1300˚C).

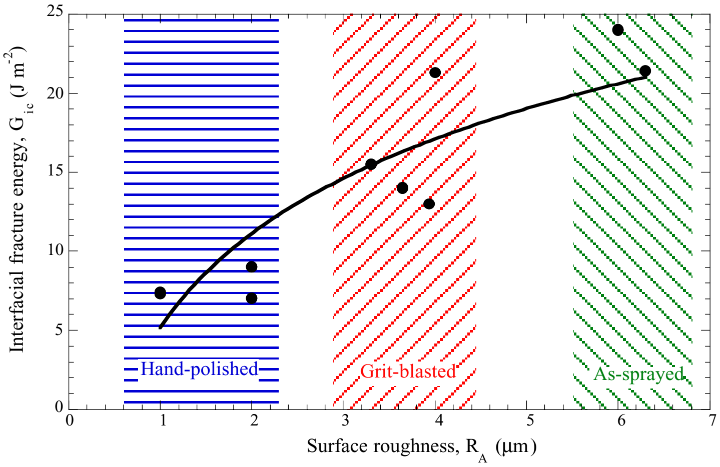
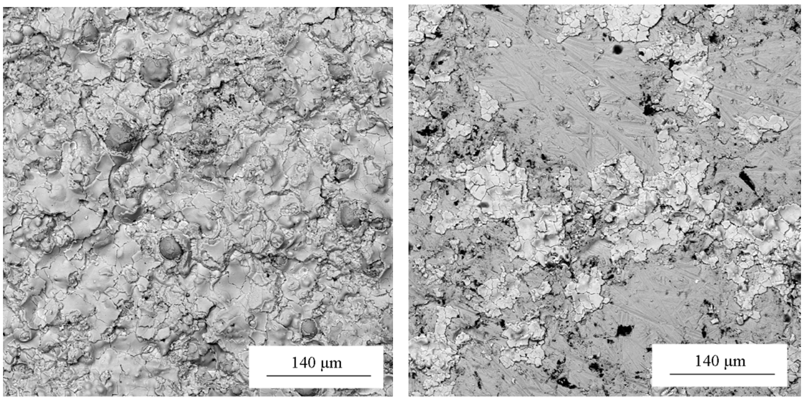


Fig.3 Measured (top coat-bond coat) interfacial fracture energy values, as a function of the surface roughness of the bond coat prior to top coat deposition.



(a) (b)

Fig.4 Fracture surfaces after top coat debonding for interfacial roughnesses of (a) 6 μm (residual top coat coverage ~90%) and (b) 2 μm (residual top coat coverage ~20%)

2.4 The Effect of Bond Coat Surface Roughness and Chemistry

A systematic study has been undertaken of the effect of bond coat roughness, by subjecting the surface to different treatments before spraying of the top coat. It has been confirmed that roughening of the bond coat raises the fracture energy of the bond coat/top coat interface up to a certain level of roughness, beyond which a plateau is reached. Data are shown in Fig.3. Study of the crack paths followed in different cases indicated that, while cracking occurs largely within the interface when it is relatively smooth, it tends to occur within the top coat, close to the interface, with higher interfacial roughnesses – see Fig.4. The effect of creep in the bond coat has also been studied[10]. It was anticipated that some systematic work on the role of bond coat creep could be undertaken using proprietary Sulzer powders with high creep resistance, but no decision has yet been taken on the provision of powder for this purpose.

2.4 The Effect of Top Coat Powder Purity

A study has been completed into the effect of top coat purity (silica content) on its sintering characteristics, using powder supplied by Sulzer. This confirmed that, within the range of purity studied, its influence was small. It was deduced that, for the range of purity obtainable without excessive cost, the difference in vitreous phase content at service temperatures was insufficient to alter the sintering kinetics significantly. This is consistent with microstructural observations.

2.5 The Effect of Top Coat Powder Morphology and PSD

Interest in the role of the powder morphology and particle size distribution (PSD) has led to a very productive line of investigation. It became clear that improved understanding of the transport phenomena occurring during spraying was essential in order to control the top coat microstructure via geometrical characteristics of the powder particles. A large part of this work[11] was focussed on modelling of the heat and momentum transfer which occur between a particle and the surrounding gas during spraying, and of the stresses which are created within the particle. Good agreement was obtained with experiment in various areas, including the effects of spraying and powder parameters on deposition efficiencies (eg see Fig.5) and also the formation of hollow particles by in-flight melting and refreezing.

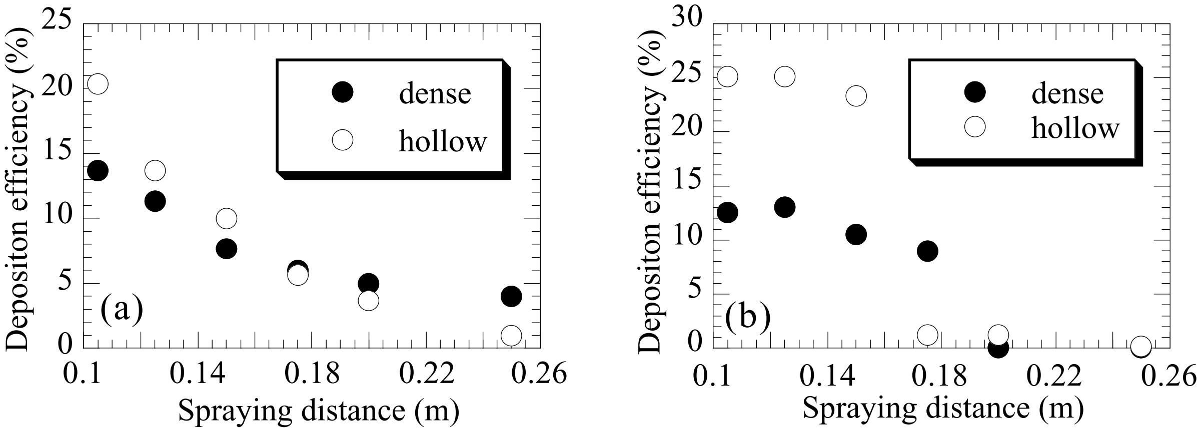


Fig.5 (a) Experimentally-observed and (b) predicted dependence of the deposition efficiency on spraying distance, for atmospheric plasma spraying of hollow and dense zirconia powders. The predicted points correspond to multi-particle modelling runs, using an experimentally measured distribution of particle sizes. It was assumed that only fully molten particles would adhere to the substrate.

2.6 Bond Coat Pre-oxidation

It has been shown[12] that prior formation of the TGO may be less deleterious that *in situ* formation during service. Study has also been made of the stresses associated with bond coat oxidation. A candidate area for further study is to preoxidise the bond coat in the VPS chamber and see whether this improves interfacial adhesion. This would probably be most effectively carried out using the transferred arc facility to locally heat the bond coat in situ, but unfortunately this facility has not been functioning correctly for some time, despite several efforts by Sulzer personnel to rectify the problem.

2.7 Production of Top Coats based on Pyrochlores

A study was planned of pyrochlores such as lanthanum zirconate, $La_2Zr_2O_7$, as alternative top coat materials to zirconia in TBCs. These materials do not appear to have been systematically studied as sprayed top coats, although there has been some work on them in PVD form. This study has not been undertaken, because of difficulties in obtaining suitable powder supplies. Interest in them appears to have decreased since the project proposal was submitted. However, work has been initiated recently at Cambridge , supported by Sulzer Metco, on the behaviour of zirconia-based top coats containing Dysprosia or Ceria. This work is not yet complete, but preliminary indications are that such formulations may offer advantages over standard YSZ.

2.8 Laser Drilling of TBCs

A line of investigation, which has partly arisen via synergy with another EPSRC-supported project, is concerned with laser drilling. Part of this study[13, 14] has been focussed on drilling of TBCs and there has been extensive work on modelling of the heat flow during laser drilling, in order to predict hole shapes (eg see Figs 6 and 7) and to understand the development of microstructural damage and possible effects on the likelihood of interfacial debonding. The work has led to improved understanding of the possible influence of laser drilling on the tendency for top coats to debond. It was concluded that laser drilling could, in fact, inhibit interfacial crack propagation slightly via the crack-arresting effect of resolidified ceramic lips around the holes. However, the exact effect observed depends on the angle of drilling, the use of assist gas and the toughnesses of the substrate / bond coat and bond coat / top coat interfaces. The presence of the top coat was found to modify the melt ejection characteristics of the substrate, which affects drilling rates etc.

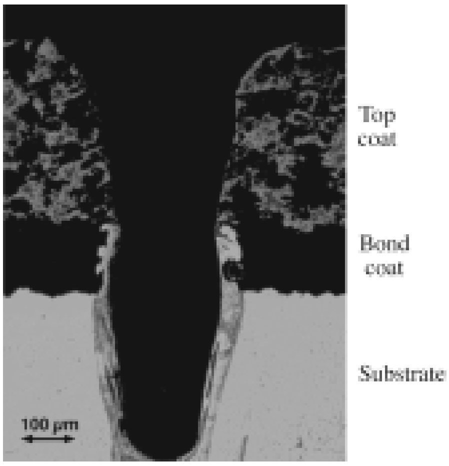
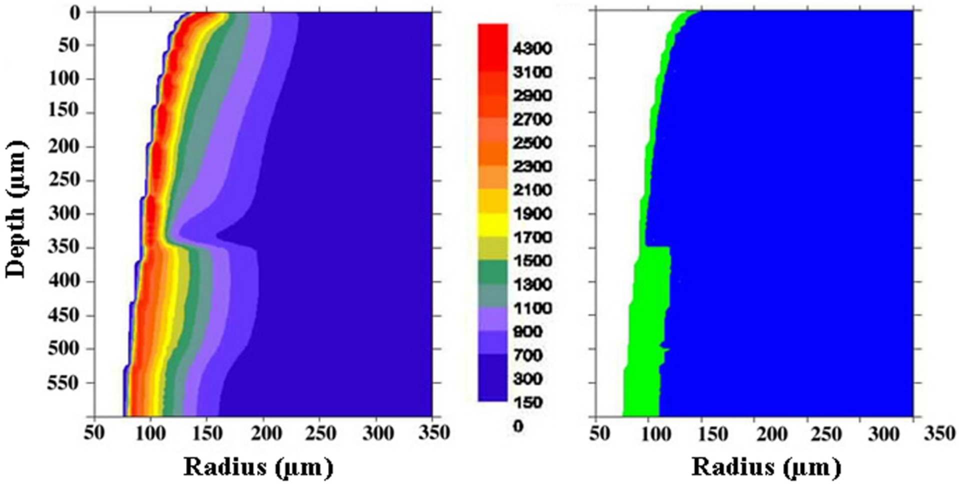


Fig.6 Optical micrograph showing undercutting of the YSZ top coat by the resolidified NiCrAlY bond coat layer, after drilling with three 1.6 J, 0.5 ms pulses.



(a) (b)

Fig.7 Predicted (a) thermal field and (b) phase field for the specimen shown in Fig.3. (White = empty cells, green = molten cells, blue = solid cells.)

References

1. Thompson, J.A. and Clyne, T.W., *The Stiffness of Plasma Sprayed Zirconia Top Coats in TBCs*, in *United Thermal Spray Conference*, (1999), Lugscheider, E. and Kammer, P.A. (ed.), Dusseldorf, DVS, p.835-840.

2. Thompson, J.A., Ji, W. and Clyne, T.W., *The Effect of Top Coat Sintering on Ceramic Spallation in Plasma-Sprayed Thermal Barrier Coatings*, in *13th Int. Conf. on Surface Modific. Techn. (SMT XIII)*, Sudarshan, T.S., Khor, K.A. and Jeandin, M. (ed.), (1999), ASM. p.177-182.

3. Thompson, J.A., Ji, W., Klocker, T. and Clyne, T.W., *Sintering of the Top Coat in Thermal Spray TBC Systems under Service Conditions*, in *Superalloys 2000*, (2000), Pollock, T.M., Kissinger, R.D., Bowman, R.R., Green, K.A., McLean, M., Olsen, S.L. and Schirra, J.J. (ed.), Seven Springs, USA, TMS, p.685-692.

4. Thompson, J.A., Matejicek, J. and Clyne, T.W., *Modelling and Neutron Diffraction Measurement of Stresses in Sprayed TBCs*, in *Superalloys 2000*, (2000), Pollock, T.M., Kissinger, R.D., Bowman, R.R., Green, K.A., McLean, M., Olsen, S.L. and Schirra, J.J. (ed.), Seven Springs, USA, TMS, p.639-647.

5. Thompson, J.A. and Clyne, T.W., *The Effect of Heat Treatment on the Stiffness of Zirconia Top Coats in Plasma-Sprayed TBCs*. Acta Mater., vol.**49** (2001) p.1565-1575.

6. Tsipas, S.A., Golosnoy, I.O. and Clyne, T.W., *The Effect of a High Thermal Gradient on Sintering and Stiffening in the Top Coat of a Thermal Barrier Coating (TBC) System*, in *Proc. 17th Int. Thermal Spray Conf.*, (2003), ASM, Orlando, in press.

7. Golosnoy, I.O., Tsipas, S.A. and Clyne, T.W., *Use of a Numerical Model to Explore Changes in the Thermal Conductivity of the Top Coat in a Thermal Barrier Coating (TBC) System during Prolonged Exposure to a High Heat Flux*, in *Proc. 17th Int. Thermal Spray Conf.*, (2003), ASM, Orlando, in press.

8. Fox, A.C. and Clyne, T.W., *Oxygen Transport Through the Zirconia Top Coat in Thermal Barrier Coating Systems*, in *Proc. 15th Int. Thermal Spray Conf.*, C.Coddet (ed.), (1999), ASM, Nice, France. p.1589-1594.

9. Fox, A.C. and Clyne, T.W., *Oxygen Transport through the Zirconia Layer in Plasma Sprayed Thermal Barrier Coatings*, in press, Surf. & Coat. Techn., (2003).

10. Thompson, J.A., Tsui, Y.C., Reed, R.C., Rickerby, D.S. and Clyne, T.W., *Creep of Plasma Sprayed CoNiCrAlY and NiCrAlY Bond Coats and its Effects on Residual Stresses During Thermal Cycling of Thermal Barrier Coating Systems*, in *High Temperature Surface Engineering*, Nicholls, J. and Rickerby, D.S. (ed.), (2000), IoM, Edinburgh, p.199-212.

11. Klocker, T., Dorfmann, M. and Clyne, T.W., *Process Modelling to Optimise the Structure of Hollow Zirconia Particles for use in Plasma Sprayed Thermal Barrier Coatings*, in *ITSC 2001*, (2001), Berndt, C.C., Khor, K.A. and Lugscheider, E.F. (ed.), Singapore, ASM, p.149-155.

12. Tsui, Y.C., Reed, R.C. and Clyne, T.W., *On the Change in Stress State Associated With Bond Coat Oxidation During Heat Treatment of a Thermal Barrier Coating System*, in *Proc. 1st United Thermal Spray Conf.*, Berndt, C.C. (ed.), (1999), ASM, Indianapolis, p.267-276.

13. Voisey, K.T., Thompson, J.A. and Clyne, T.W., *Damage Caused during Laser Drilling of Thermal Spray TBCs on Superalloy Substrates*, in *ICALEO*, (2001), X.Chen (ed.), Jacksonville Florida, USA, Laser Institute of America, p.1802.

14. Voisey, K.T. and Clyne, T.W., *Laser Drilling Of Cooling Holes Through Plasma Sprayed Thermal Barrier Coatings*, in press, Surf. & Coat. Techn., (2003).