Erosion of gadolinia doped EB-PVD TBCs

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Abstract

Gadolinia additions have been shown to significantly reduce the thermal conductivity of EB-PVD TBCs. The aim of this paper is to further the understanding on the effects of dopants on the erosion resistance of EB-PVD TBCs by studying the effects of 2 mol% Gd_2O_3 additions on the room and high temperature erosion resistance of as received and aged EB-PVD TBCs. Previously it has been reported that gadolinia additions increased the erosion rate of EB-PVD TBCs, this is indeed the case for room temperature erosion, however under high temperature (825 °C) erosion conditions this is not the case and the doped TBCs have a slightly lower erosion rate than the standard YSZ EB-PVD TBCs. This has been attributed to a change in the erosion mechanisms that operate at the different temperatures. This change in mechanism was not expected under the impact conditions used and has been attributed to a change in the column diameter, and how this influences the dynamics of particle impaction.
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1. Introduction

Thermal barrier coatings using 8 wt.% yttria partially stabilised zirconia as the top coat have been used in gas turbine engines for a number of decades and it is widely accepted that EB-PVD TBCs offer high strain compliance and good erosion resistance compared to APS TBCs. Erosion is seen as a secondary cause of failure, small ingested particles can cause significant damage to the coating and consequently EB-PVD TBCs' mechanical properties are very important. Unfortunately EB-PVD technique also leads to a coating with a higher thermal conductivity hence the challenge was to lower the thermal conductivity of EB-PVD TBCs to match that of plasma sprayed system to provide a coating with excellent thermal properties.

The mechanisms and techniques to further decrease the thermal conductivity of the EB-PVD TBCs by adding rare earth oxides are well documented [1–4]. It has been shown that rare earth oxide additions can significantly lower the thermal conductivity of EB-PVD TBCs and thermal conductivity close to that of APS TBCs has been achieved by doping the coating with 2 mol% of gadolinia [2].

A fair amount of work has been published on the erosion of EB-PVD TBCs in the as-received condition under various conditions of temperature, velocity, impact angles and with different types of erodent [5–11]. The erosion mechanisms of EB-PVD TBCs have also been well described by Wellman and Nicholls [5,9] and Chen et al. [7,8], the effect of heat treatments on the properties of TBCs has also been studied [12] and work has been done on the erosion of aged samples at room temperature. However the authors are not aware of any work published on the erosion of aged EB-PVD TBCs at high temperature.

The purpose of this work was to determine whether rare earth additions modified the erosion resistance and mechanisms of erosion for an EB-PVD TBCs. If the erosion resistance of doped EB-PVD TBCs were unchanged it would provide a coating with

Table 1
Table of the different samples used for the experiments

Sample	Substrate	Coating	Ageing
A	Al_2O_3	Std YSZ	–
B & C	Al_2O_3	Std YSZ	100 h at 1100 °C
D	Al_2O_3	Std YSZ	24 h at 1500 °C
E & F	ZrO_2	Doped	–
G & H	ZrO_2	Doped	100 h at 1100 °C
I & J	ZrO_2	Doped	24 h at 1500 °C
K & L	Aluminised C263	Doped	–

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Table 2
Test conditions

Erodent	Alumina
Impact angle	90°
Particle size	90–125 μm
Velocity	RT: 100 m/s HT: 190 m/s
Feed rate	0.495 g/min
Temperature	Room temperature: A, B, E, G, I and K
	825 °C: C, D, F, H, J and L

excellent mechanical and thermal properties and doped TBCs would be the material of choice for high pressure turbine blade applications.

2. Testing

For the experiments two types of coating were used, a standard ZrO_2–8 wt.% Y_2O_3 and a standard YSZ doped with 2 mol% of Gd_2O_3. The standard YSZ coatings were deposited on alumina substrate 96% purity and the doped coatings on zirconia and aluminised C263 substrate all by EB-PVD. To determine the effect of ageing on the erosion rate, two different sets of ageing times and temperature were used: 100 h at 1100 °C and 24 h at 1500 °C. The different types of specimens are listed in Table 1.

The erosion tests were carried out using alumina particles with a size range between 90–125 μm for an impact angle of 90 °C and a feed rate of 0.5 g/min. The samples were tested at room temperature and at 825 °C. The erosion conditions are given in Table 2. The erosion tests were carried out using the high pressure gas gun erosion rig at Cranfield University, a description of which can be found in a previous publication by Wellman and Nicholls [12]. Standard and doped samples were eroded at room temperature and high temperature in the as deposited condition and after heat treatment.

3. Results and discussion

3.1. Erosion at room temperature

The results are presented in Fig. 1. These results show that the erosion rate at normal impact of standard YSZ increases by circa 50% when the sample is aged for 100 h at 1100 °C, this is consistent with the results published by Wellman and Nicholls [12]. This trend is also observed for the doped TBCs with a dramatic increase the erosion rate for the sample aged for 24 h at 1500 °C. After the first cycle of the erosion run this sample was completely cracked and after the third cycle the coating was penetrated. This increase in erosion rate with ageing is linked with sintering: cracks can propagate to neighbouring columns as they are sintered together resulting in a greater material loss per impact [12].

It was also noted that the doped TBCs on the zirconia and aluminised C263 substrate have about the same the erosion rates. Moreover these results show that the erosion rate is greater for the doped TBCs for the samples tested in the as-received condition as well as the aged samples. The erosion rate increases by between 70% and 80% when the TBC is doped with Gd_2O_3.

After erosion testing each sample was sectioned, mounted, polished and examined in the scanning electron microscope (SEM). Standard ZrO_2–8 wt.% Y_2O_3 coatings showed the same erosion behaviour as presented by Wellman and Nicholls [5] that is to say near surface cracking and dendrite initiated cracking.

However a new erosion mechanism has been observed for the doped sample tested in the as received condition at room temperature and is illustrated in Fig. 2. As it can be seen from the micrographs, lateral cracks run parallel to the surface of the coating at different depths. Furthermore cracks do not stop at the column boundaries and propagate across several columns. It looks like "a step erosion", on impact a crack at a depth between 10–20 μm is formed and propagates across multiple columns parallel to the surface. Then the layer is removed exposing the
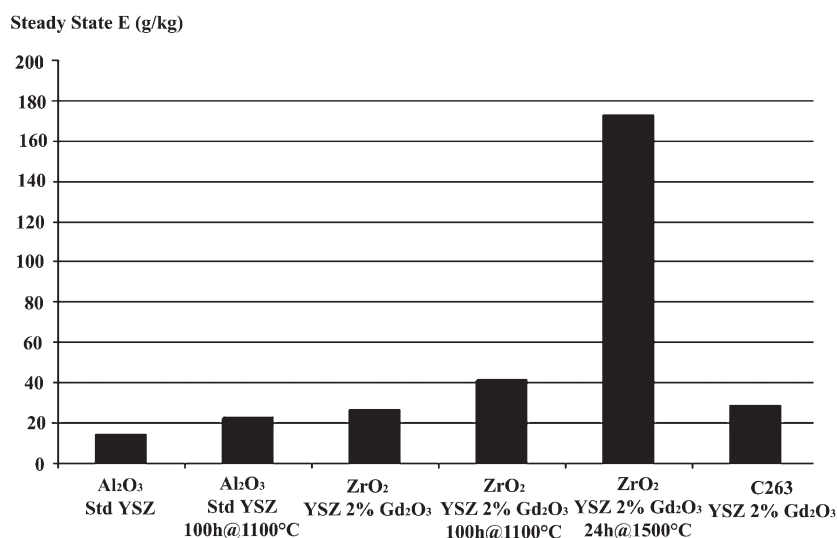

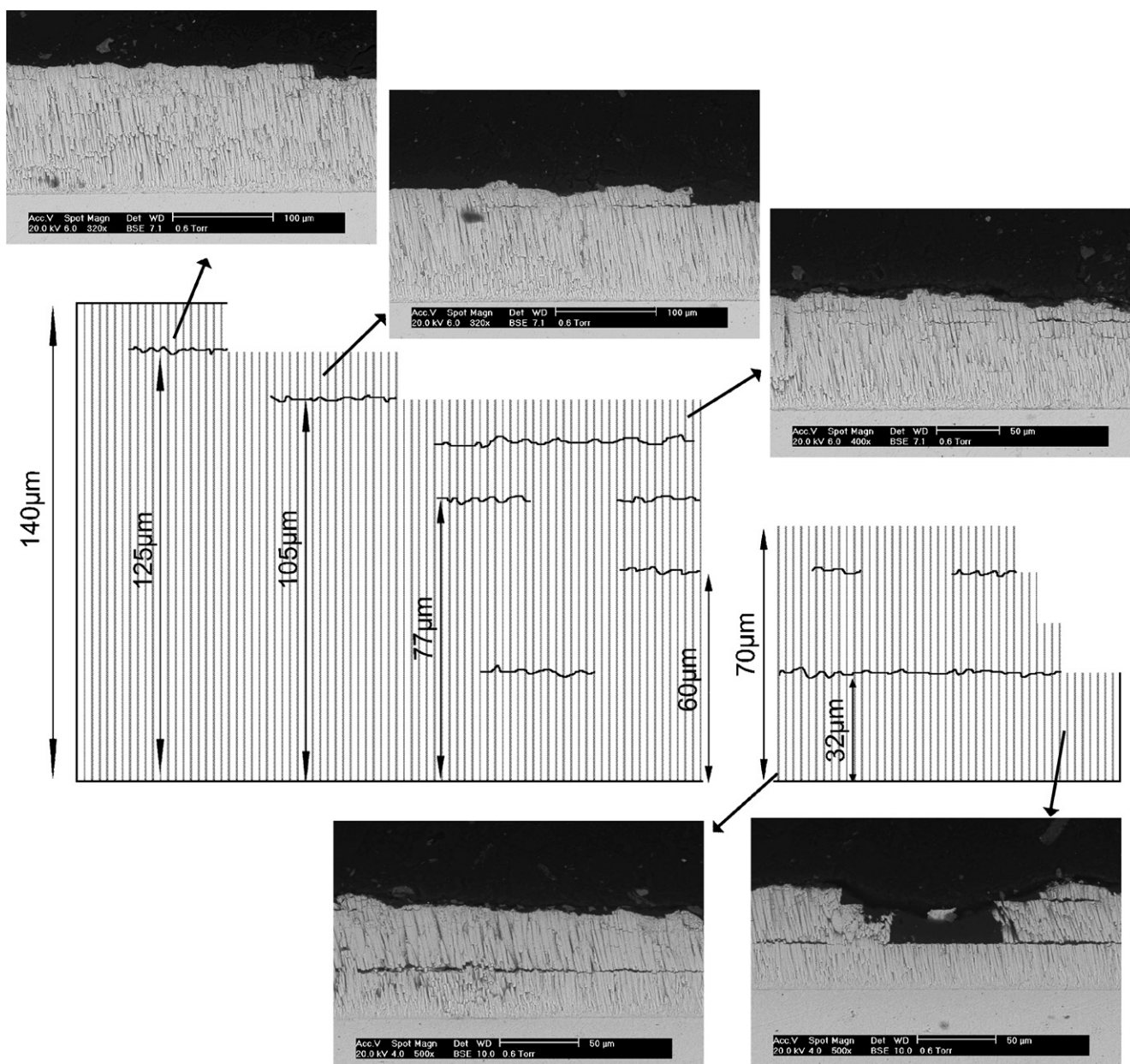Fig. 1. Erosion rate of TBC at room temperature.

Fig. 2. Schematic representation and micrographs of the new erosion mechanism observed for doped TBCs.

underneath layer to the flow of particles and so on. Cracks can also be observed much deeper in the coating. This particular erosion mechanism was observed for the doped TBCs on both the zirconia and the aluminised C263 substrate in the as-received condition. There was no evidence of this type of cracking in the aged samples. Erosion in the aged samples occurs in the same manner as the standard TBC.

It was believed that cracks propagated in layers rich in gadolinia which could have been due to a non-homogenous deposition. However EDS elemental mapping revealed no segregation detectable by this method, gadolinia appeared to be uniformly distributed in the coating.

It is proposed that during initial impact elastic compression waves are induced beneath the impacting particle. The columns are around 3–5 μm in diameter and the alumina particles size is

100 μm therefore a single impact could affect about 20 columns. The compression waves propagate down the columns and at the interface with the TGO they reflect in diffuse tensile waves and propagate back toward the top of the coating. The tensile stresses generated could cause cracks to form from the dendrites at the edge of the columns and extend across the columns. Once the crack is formed it will grow due to the stresses generated by further impacts and this will lead to the spallation of a complete layer of columns. Moreover further impacts will induce compressive waves which could close the crack hence producing another impact which could generate stress waves causing cracks much deeper in the coating. This erosion mechanism seems to be more detrimental for the coating compared to the one observed for standard samples as it results in a large increase in erosion rate. Indeed, it is evident from Fig. 2 that, after a certain level of
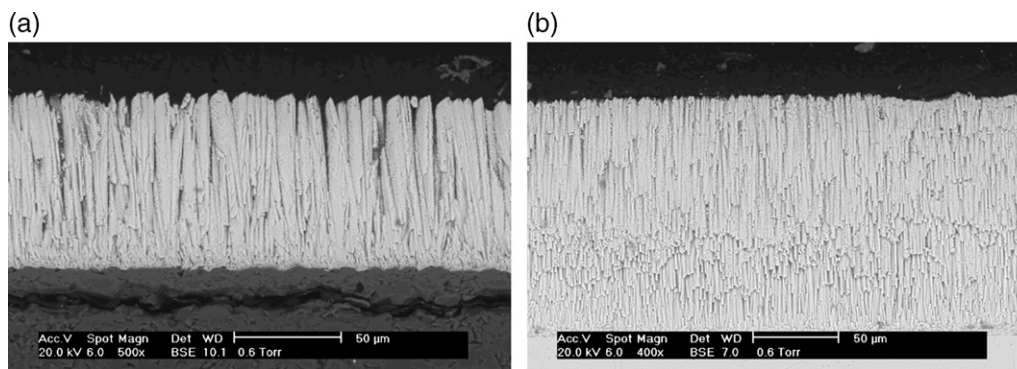
Fig. 3. (a) Microstructure of a standard EB-PVD TBC, (b) finer microstructure of the doped EB-PVD TBC.

damage, a cracked layer is not held anymore by the rest of the coating and is removed from the coating resulting in a great material loss.

If the column diameters of the standard and doped TBCs are compared, the doped TBC has much finer columns in the range of 3–5 μm against 6–8 μm for the standard one. From the micrograph Fig. 3 it can be seen that the doped TBC has a "needle like" microstructure and the columns seem to be packed closer together. Consequently the "saw teeth" which give this particular "featherlike" structure to the columns must be closely entangled and this could explain why the cracks can propagate to the neighbouring columns.

A finer columnar microstructure has also been observed by the author when co-doping with europia and dysprosia using different amount of dopant: as the percentage of dopant increases the columns become finer. The microstructure of the coating can be roughly predicted using the Movchan and Demchishin structure diagram represented in Fig. 4 [13]. In this diagram the coating texture is divided into different zones according to the processing temperatures normalized to the melting point of the coating material (T/T_m). Since the deposition temperature of the standard and doped coatings was around 1000 °C the coating microstructure can be characterized as "Zone 2" in which, the higher the melting point of the coating material, the finer the columns. According to Rouanet [14] adding yttria or rare-earth oxides to zirconia (up to 50 mol% in the case of Y_2O_3) increases the melting temperature however gadolinia is the exception and additions up to 10 mol% have no significant effect on the melting
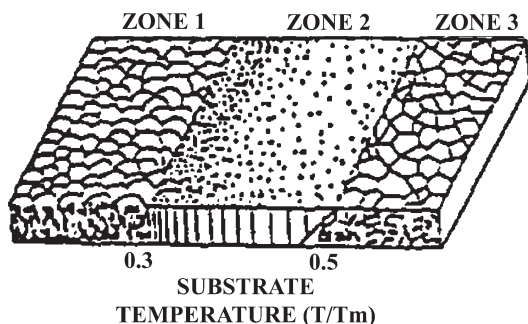
temperature (Fig. 5). Standard YSZ coatings and coatings co-doped with gadolinia but also dysprosia and europia were deposited using the same deposition parameters onto similar substrates therefore it is believed that the finer columnar microstructure is the result of ternary additions of rare-earth oxides. The Rouanet diagram presents only the effect a single dopant addition but co-doping standard YSZ material could result in an increase of its melting point and it could result in a coating with a finer microstructure.

3.2. Erosion at high temperature

The results are presented graphically in Fig. 6. The erosion rate of the standard YSZ aged 24 h at 1500 °C was surprisingly low with an erosion rate of 7.4 g/kg. The trend of the erosion results at room temperature indicates that the erosion rate of the standard YSZ aged 24 h at 1500 °C should be higher than the erosion rate of the standard YSZ aged 100 h at 1100 °C,

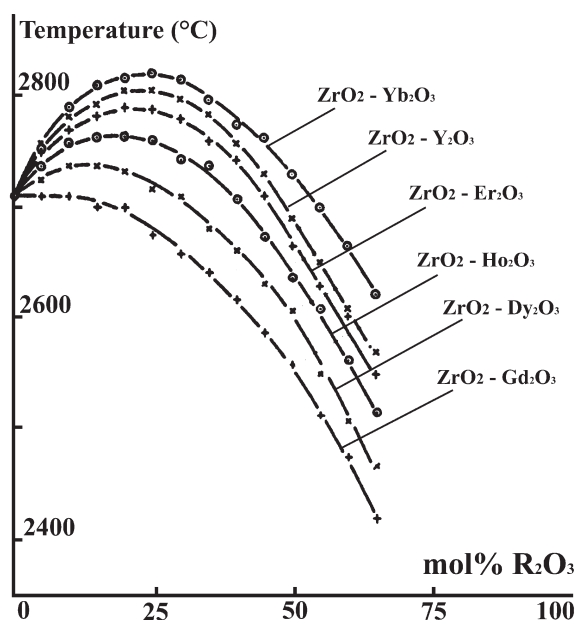Fig. 4. Movchan and Demchishin structure diagram (Ref. [13]).

Fig. 5. Melting temperature of zirconia as a function of secondary addition of rare earth oxides (Ref. [14]).
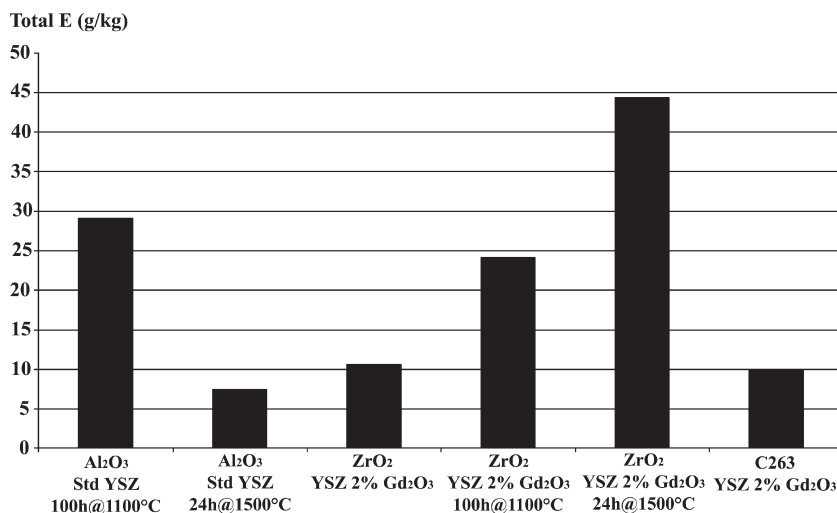
Fig. 6. Erosion rate of TBC at 825 °C.

however, when tested at 825 °C it was found to be four times lower. It can be seen from Fig. 7 that the sintering is very different for this sample and it is very difficult to distinguish individual columns. It is believed this loss in columnar microstructure is caused by liquid phase sintering due to impurities in the alumina substrate such as silicon, calcium or magnesium in a manner very similar to CMAS attack. Further experiments revealed that coatings deposited on alumina substrates 96% purity exhibit liquid phase sintering and monoclinic phase formation only after aging 8 h at 1500 °C whereas coatings deposited on high purity alumina have a normal sintering behaviour and no monoclinic phase was present in the coating after ageing 500 h at 1500 °C. This observation will be the subject of another paper. Consequently the erosion rate of this sample is closer to that of bulk zirconia than an aged EB-PVD TBC. This is significantly lower than that observed by Wellman and Nicholls [12] in a similar test. However, the substrate used was zirconia and not alumina and consequently this impurity effect did not affect the sintering of the TBC on zirconia substrates.

The high temperature erosion rate of the doped TBCs increases with the ageing temperature exactly like for the test at room temperature, however when comparing the doped and the standard TBCs aged 100 h at 1100 °C the erosion resistance of the doped TBC is better than the standard TBC. At room temperature the opposite behaviour is observed with the standard TBC a lot more erosion resistant than the doped one. If the results at room temperature and high temperature are compared for the doped TBCs it can be noted that the erosion rates are lower when tested at high temperature. The velocity of the impacting particles was higher for the test at high temperature therefore the samples tested at high temperature should have a higher erosion rate compared to those tested at room temperature. Moreover the erosion rate of the doped TBC in the as-received conditions at high temperature (10.5 g/kg) is also lower than the erosion rate of the standard sample tested at room temperature (13.1 g/kg). These "anomalies" have been attributed to changes in the erosion mechanisms.

In their work on Foreign Object Damage (FOD), Wellman et al. [9] have clearly identified that plastic deformation can occur during large particle impact in the form of buckling at high temperature. SEM analysis of sectioned samples (Fig. 8) revealed that material loss in the doped TBCs eroded at high temperature was via a FOD type II mechanism (buckling of columns without significant cracking) rather than an erosion
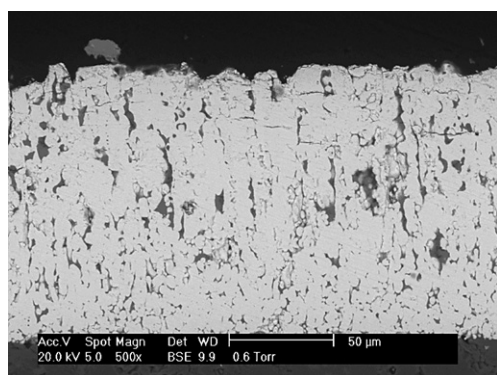

Fig. 7. Micrograph of the standard sample heat treated 24 h at 1500 °C tested at high temperature.
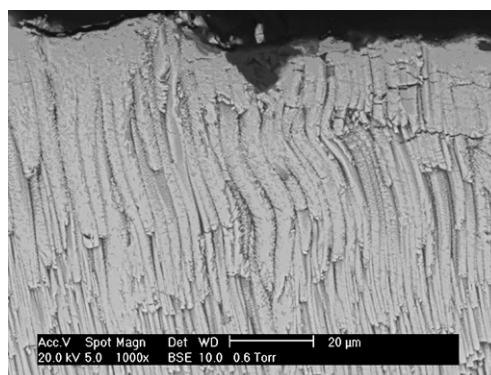

Fig. 8. Buckling in the columns of a doped TBC tested at high temperature.

(lateral cracking) mechanism. The micrograph Fig. 8 shows that at high temperature, due to impacts, the columns of the doped coating buckled almost without cracking. Consequently doped TBC has the ability to plastically deform at high temperature hence absorbing the kinetic energy of the impacting particles. When a particle impacts the coating it decelerates progressively as the columns buckle therefore the damage caused by the impact is reduced; moreover buckling occurred without significant cracking hence reducing the erosion rate of the doped TBC. Further impacts will increase the degree of buckling in the columns, cracks will start to form and it will be followed by material loss. Kink bands, as described by Chen [7], were also found in the doped TBCs eroded at high temperature (Fig. 9). When the plastic zone penetrates deeply in the coating the stresses generated can be very damaging and plastic deformation can be accompanied with kink bands that initiate around the perimeter of the plastic zone and large-scale delamination can be formed [7]. Buckling occurred in the sample tested in the as received condition and in the one aged 100 h at 1100 °C however there was no evidence of buckling in the sample aged for 24 h at 1500 °C. As the erosion rate for this sample is also reduced compared to the test at room temperature it is believed that there was a certain amount of buckling but it was not evident on the micrographs that were examined.

Plastic deformation in the form of densification was also evident on the doped samples tested at high temperature (Fig. 10). Successive impacts generate hydrostatic compression in the columns removing porosity by "dynamic hot pressing" hence forming a densified layer [7]. Further impacts induce elastic stress waves building tensile stresses at the interface between the dense layer and the underlying columnar microstructure that can initiate cracks. These cracks can propagate under subsequent impacts causing partial detachment of the dense layer and material removal as it is shown in Fig. 10. Plastic deformation in the form of densification or buckling absorbs the energy of the impacting particles therefore significantly reducing cracking and the damage in the coating and increasing the erosion resistance of the doped coating at high temperature.

The switch from "Mode I: erosion" for standard TBCs to "FOD type II" for the doped TBCs tested at high temperature is believed to be linked to the finer microstructure observed for doped TBCs and the higher degree of plasticity under the high
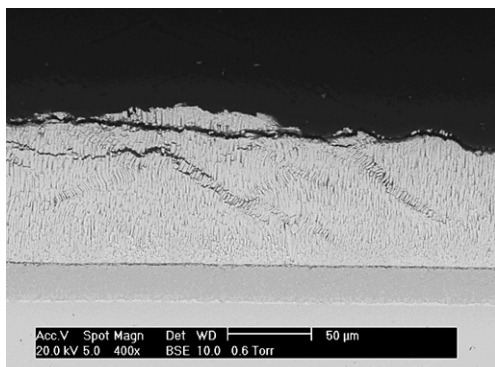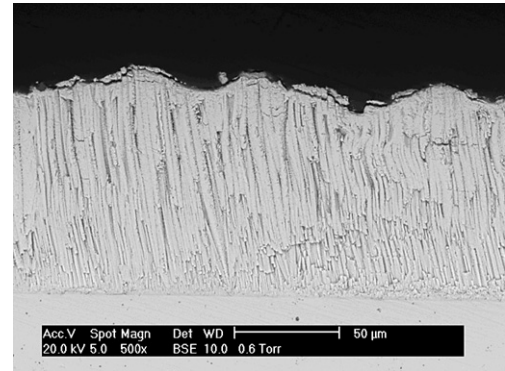

Fig. 10. Densification due to successive impacts.

temperature test conditions. Analyses of a number of samples impacted under various test conditions have shown that for standard YSZ, a D/d ratio, where D is the contact footprint diameter and d is the column diameter, less than one results in "Mode I: erosion" while a D/d ratio of about 2 to 10 results in compaction damage and a ratio greater than 10 results in FOD with the associated kink bands, densification and in some cases buckling of the columns [15]. The size of impacting particles being the same, the ratio between the contact foot print of the impact (D) and the column diameter (d) is higher for doped TBCs consequently the load created by impacting particles is shared between a higher number of columns therefore the applied load is accommodated more efficiently than if it was contained within a smaller number of columns. The importance of contact area relative to column diameter has also been noted in the micro hardness testing of EB-PVD TBCs [16].

4. Conclusion

The erosion rates found in this research suggested that gadolinia addition has the detrimental effect of lowering the erosion resistance of the coating at room temperature. This decrease in erosion resistance is believed to be linked with the new erosion mechanism observed for the doped TBCs tested at room temperature in the as-received condition. Large cracks propagate across a significant number of columns parallel to the surface at various depths in the coating. These cracks could be caused by elastic stress waves and can propagate to a significant number of columns due to the fact that columns in the doped coating are narrow and tightly packed.

It has also been shown that doped coatings can plastically deform at high temperature in the form of densification and buckling without significant cracking. Such behaviour is advantageous as it reduces the damage caused by the impact and therefore reduces the erosion rates at high temperature. It was found that the doped TBC tested in the as-received condition at high temperature has a higher erosion resistance than the standard sample tested at room temperature highlighting the significant effect of plastic deformation in the reduction of erosion rates. The finer microstructure observed for doped TBCs is believed to be responsible for this change in erosion mechanism.

Fig. 9. Kink bands formed in the doped TBCs.

Acknowledgements

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