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Effect of Microstructure and Temperature on the Erosion Rates and Mechanisms of Modified EB PVD TBCs

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Thermal barrier coatings (TBCs) have now been used in gas turbine engines for a number of decades and are now considered to be an accepted technology. As there is a constant drive to increase the turbine entry temperature, in order to increase engine efficiency, the coatings operate in increasingly hostile environments. Thus there is a constant drive to both increase the temperature capabilities of TBCs while at the same time reducing their thermal conductivities. The thermal conductivity of standard 7wt% yttria stabilized zirconia (7YSZ) electron beam (EB) physical vapour deposited (PVD) TBCs can be reduced in two ways: the first by modification of the microstructure of the TBC and the second by addition of ternary oxides. By modifying the microstructure of the TBC such that there are more fine pores, more photon scattering centres are introduced into the coatings, which reduce the heat transfer by radiation. While ternary oxides will introduce lattice defects into the coating, which increases the phonon scattering, thus reducing the thermal conductivity via lattice vibrations. Unfortunately, both of these methods can have a negative effect on the erosion resistance of EB PVD TBCs.

This paper compares the relative erosion rates of ten different EB PVD TBCs tested at 90° impact at room temperature and at high temperature and discusses the results in term of microstructural and temperature effects. It was found that by modifying the coating deposition, such that a low density coating with a highly ‘feathered’ microstructure formed, generally resulted in an increase in the erosion rate at room temperature. When there was a significant change between the room temperature and the high temperature erosion mechanism it was accompanied by a significant decrease in the erosion rate, while additions of dopants was found to significantly increase the erosion rate at room and high temperature. However, all the modified coatings still had a lower erosion rate than a plasma sprayed coatings. So, although, relative to a standard 7YSZ coating, the modified coatings have a lower erosion resistance, they still perform better than PS TBCs and their lower thermal conductivities could make them viable alternatives to 7YSZ for use in gas turbine engines.

Introduction

Since they were first introduced into gas turbine engines thermal barrier coatings (TBCs) have been the subject of numerous research papers generally concentrating on one of three issues: thermal cyclic life [1,2], erosion performance (or lack thereof) [3,4] and thermal conductivity (and how to reduce it) [5,6]. Thermal barrier coatings consist of a bond coat, an alumina thermally grown oxide (TGO) and a ceramic top coat (typically 7-8wt% yttria partially stabilised zirconia), which has a thermal conductivity of 1.8-2.0 W/mK for electron beam (EB) physical vapour deposited (PVD) TBCs and 0.8 W/mK for plasma sprayed (PS) TBCs and is what gives the TBC its thermal barrier properties[5]. These differences in thermal conductivities are purely attributed to the differences in the microstructure of the two types of TBCs. However, the very microstructure that gives the PS TBCs a lower thermal conductivity, compared to their EB PVD counter parts, also reduces their strain compliance and erosion resistance which means that they are not widely used on aerospace gas turbine blades. The research into the performance of TBCs has been primarily driven by two distinct factors; reliability and efficiency, which to a certain degree are interrelated. The drive to improve efficiency of gas turbines is essentially a drive to increase the operating temperature capabilities of the various components (increased turbine entry temperature) results in an increase in engine efficiency. To this end more efficient TBCs are required to protect the components from the increase in operating temperatures.

In order to lower the thermal conductivity of a material it is necessary to either reduce the specific heat capacity, density, refractive index phonon velocity or mean free path. Since the specific heat capacity of a material is an intrinsic material property the only viable options to reduce the thermal conductivity of zirconia based TBCs is to reduce the density of the material or to reduce the velocity and or mean free path of the heat carriers, i.e. photons and phonons. Phonon scattering occurs in crystal structures when phonons interact with crystal defects such as vacancies, grain boundaries, dislocations and impurities (which cause lattice distortions). Generally grain boundaries do not contribute significantly to phonon scattering however it has been shown [6,7] that for TBCs grain boundary scattering can have a significant effect on the thermal conductivity, these issues are comprehensively covered in a paper by Nicholls et al in 2002 [5]. Essentially there are two methods to reduce the thermal conductivity of TBCs one is the addition of dopants, to introduce more scattering centres at the atomic scale and the other is to modify the coatings structure, again to introduce voids and reduce the coating density on a micro-scale. TBCs are not very erosion resistant, typically a 7YSZ TBC has an erosion rate 2-3 times greater than the superalloy on which it is applied. Although EB PVD TBCs perform better than PS TBCs the addition of 2-4% of rare earth oxide dopants can significantly increase the erosion rates of EB PVD TBCs [8]. Furthermore, the

microstructure of the TBC can also have a significant effect on the erosion mechanism which in turn affects the erosion rate; there are a number of papers in the open literature which discuss the various erosion mechanisms of TBCs[3,4,9].

This paper examines the erosion performance of a number of different TBCs that have been produced with the aim of reducing their thermal conductivities; the coatings have been produced with additions of dopants and or modifications to their microstructure, all the doped coatings were applied on top of a thin layer of standard 7YSZ to ensure that there were no adhesion issues. The aim of this paper was to examine the affects of these modifications on the erosion rates of the coatings and to determine any changes in the erosion mechanisms.

The coatings investigated are shown in Figure 2 and can be categorized into 3 groupings. Group 1 consists of baseline t' 7YSZ with density variations. Group 2 has substitution of ZrO_2 with HfO_2 and Y_2O_3 levels to produce t' and c (cubic) coatings. Group 3 comprises two coatings that have significant amount of REO (Rare Earth Oxides) other than Y_2O_3 . Figure 2 shows these systems. The letter designation shows which samples were tested at 25°C and 850°C.

Testing

The erosion tests were all carried out in the high-temperature erosion test facility at Cranfield University. The tests were carried out at room temperature and at 850°C using 90-125µm angular alumina particles at mean velocity of 100m/s impacting the samples at 90°.

The following figure is a schematic of the high temperature erosion facility at Cranfield University that was used for the erosion testing. It consists of a number of key components starting with the compressor (C), which supplies a pressure vessel (P). This is there to ensure that a constant amount of compressed air is supplied to the heating system (H). The air passes through a convoluted path in the pressurised heating system, which is electrically heated, before entering the acceleration tube (T). The erodent material, in this case alumina, is fed via a screw feeder and a venturi nozzle into the acceleration tube, where the compressed air accelerates the particles before they impact the test specimen in the chamber (S). When using alumina as an erodent the resident time of the particles in the hot gas stream is not sufficient to heat the particles to a significant degree so they do not soften. The test samples are attached to a carousel, which is capable of holding six different specimens at different angles with respect to the impacting particles.

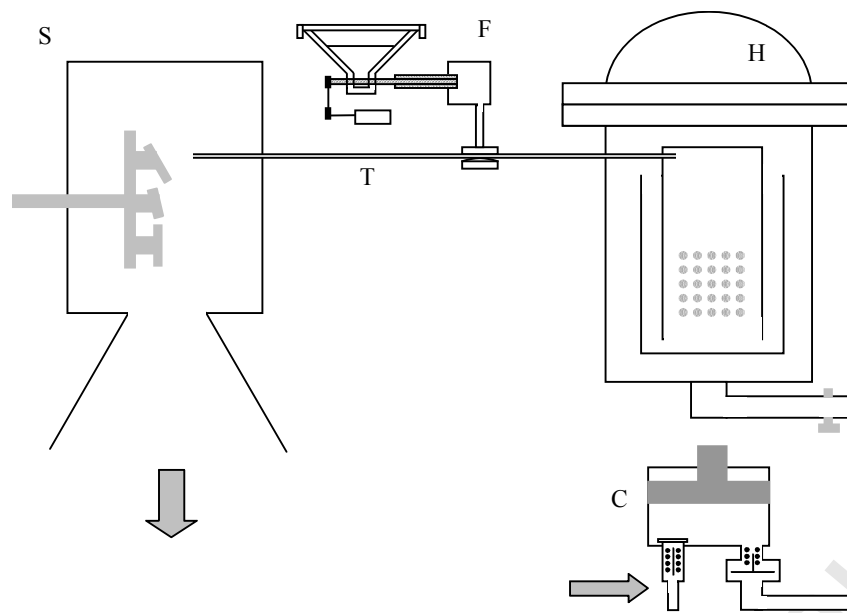


Figure 1: Schematic of the erosion rig.

Temperature Range	RT-850°C
Particle Velocities	50-400 m/s (depending on particle size)
Particle Size Range	50-1,000 μm (affects the max velocity)
Impact Angles	30, 45, 60, 75 & 90°
Particle Feed Rate	0.2-1 g/min

Table 1: Operating conditions of the test rig.

The maximum velocity of the erodent is dependent on its size and density. Small, low-density particles are capable of the highest velocities and almost attain the gas velocity.

Results

The results of the erosion testing are given in the following table and graph. As can be seen, in Figure 2 there is a large variation in steady state erosion rates between 11 and 51 g/kg for the EB PVD TBCs. The room temperature tests can be divided into two groups those with an erosion rate above 40g/kg and those

with an erosion rate between 10-22g/kg. The high temperature tests can also be divided into two main groups: the two samples with steady state erosion rates between 35 and 51 g/kg and those with steady state erosion rates between 11 and 14 g/kg with one sample set, the cubic (c) Hf modified TBC, sitting between the two groups with an erosion rate of 20g/kg. Another important feature is the extremely large reduction in the erosion rate of the Hf modified coatings between the RT and 850°C tests.

The bar chart in Figure 2 compares the HT and the RT steady state erosion rates. In all except two cases, the two standard 7YSZ samples (CC & E/F), the high temperature erosion rate is lower than the room temperature erosion rate, indicating possible changes in the erosion mechanisms. Importantly, if unsurprisingly, the two sets of standard 7YSZ samples have very similar erosion rates for both the RT and the HT tests, indicating that there is no significant change in the erosion mechanisms do to the increase in temperature. (Also shows two unrelated coating suppliers can have same erosion resistance for their standard coating). The results from the literature are the maximum and minimum erosion rates measured around a blade that was section into 6 pieces for room temperature erosion testing.

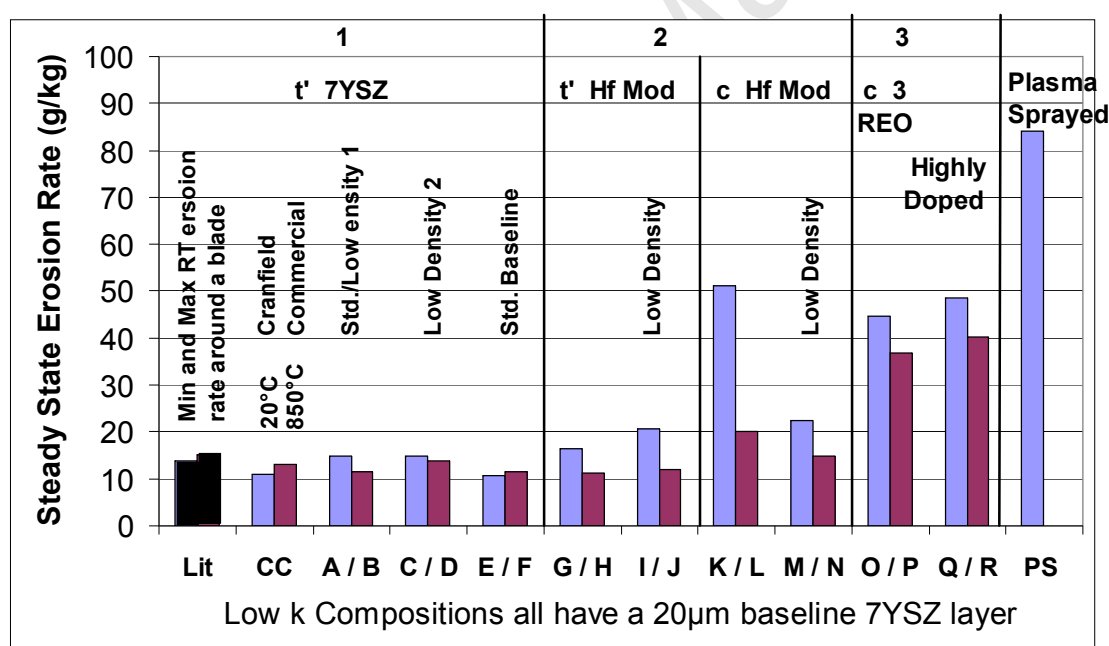


Figure 2: Bar chart comparing the HT and the RT steady state erosion rates (results of the plasma sprayed TBC is from previous work conducted at Cranfield University, t' = metastable tetragonal and c = cubic, lit = results from literature [10]).

The erosion results and the percent reduction between the RT and the HT erosion rates are given, as mass loss in g per kg of erodent impacting the sample, in Table 2. Unfortunately, the relative densities of the

different coatings are not known so it is not possible to calculate and compare the volumetric erosion rates, which is of interest as it will be proportional to thickness loss which is important for TBC coating performance.

		SS E-rate (g/kg) RT HT	% reduction 100*(RT- HT)/RT	
A/B	Thin Std 7YSZ / low density 7YSZ	14.84 / 11.60	22	Group 1 7YSZ with density variations
C/D	Low density 7YSZ	14.83 / 13.89	6	
CC/CC	Standard 7YSZ	10.92 / 12.94	-18	
E/F	Standard baseline 7YSZ	10.72 / 11.54	-8	
G/H	Thin Std 7YSZ / t' Hf mod YSZ	16.51 / 11.26	32	Group 2 HfO₂ modified coatings with t' and c crystal structures
I/J	Thin Std 7YSZ / Low density t' Hf mod YSZ	20.65 / 11.95	42	
K/L	Thin Std 7YSZ / c Hf mod YSZ	51.19 / 20.15	61	
M/N	Thin Std 7YSZ / Low density c Hf mod YSZ	22.50 / 14.75	34	
O/P	Thin Std 7YSZ / c 3 REO	44.72 / 36.93	17	Group 3 Significant additions of REOs
Q/R	Thin Std 7YSZ / Highly doped TBC	48.67 / 40.09	18	
PS *	Plasma Sprayed YSZ	84 / -		

Table 2: Table of erosion rates and % change between the **RT** and the *HT* erosion testing (* - from previous testing conducted at Cranfield University).

Discussion and Microstructural Evaluation

It is currently accepted that there is some loss of erosion resistance when one modifies 7YSZ in order to achieve a lower thermal conductivity, this was also the case for all the coatings tested in this programme, although it must be noted that they were all still more erosion resistant than APS YSZ. However, some

low thermal conductivity coatings are currently being used, even with the slight compromise in their erosion performance, for example the PWA low thermal conductivity coating. Unfortunately, the current situation with EB PVD TBCs is such that any effort to modify the TBC in order to lower the thermal conductivity results in an increase, sometimes a significant increase, in erosion rates. Since TBCs erode via a fracture dominated mechanism, both the hardness and the fracture toughness are important values, and extremely difficult to measure, as yet no one has managed to produce 7YSZ TBCs with higher fracture toughness.

After erosion testing, the samples were all cross sectioned, mounted and then polished for E-SEM evaluation in order to determine the various erosion mechanisms that were taking place. As is evident from the graph of erosion rates in Figure 2 the results can be broadly split along the lines of composition and the results will be discussed in groups according to composition.

t'-7YSZ:

All of the t' 7YSZ erosion rates are lower than 15g/kg while the two standard coatings (Cranfield Commercial, CC, and std baseline, E/F) had virtually identical erosion rates at just under 11g/kg. The low density t'-7YSZ coatings had an erosion rate higher than the standard t'-7YSZ under room temperature conditions, however, more importantly, under high temperature conditions their erosion rates were very similar to the t'-7YSZ coatings, in one case within experimental error. It is also worth noting that the low density 7YSZ TBCs had erosion rates that fell between the minimum and maximum erosion rates of 13.9 and 15.2g/kg reported in the literature [10] for room temperature erosion testing around a turbine blade sectioned into six samples.

As can be seen from the SEM micrograph in Figure 3a the high temperature erosion of the low density 7YSZ coating resulted in a fairly high degree of compaction damage, with near surface cracking running across the columns just into the region of the compaction damage.

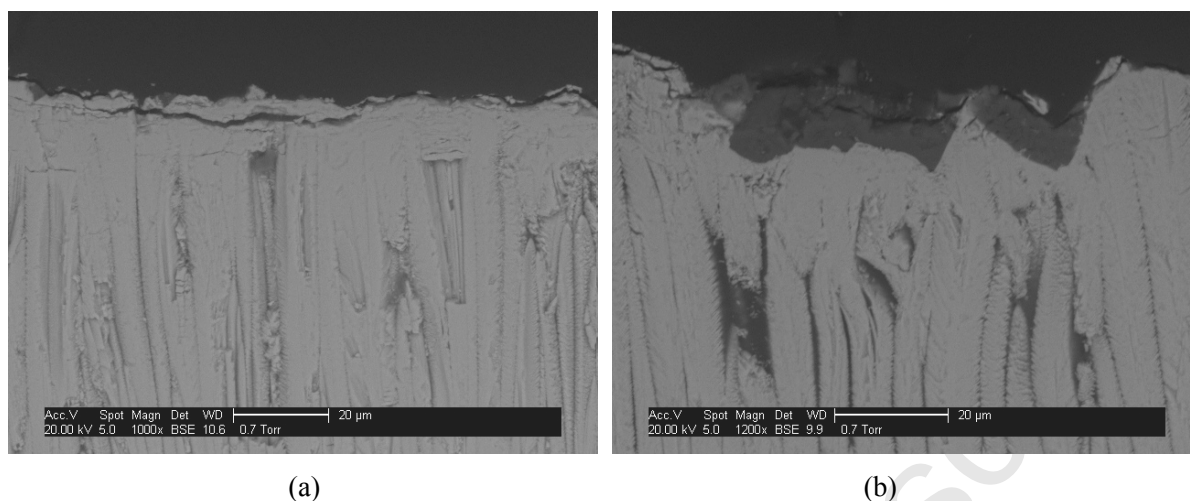


Figure 3: SEM micrograph showing HT erosion damage to (a) Coating B and (b) Coating D, the two t' -7YSZ low density coatings.

The SEM micrograph in Figure 3b shows an example of plastic deformation in the form of ‘S’ bending (Type II FOD) as well as some compaction damage. In other areas Coating D, a low density t' -7YSZ, also showed a compaction and cracking damage mechanism similar to that illustrated in Figure 3b. When examined in cross section the low density t' -7YSZ coatings have a more noticeable dendritic growth on the edges of the columns compared to the baseline coating, which is likely to affect the fracture toughness and hardness of the coatings. However, under high temperature conditions the erosion mechanism of the two low density coatings changes from near surface cracking to compaction damage with some evidence of FOD type II damage, which results in a lower erosion rate. This compaction damage and the ‘S’ bending of Type II FOD allows the coating to ‘absorb’ more damage plastically under impact conditions resulting in a lower erosion rate compared to the RT testing.

The baseline t' -7YSZ coating on the other hand exhibited very little sign of compaction damage with material removal occurring via a near surface cracking mechanism with evidence of some cross column cracking. The SEM micrographs, in Figure 4, show the slight difference in the erosion mechanism between the RT and the HT erosion of the baseline t' -7YSZ coating. In both cases predominantly near surface cracking is evident with some cross column cracking evident in the case of the HT erosion sample (F), which accounts for the slight increase in the HT erosion rate. The effect of the standard 7YSZ on the low density t' is insignificant relative to erosion resistance (A/B vs. C/D).

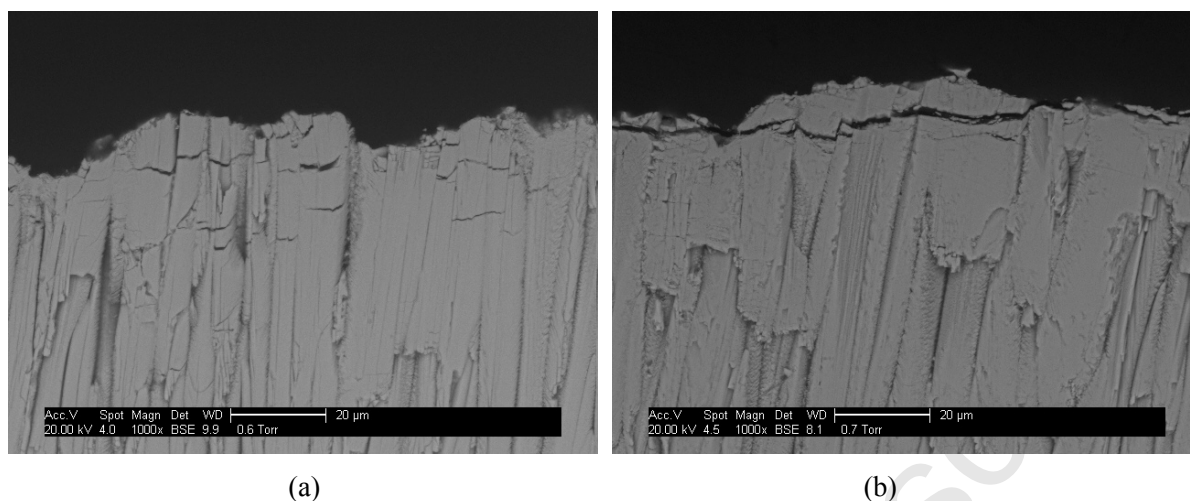


Figure 4: Near surface cracking in the base line t' -7YSZ coating (a) at RT and (b) eroded at high temperature.

Hf Modified TBCs:

In examining the erosion of the Hf modified TBCs there are three different issues to consider: how the Hf addition affects the erosion, how the microstructure affects erosion and thirdly how the crystal structure affects the erosion.

t' -Hf Modified TBCs: Both the t' -Hf modified TBCs have a higher erosion rate than their 7YSZ counterparts under room temperature conditions. Previous research has shown that additions of rare earth oxides of Gd and Dy to 7YSZ TBCs results in an increase in their erosion rates[11], but Gd / Dy additions substitute for the Y sites thus increasing the overall stabiliser content, while Hf substitutes for the Zr and does not affect the stabiliser content. In a similar manner to the t' -7YSZ coatings, the low density t' -Hf mod TBC has a higher erosion rate at RT and a virtually identical erosion rate at high temperature when compared to its standard density counterpart. But, most importantly, both of the t' Hf modified TBCs had high temperature erosion rates similar to the standard baseline 7YSZ, in fact the t' Hf mod TBC with a standard density had a lower erosion rate than any of the other coatings tested under high temperature conditions.

The SEM micrographs in Figure 5 show the near surface cracking in the t' -Hf mod coatings under RT erosion while under the HT erosion conditions there is significant densification of the TBC and associated plastic deformation/compaction, which results in a decrease in the erosion rates. Under high temperature erosion conditions the both of the t' -Hf mod coatings showed a far greater reduction in their erosion rate to almost match that of the baseline t' -7YSZ coating.

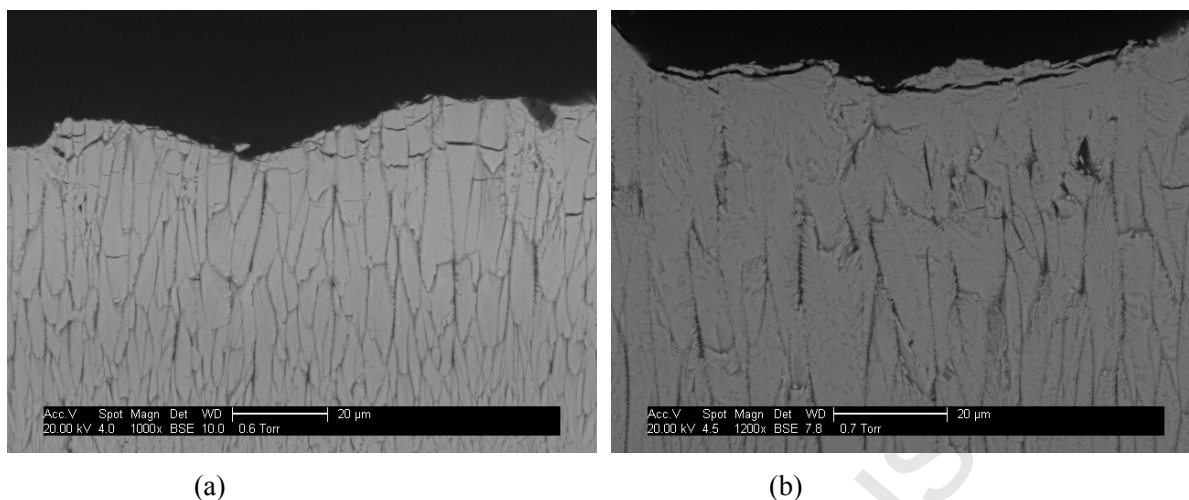


Figure 5: Near surface cracking in the t' -Hf mod coatings (a) G at RT and (b) H at high temperature.

The SEM micrographs in Figure 6 show cross column cracking as well as near surface cracking in t' -Hf mod low density coating eroded under RT conditions. Under HT conditions, as can be seen in the micrograph, 6b, there is a significant degree of densification of the coating and 'S' bending (type II FOD). Under impact conditions when densification and/or type II FOD occurs a significant amount of the impact energy is used during the densification and plastic deformation of the coating resulting in a smaller degree of cracking and hence a lower erosion rate when compared to a near surface cracking type erosion mechanism.

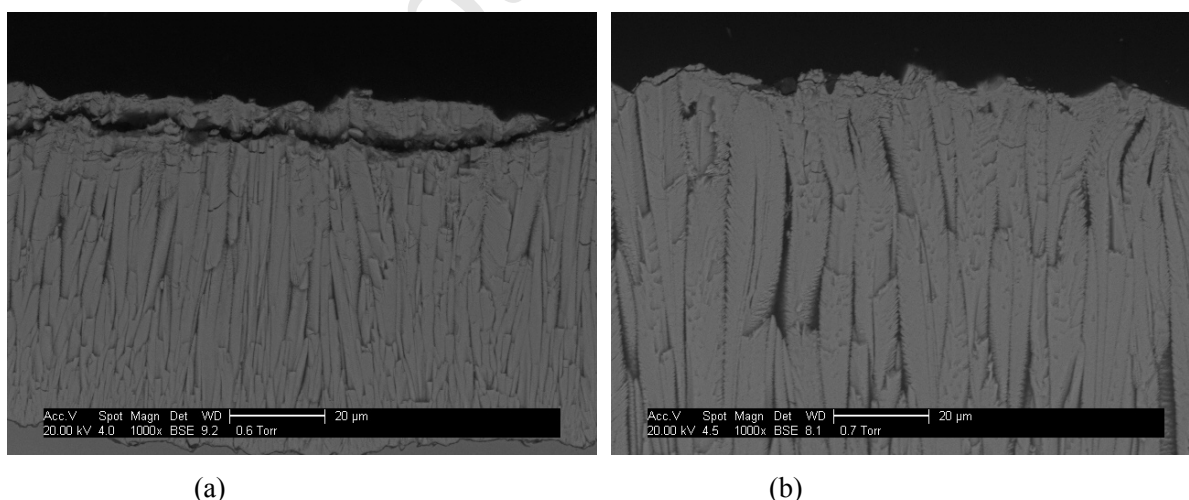


Figure 6: Near surface cracking in (a) Coating I at RT and (b) Coating J eroded at high temperature.

c-Hf Modified TBC: There are a number of issues that are immediately apparent when looking at the erosion results of these coatings. In all cases the Hf modified TBC with a cubic crystal structure has a higher, in some cases significantly higher, erosion rate than their t' counterparts, for both room and high temperature testing. This supports the assertion [12] [13] that due to the fact the t' YSZ has a substantially higher toughness than c YSZ, toughness of a material will have a great influence on the erosion rate, the t' structure is preferable. The c-Hf mod coating shows a significant reduction in erosion rate between room temperature and high temperature and this is the first system where the low density version of the coating has a lower erosion rate.

The large change in the erosion rate between RT and HT for the c-Hf Mod coatings can be ascribed to the change in erosion mechanism from cross column cracking (the mechanism giving the highest erosion rate) at RT to densification and compaction with some cross column cracking at HT. The densification, compaction and type II FOD mechanisms all absorb a significant amount of the impact energy hence reducing the degree of cracking and the erosion rate. So the more plastic deformation that the coatings can accommodate on impact, the lower the erosion rate relative to the other fracture dominated mechanisms.

The fact that, for the c-Hf mod coatings, the low density coating has a lower erosion rate is also explained in terms of erosion mechanisms. Table 3 gives the erosion mechanisms for the coatings at RT and HT. Although one would expect that the low density version of the coating will have a lower fracture toughness than the dense version of the coating and hence a higher degree of cracking and thus a higher erosion rate, this is not the case when the mechanism changes. The low density c-Hf Mod coating is the only sample that eroded via a densification and compaction mechanism at RT in this set of tests and hence had a lower erosion rate than the dense sample which eroded via a cross column cracking mechanism. The low density c-Hf Mod coating, eroded at HT, had a slightly lower erosion rate than the equivalent sample eroded at room temperature due to the fact that at the higher temperature it exhibited a greater degree of densification and plastic deformation of the coating.

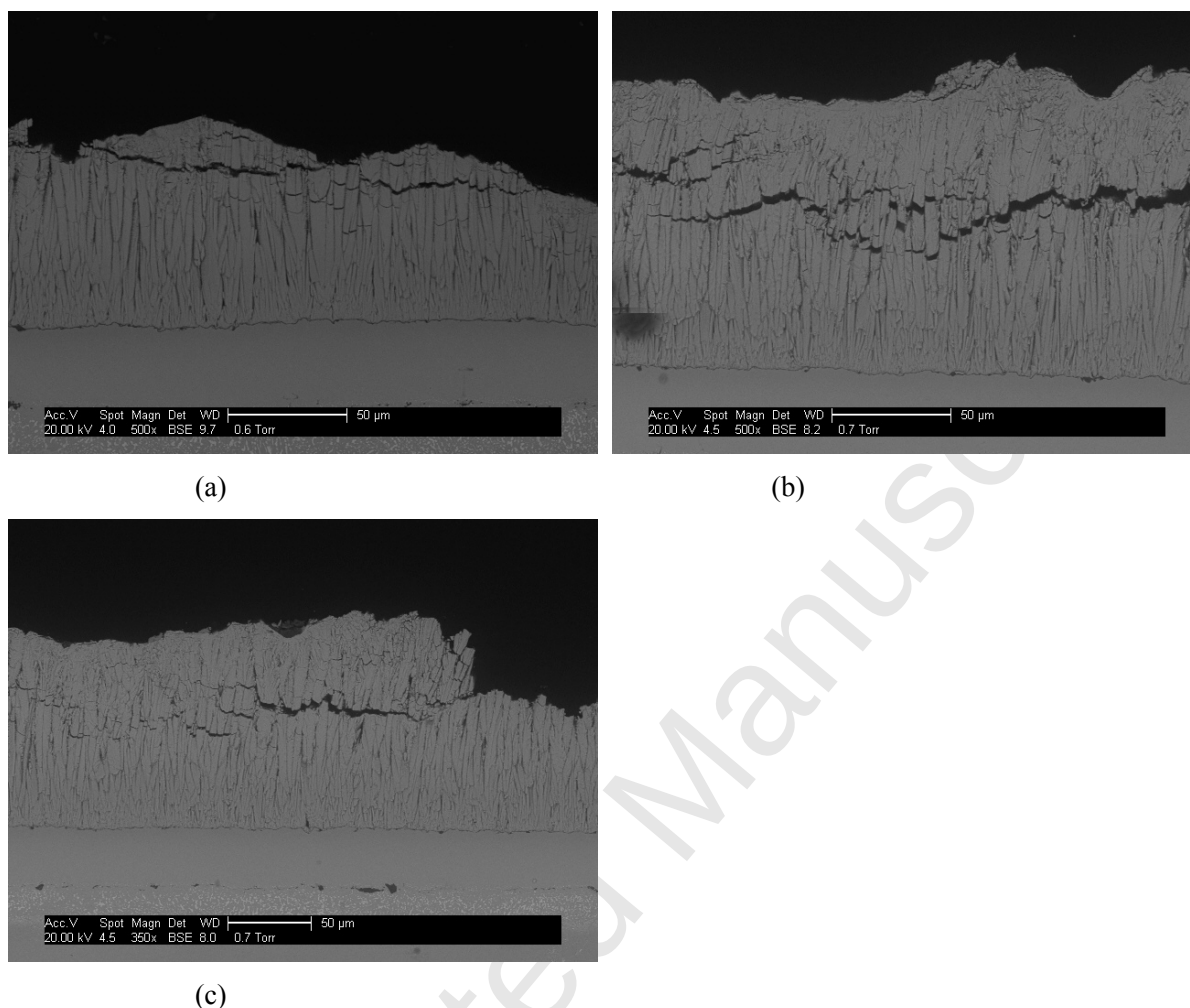


Figure 7: Erosion damage in the c-Hf Mod coating K (a) at RT, (b) and (c) Coating L at high temperature.

The SEM micrographs in Figure 7 show cross column cracking in the c-Hf Mod coating eroded under RT conditions. Under high temperature erosion conditions there is some evidence of compaction damage and densification; however, there is also evidence of significant subsurface damage which appears to accumulate for a long time before a significant amount of material is suddenly lost from the coating. This is illustrated by the step in the coating in Figure 7c and was accompanied by a sudden increase in mass loss. Such a sudden increase in mass loss normally indicates penetration to the bond coat, which is the point at which the test is stopped. On the other hand under room temperature conditions (sample K) had an initial incubation period of low material loss followed by a steady state erosion rate that was very high.

As can be seen from the micrographs in Figure 8 both coatings erode via the same mechanism of compaction damage and cross column cracking, with the sample tested at high temperature showing a

higher degree of densification and compaction, i.e. at HT the coating is able to absorb more of the impact energy plastically, resulting in a decrease in the degree of cracking and hence a slight decrease in erosion rate. This is very similar to erosion mechanism identified by Steenbakker while conducting erosion testing at RT and HT on gadolinia doped TBCs, although in that case the mechanism was only observed to occur during the HT erosion testing[8].

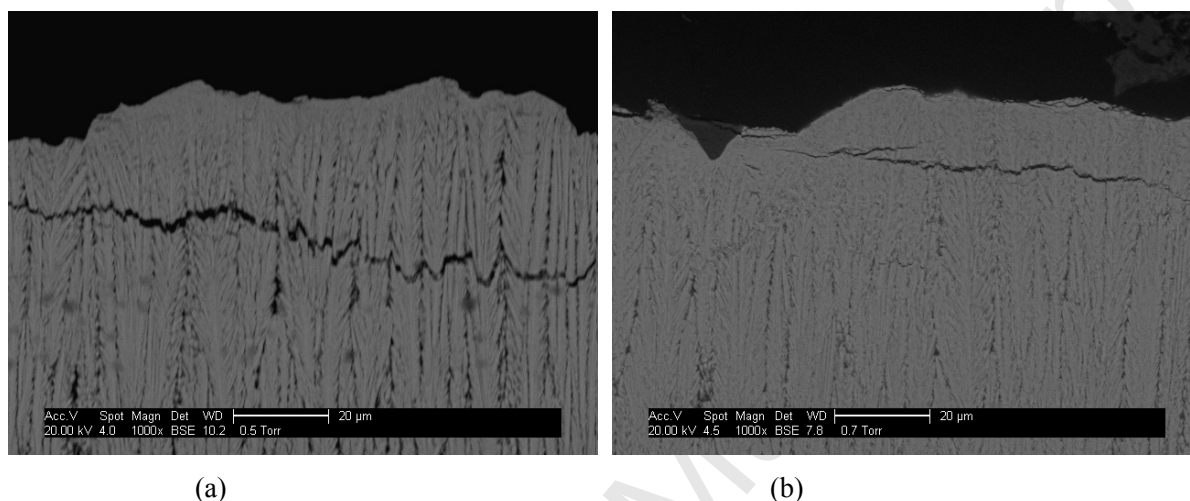


Figure 8: Near surface and cross column cracking with associated surface regions of densification in the c-Hf mod TBC Coating M (a) at RT and (b) Coating N at high temperature.

c-3 REOs and Highly Doped TBCs:

The final modified coatings to discuss all had highly modified top coats compared to a standard 7YSZ TBC. All four samples had high erosion rates with the predominant mechanism being cross column cracking. There appears to be no difference between the erosion mechanisms at RT and HT for the coating with 3 REOs as illustrated in the SEM micrographs in Figure 9, with both samples eroding via a cross column cracking mechanism. However, one could argue that there is evidence of a small degree of densification occurring under the HT erosion conditions, which would account for the slight reduction in erosion rate at the higher temperature.

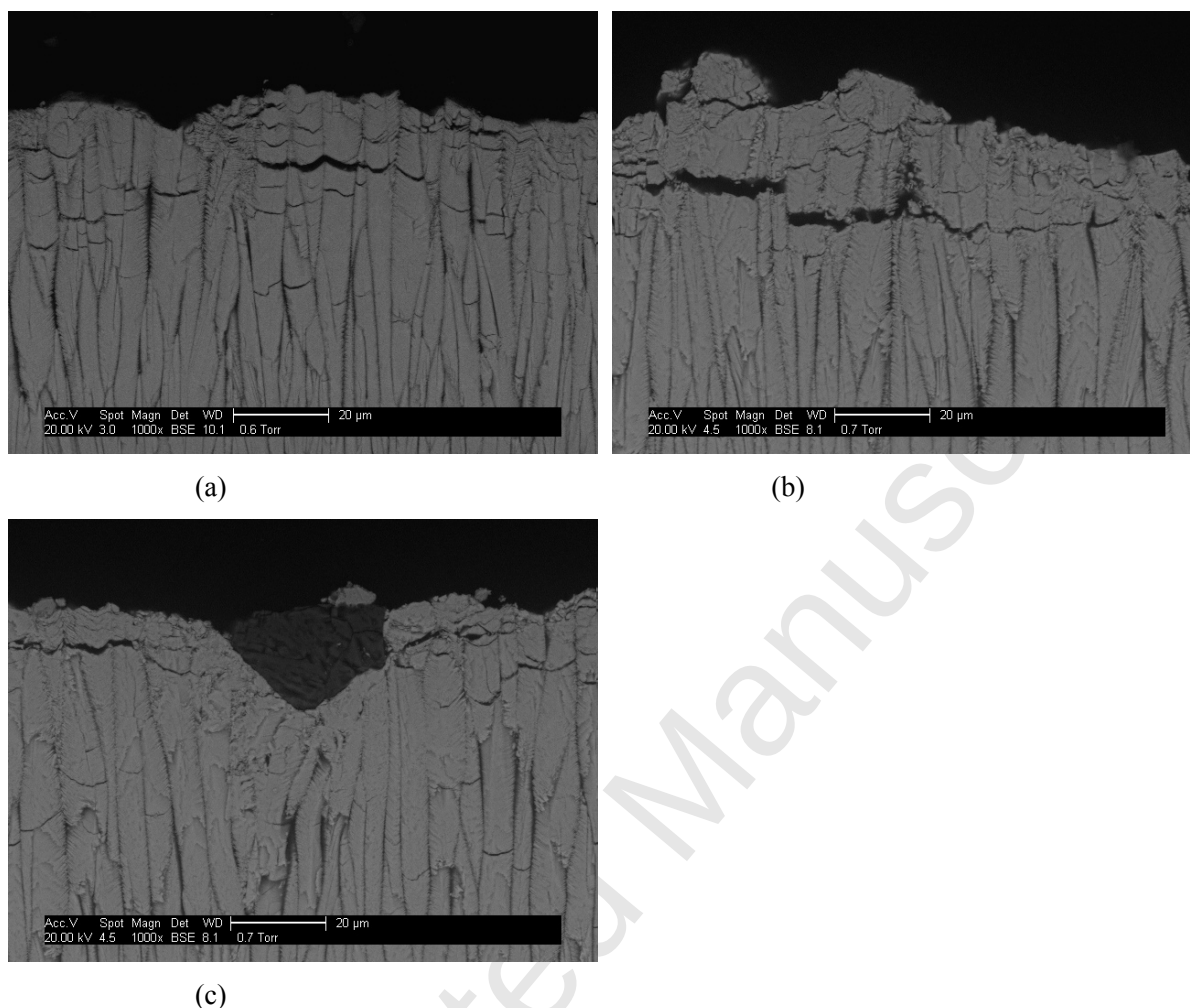


Figure 9: Near surface and cross column cracking in the coatings with 3 REO additions (a) Coating O at RT, (b) and (c) Coating P at high temperature.

Again as illustrated in the two SEM micrographs in Figure 10 in the highly doped coating there is very little difference in the erosion mechanisms between the two samples, one tested at room temperature the second at high temperature, with both eroding via a cross column type mechanism with associated near surface cracking. However, as can be seen in the left hand side of the micrograph of coating R there is evidence of the columns bending in a Type II FOD manner. Although the bending has resulted in cracking it still shows some degree of plasticity, and again this would account for the slight drop in erosion rate between RT and HT for these coatings.

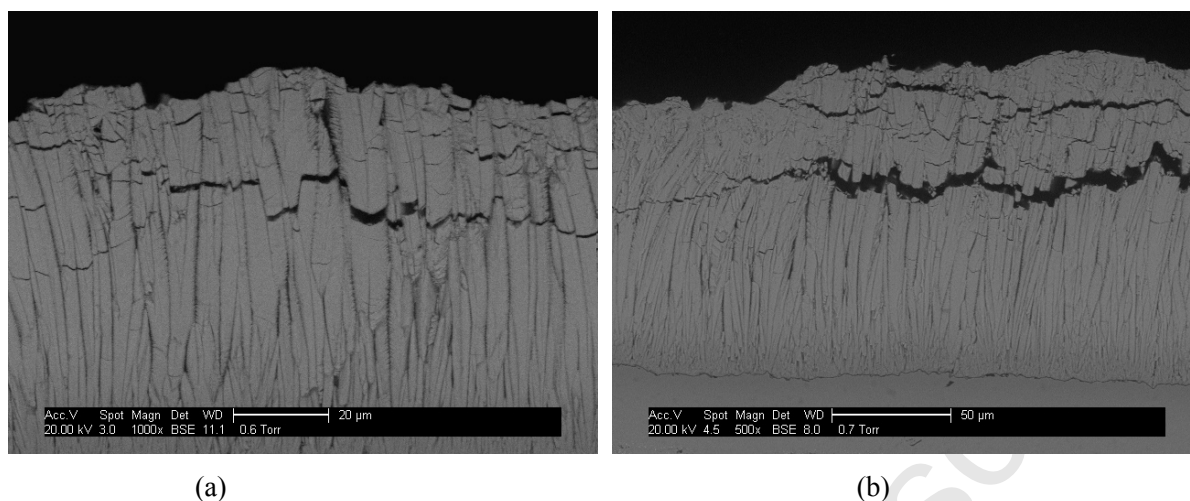


Figure 10: Near surface cracking in (a) Coating Q at RT and (b) Coating R eroded at high temperature.

Under both the RT and the HT test conditions, these four coatings exhibited erosion rates which were significantly higher than all of the t' coatings.

Erosion mechanisms:

The data in Table 3 summarises the various erosion mechanisms that have been observed during the course of this investigation. The results support previous work which suggested that material loss via a near surface cracking mechanism results in the lowest erosion rates and that loss via cross column cracking results in high erosion rates, while a densification / compaction type mechanism operating in conjunction with other mechanisms can help to reduce the erosion rate.

Foreign object damage (FOD) can occur as two distinct mechanisms Type I and Type II [9] and while it is well known that FOD type I results in significant damage to the coating with high mass loss rates, especially when the impact damage penetrates to the ceramic/TGO interface, the severity of FOD type II has been less well understood. This paper has shown that, as long as the damage does not extend to the interface, the FOD type II erosion mechanism, due to its ability to dissipate impact energy via densification and plastic deformation (in the form of 'S' buckling) can act to reduce the erosion rate of EB PVD TBCs.

Sample	Erosion Mechanism/s	Rate
A	Near surface cracking	Low
B	<i>Densification with compaction and cracking with some Type II FOD</i>	<i>Low</i>
C	Near surface cracking	Low
D	<i>Densification with compaction and cracking with some Type II FOD</i>	<i>Low</i>
E	Near surface Cracking	Low
F	<i>Near surface cracking with some cross cracking</i>	<i>Low</i>
G	Near surface cracking	Low
H	<i>Densification with compaction and cracking</i>	<i>Low</i>
I	Near surface cracking and cross column cracking	Medium
J	<i>Densification and compaction with some Type II FOD</i>	<i>Low</i>
K	Cross column cracking	High
L	<i>Densification and compaction with cross column cracking</i>	<i>Medium</i>
M	Compaction damage and cross column cracking	Medium
N	<i>Significant densification and compaction with cross column cracking</i>	<i>Low</i>
O	Cross column Cracking	High
P	<i>Cross Column cracking (with possibly a small amount of densification)</i>	<i>High</i>
Q	Cross column cracking	High
R	<i>Cross Column cracking (with a small degree of FOD Type II damage)</i>	<i>High</i>

Table 3: Erosion mechanisms for the different samples under **RT** and *HT* conditions.

6. Conclusions

With one exception, the t' Hf modified coating tested at 850°C, all the low thermal conductivity coatings had a higher erosion rate than the baseline 7YSZ. The t' Hf modified coating tested at 850°C showed a reduction in erosion rate due to a change in mechanism. Essentially this paper has shown that trying to reduce the thermal conductivity of TBCs by changing the density (and hence the microstructure), adding one or more rare earth oxide dopants and / or changing the crystal structure all result in an increase in the erosion rate of TBCs by different degrees. More specifically this paper has demonstrated that:

- All the EB PVD coatings tested had an erosion rate lower than that of plasma sprayed 7YSZ TBCs.

- Under room temperature erosion conditions the modified TBC systems all had a higher erosion rate than the standard 7YSZ TBC.
- Under high temperature erosion conditions all the doped TBCs had a higher erosion rate than the standard 7YSZ TBC, except for sample H (the t' Hf modified coating) which had a very slightly lower erosion rate.
- The standard 7YSZ TBCs showed a very slight increase in erosion rate with temperature.
- The doped TBC systems all showed a significant decrease in erosion rate with temperature.
- The decrease in the erosion rate under high temperature conditions was attributed to either a complete change in erosion mechanism and/or the introduction of densification and plastic deformation within the coatings during high temperature erosion.
- Under high temperature erosion conditions the Hf modified t' coatings performed as well or better than the standard 7YSZ coatings.

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