The role that hydrogen and sulfur play in desktop failure of thermal barrier coatings

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Introduction

Thermal barrier coatings (TBC) are widely used in high temperature applications such as airplane engines or land-based gas turbines to create a temperature gradient between the hot working gas and the component material. Typically breakdown (i. e. spallation) of the protective TBC occurs at the end of their lifetime during cooldown due to thermal expansion mismatch stresses. However, sometimes spallation occurs delayed for minutes, hours, or even days after the sample is cold [1-3]. This special type of failure, called “desk top spallation” is, up to now, not fully understood and therefore a field of great interest.

Because desk top failure occurs in ambient air, one working hypothesis is that water vapor from the office environment plays a role. The detrimental effect of water (vapor) on TBCs is therefore of great interest. Furthermore, it is well known that sulfur, e g. from the gas environment or from the bond coat and substrate, has a detrimental effect on alumina scale adhesion [4-7]. Locus of failure in desk top spallation is predominantly the thermally grown (alumina) oxide (TGO) layer. Therefore the role of sulfur might also be of critical importance.

The Aim of this work is therefore to study the effects of water and SO_2 containing environments on delayed spallation and the lifetime of TBCs.

Experimental

System investigated:

Substrate	Bond coat	Top Coat
CM 247	**150 µm VPS NiCoCrAlY**	**250 µm APS Yttria Stabilized Zirconia (YSZ)**

Oxidation parameters:

- Isothermal oxidation at 1100 °C for up to 1200 h
- Atmospheres: Synthetic air, Synth. air & 10 Vol.% H_2O (dewpoint 46 °C), and
  Synth. air & 50 Vol.% H_2O (dewpoint 82 °C)

Results — Mechanical Properties

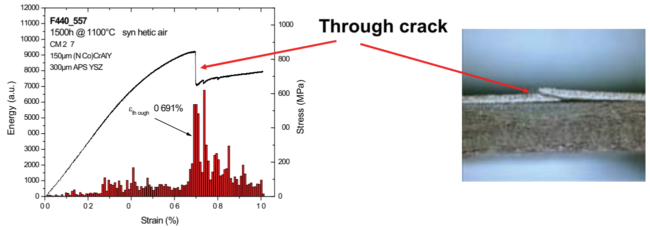

Figure 1
Acoustic emission during 4-point bend testing (at RT) of a pre-oxidized TBC specimen. The drop in the stress curve and the peak in acoustic emission indicate where through cracking of the top coating occurs.

The mechanical properties were investigated with 4 point bend testing at room temperature as a function of exposure time and environment. A typical example of the stress/strain curve and acoustic emission signals is given in figure 1. The drop in the stress/strain curve and the peak in the acoustic emission indicate where failure (i.e. through cracking) of the top coating occurs.

The critical strain for through cracking is given as a function of exposure time and environment in figure 2. The specimens that were pre-oxidized in humid environment show a tendency towards slightly lower critical strain values.

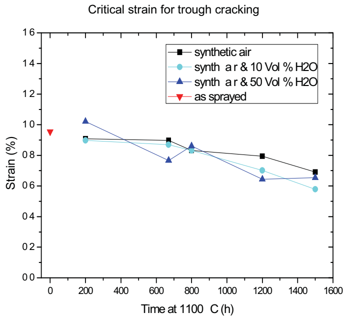

Figure 2
The critical strain for through cracking as a function of exposure time and exposure environment.

Results — Delayed Failure in humid environment

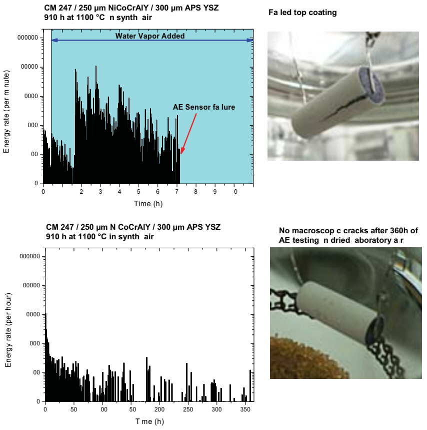

Figure 3
Acoustic Emission of two identical pre-oxidized samples in humid environment (top) and dried air (bottom). The sample in humid environment showed top coat spallation after less than 7 hours, whereas the sample in dried air remained intact for 360 hours.

As the desktop effect occurs at room temperature and one hypothesis is that humidity from the office environment plays a role, the influence of water vapor on (pre-oxidized) cold samples was investigated Two samples were pre-oxidized for 910h at 1100°C and rapidly cooled to room temperature within 20 minutes. Subsequently, the samples were connected to acoustic emission sensors and put into hermetically sealed crucibles. One crucible was filled with water vapor, the other contained molecular sieve pellets to create a dry atmosphere. As can be seen in figure 4 the sample in the humid environment spalled catastrophically, whereas the sample in dry air remained intact even after 360 hours of monitoring.

Results — Hydrogen detection with PIGE

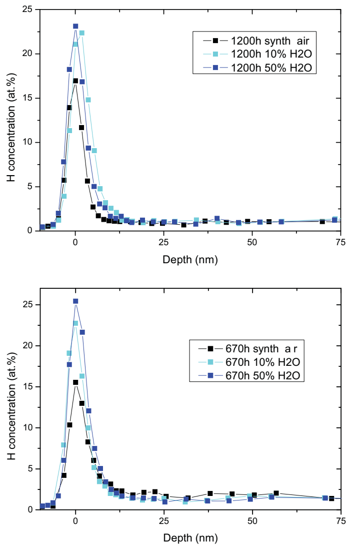

Figure 4
Hydrogen concentration depth profile of crack surfaces produced by in-vacuum forced spallation. A surface contamination peak is visible after isothermal oxidation in water-free and high water vapor atmospheres.

Hydrogen detection in the TBC system was performed by ion beam analysis using the nuclear reaction $^{1}H(^{15}N,\alpha\gamma)^{12}C$. First results verified the inward diffusion of hydrogen into the TBC after isothermal oxidation at 1100°C in water vapor environments [8]. Hydrogen analysis after top coat spallation under vacuum with a custom built vacuum chamber (SDIBA) revealed that even cracking under high vacuum conditions leads to a surface contamination peak in the hydrogen concentration depth profile (see figure 4). The hydrogen profile in a depth region >25nm showed similar amounts of hydrogen ~2 at.% independent of the exposure environment. Due to the unavoidable surface contamination no evidence of increased hydrogen could be found at the crack surface with this technique.

Conclusions

Mechanical 4 point bend testing revealed a tendency towards slightly decreased critical strains for through cracking for samples that were oxidized in humid environment. Delayed spallation was triggered in controlled experiments on APS sprayed TBC systems by room temperature exposures in humid environment. The acoustic emission revealed an increased cracking in humid environment and after only few hours of exposure the top coating spalled. On the contrary the specimen stored in dried air did not spall and acoustic emission was significantly lower. Hydrogen detection on vacuum-cracked surfaces was impossible to show hydrogen accumulation at the crack surface due to an unavoidable surface contamination peak.
Nevertheless, the results strengthen the hypothesis that hydrogen species (e.g. water molecules) weaken the mechanical strength of alumina oxide; and that water (i e. humidity) in conjunction with high mechanical stress in the oxide can lead to desk top spallation.

References

[1] V Sergo, D R Clarke, J Am Ceram Soc , 81 (1998) 3237-3242
[2] V Tolpygo, D R Clarke, Mater Sci Eng , A278 (2000) 142-161
[3] D Renusch, H Echsler, M Schütze, Mat High Temp , 21 (2004) 65-76
[4] J L Smialek, Metallurgical Transactions A 22A (1991) 739-752
[5] J L Smialek, Ceramic Engineering and Science Proceedings 23 (2002) 485-495
[6] J L Smialek, G N Morscher, Mater Sci Eng , A332 (2002) 11-24
[7] J L Smialek, Scripta Materialia 45 (2001) 1327-1333
[8] M Rudolphi, D Renusch, H -E Zschau, M Schütze, J Meijer, Poster KWI-Jahreskolloquium 2008