# The Role of Bond Coat Oxidation for the Life Time of Thermal Barrier Coatings

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### Deutsche Forschungsgemeinschaft

### Summary

The aim of this project is to develop a life time prediction model for the top coats of the air plasma sprayed thermal barrier coating systems (APS-TBC) for both isothermal and cyclic oxidation conditions. These coatings are made from yttria stabilized zirconia (YSZ) and are currently used to protect the superalloy components (i.e. blades and vanes) found in land based gas turbines and aero engines.

# 20mm

Fig. 1: A real turbine blade and smaller laboratory oxidation sample.

### Introduction

The increase of turbine inlet temperatures achieved by the use of thermal barrier coating systems has beneficial effects, like increased efficiency and reduced  $\mathrm{CO}_2$ -emission. This calls for a reliable life time prediction model. Such life time prediction models that can ensure inspection intervals in excess of for example 25000 hr in the case of land based gas turbines are still under development and research activities of all potential users are focused on the improvement of these life time prediction models.

Zirconia,  $ZrO_2$ , is known to be a fast oxygen-ion conductor at high temperatures. Consequently, oxidation of the underlying superalloy occurs, and a thermally grown oxide (TGO) film forms at the TBC/alloy interface. In an effort to provide corrosion resistance an aluminum-rich metallic coating (termed a bond coat) is applied to the superalloy prior to the deposition of the TBC top coat. During corrosion the oxidized bond coat produces a protective  $Al_2O_3$  TGO.

For the last 15 years the influence that the oxidation behavior has on spallation life time has been described by simply the thermally grown oxide (TGO) thickness (See NASA report CR 182230, 1989). This project has proven that the accuracy of spallation prediction models can be improved by taking a closer look at the phenomena of oxidation. Bond coat oxidation as well as bond coat depletion of AI are still believed to be the major degradation mechanisms with respect to the life time of thermal barrier coating systems. Additionally, the mechanical reliability of the partially yttria stabilized zirconia top coat has an influence on the spallation life time of the TBC system.

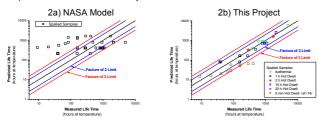


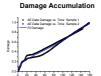
Fig 2: a) Accuracy assessment of the NASA life time model. b) Accuracy assessment of the life time model produced by this project.

In Fig. 2a is an accuracy assessment plot for top coat oxidation failure, where the predicated life times calculated from a NASA model are compared to the measured life times of laboratory oxidation samples. What is shown in this figure is that the predictions are really not very accurate. The red lines in the figure represent an accuracy of a factor of 3, which is considered by NASA to be a reasonable accuracy limit. There is a German research project funded by BMBF-BEO (Project Nr. 0327068E) in which KWI had participated, that had as a project goal a factor of two accuracy (the blue lines in Fig. 2). The criterion for oxidation failure, for this NASA model, is just the critical oxide thickness and whether the sample is thermally cycled is not taken into account. The data point plotted in Fig. 1a at 5000hr is from a sample that spalled after isothermal oxidation and actually failed because the bond coat had become depleted of the TGO forming element aluminum, where Al depletion is also not part of this NASA model. It has been argued that the accuracy of life time prediction models could be improved if the life time model took a closer look at the phenomena of oxidation, which is exactly what this project has done.

In Fig. 2b is the accuracy assessment of the life time model developed by this project. This model views spallation due to oxidation as a superposition of three mechanisms namely, thermal fatigue, thermal ageing, and bond coat depletion of aluminum, which is much more sophisticated than simply using a critical oxide thickness as a spallation criteria. The details of this modeling approach have been published and are in the project reports. In Fig. 2b it is clearly shown that this approach produces a more accurate result compared to Fig. 2a. The spalled samples produced by this project were isothermal and cyclically oxidized. The hot dwell times tested were 1, 2, 10, and 20 hr. The data points plotted in Fig. 2b with the 5min hot dwell were taken from the literature as an exercise and for the purpose of model verification. From the figure the model produced by this project makes qualitative life time predictions that match the life time reported in the literature. Ultimately, one would like to produce a life time model based on laboratory samples and laboratory data that could predict the life time of the in-service components.

### **Acoustic Emission During Oxidation**

The current study is using acoustic emission (AE) during oxidation of the TBC systems in order to assess the role of TGO and top coat micro-cracking. In order to quantify this micro-cracking a concept of damage accumulation is being used, which is defined as a function that varies from zero to one. When the damage accumulation function becomes equal to one the TBC top coat begins to spall. On the left side of Fig. 3 is plotted two sets of AE data and a line from a fitted damage accumulation equation. The right side of Fig. 3 represents a concept of residual life, which is equal to one minus the damage accumulation.



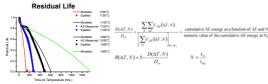


Fig. 3: Thermal cyclic oxidation with in-situ acoustic emission testing . Left Side: Modeled and measured damage accumulation. Right Side: Modeled and measured residual life.

### Acoustic Emission During Four Point Bending

A four point bend test that also uses acoustic emission is being used to measure the critical strains that produced macro-cracking in TBC top coats. In Fig. 4a is plotted the measured bending moment and the acoustic emission energy as a function of the TBC/bond coat interface strain for two samples that have been bent so that the TBC experiences compressive strains. Figs. 4b and 4c are edge wise photos of the resulting damage. What is observed is that at a strain of ~0.004 there is a sharp rise in the acoustic emission energy which is caused by the onset of delamination macro-cracking. For sample A the test was stopped at a strain of ~0.006 and the photograph (Fig. 4b) shows a large delamination crack near the TBC/bond coat interface. What has also been found is that at a strain level of ~0.0115 a second rise in the AE data shows the critical strain for through cracking.

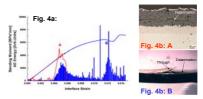


Fig. 4a: Plot of the compressive bending moment and acoustic emission energy as a function of the TBC/bond coat interface strain for two samples. 4b: and 4c: Edge-wise photos of the damage in samples A and B respectively.

### **Bond Coat Depletion of Al**

Bond coat depletion of Al is assumed to be caused by both the outward diffusion of Al into the TGO and inward diffusion of Al into the substrate. This behavior is currently being modeled by considering the average bond coat Al content after an exposure time and at a position within the bond coat and substrate. The modeled average distribution of Al within the bond coat and substrate for a sample oxidized at 1050°C is plotted in Fig. 5a. Eq. 1 was used to produce the curves. In order to use the Al depletion model for the purpose of determining when spallation will occur the Al depletion kinetics have to be calculated and compared to a critical Al concentration. This comparison is made in Fig. 5b.

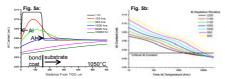


Fig. 5a: Modeled average AI distribution in the bond coat and substrate after high temperature oxidation. 5b: Modeled bond coat AI depletion kinetics for a point 10µm below the TGO for exposure temperatures 900 through 1200°C.

**Eq. 1**  $C(X, t_w, T) = \frac{C_{t_w}}{2} erf(\frac{X}{2\sqrt{D_{vin}(T)t_w}}) + (\frac{C_{t_w}}{2} + \frac{C_{vin}}{2}) erf(\frac{d_{t_w} - X - d_{t_w}}{2\sqrt{D_{vin}(T)t_w}}) + \frac{C_{vin}}{2}$ 

## **Discussion of Interacting Failure Mechanisms**

The ramifications that the observed results may have on top coat life time are schematically plotted in Fig. 6. What is considered here is the temperature dependence of the spallation life time. Here the "maximum potential top coat life time" is expected to be limited by the bond coat depletion of Al. For this type of failure it is expected that the life time is limited by the bond coat properties such as, the temperature dependent oxidation kinetics, the BC thickness, the BC Al content, the inter-diffusion of Al into the substrate etc. The dashed line labelled isothermal oxidation is based on samples that showed TBC thermal ageing failure. The degradation of the top coat under isothermal condition is likely to be caused by sintering of the YSZ and TGO growth. As depicted in Fig. 6 this failure mode has a different temperature dependence than the bond coat depletion failure mode. This is to be expected because the degradation of the top coat due to sintering, TGO growth and bond coat depletion of Al should have different kinetics. The dashed-dot line labelled cyclic oxidation is based on the spallation life times of samples that showed TBC thermal fatigue failure. The AE measurement data shows that the TGO and top coat suffers from cracking every time the sample is cooled during thermal cycling. The consequence of the repeated cracking is thermal fatigue and accelerated damage accumulation, which in turn causes the top coat life time to shorten. The driving force behind the thermal fatigue is mostly the thermal expansion mismatch stresses/strains, which will have a different temperature dependence than Al depletion at TBC thermal ageing mechanisms and is why the cyclic oxidation line has a different slope than the isothermal oxidation and BC depletion lines in Fig. 6. The solid line labeled burner rig is a modeled result. Here it is expected that the rapid cycle frequency of the burner rig, where the sample is cooled every 5 min, causes much more thermal fatigue than cyclic oxidation, which in turn produces a considerably shorter top coat life time.

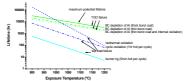


Fig. 6: Schematic of the temperature dependence of the spallation life time of APS TBC top coats. (a thick BC is 300µm, a thin BC is 150µm)