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Cracking in and around the thermally grown oxide in thermal barrier coatings: A comparison of isothermal and cyclic oxidation

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In the present paper the time and temperature dependent evolution of the microstructure of TBC systems and especially of post-experimentally determined physical defects in and around the TGO for both isothermal and cyclic exposure conditions are investigated. Specimens with APS- as well as with PVD-topcoats have been oxidised between 950 and 1100°C up to a maximum duration of 5000 h followed by extensive scanning electron microscopy and subsequent interactive image analysis to measure the maximum crack lengths in and around the TGO. These cracks are additionally classified with respect to their local orientation in the TGO or its vicinity. The results of isothermal and cyclic test conditions show a number of similarities in results e.g. an unsystematic occurrence of inwardly growing, "cauliflower like" oxide or the most frequently occurring type of cracks in APS systems. Nevertheless substantial differences concerning the final failure, microstructure, crack growth behaviour and finally life time of the component between isothermal and cyclic test conditions exist. Some indications were found, that for this particular bond coat occurance of inwardly growing oxide intrusions increases the adherence of the TGO. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

To lower their temperature, front stage blades and vanes of land based gas turbines or aero engines are nowadays covered by a ceramic thermal barrier coating (TBC) of partially yttria stabilised zirconia (P-YSZ). The ceramic coating is applied to an oxidation resistant bond coat (BC), frequently a vacuum plasma sprayed coating of the NiCoCrAlY-type. The life time of such TBC systems is limited by the mechanical integrity of the ceramic P-YSZ topcoat as well as that of the thermally grown oxide (TGO), which forms during high temperature service on the BC surface. Especially the TGO is believed to play a major role with respect to the life time of the TBC [1, 2]. cal defects for the mechanical aspects of damage or failure of thermally grown oxide scales is summarised in [6].

In the present Paper such a fracture mechanics approach is picked up and applied to complete TBC systems. Maximum (micro-) crack length values within and near the TGO that may serve as input data for new modelling approaches are measured and additionally classified with respect to the local orientation in and around the TGO.

2. Experimental

The specimens (Fig. 1) consisted of cylindrical rods of a ⟨001⟩-oriented single crystal Ni-based superalloy

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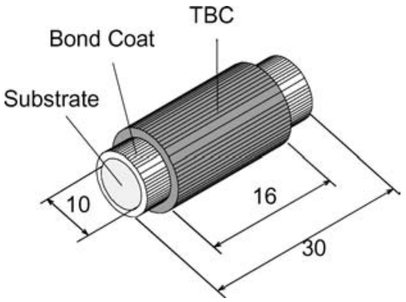

Figure 1 Schematic illustration of used test specimen (all dimensions in mm).

(CMSX-4) with a diameter of 10 mm. The rods were first completely coated via VPS-spraying with a 150 μm thick NiCoCrAlY bond coat. Subsequently, they were partly covered over a length of ca. 15 mm, either by APS or EB-PVD, with a 150 or 300 μm thick TBC of zirconia, stabilised with 7–8 wt.% yttria. Specimens, 30 mm in length were then cut from the rods. The used bond coat was a commercially available NiCoCrAlY-type coating with 12 wt.% Al and minor additions of Y and Hf.

Isothermal and cyclic exposure tests were carried out at 950, 1000, 1050 and 1100°C up to 5000 h in resistance heated furnaces for both types of TBC coated specimens. Each cycle during cyclic testing consisted of 2 h at maximum temperature and 15 min forced air-cooling to room temperature. In case of a maximum temperature of 1000°C this temperature is reached at the metal/ceramic interface within approximately 4 min, cooling down to room temperature (less than 30°C) also needs around 4 min. Details of the cyclic testing method were presented in [2]. The specimens oxidised isothermally were removed from the hot furnace and simply air-cooled. Here it must be kept in mind that for every exposure duration a single specimen was used so that every isothermally oxidised specimen experienced only one single heating and cooling step.

For the isothermally oxidised specimens postexperimental metallographic investigations were carried out after exposure periods of 100, 300, 1000, 3000 h and, for lower temperatures additionally, after 5000 h. Cyclically oxidised specimens were examined after 100, 300, 1000 and 3000 h or after failure occurred. The specimens were mounted in a low viscosity, two-component epoxy resin and then cut transversally and in some cases longitudinally. Preparation of the cross sections was carried out on an automatic grinding and polishing machine and details of the procedure are described in [7]. In order to characterise the microstructure of the TBC systems, the specimens were examined by using both light optical (LOM) and scanning electron microscopy (SEM). The determination of the maximum length and the local orientation of (micro-) cracks in the TGO and its vicinity, as illustrated in Fig. 2, were carried out using an interactive semi-automatic image analysis software package.

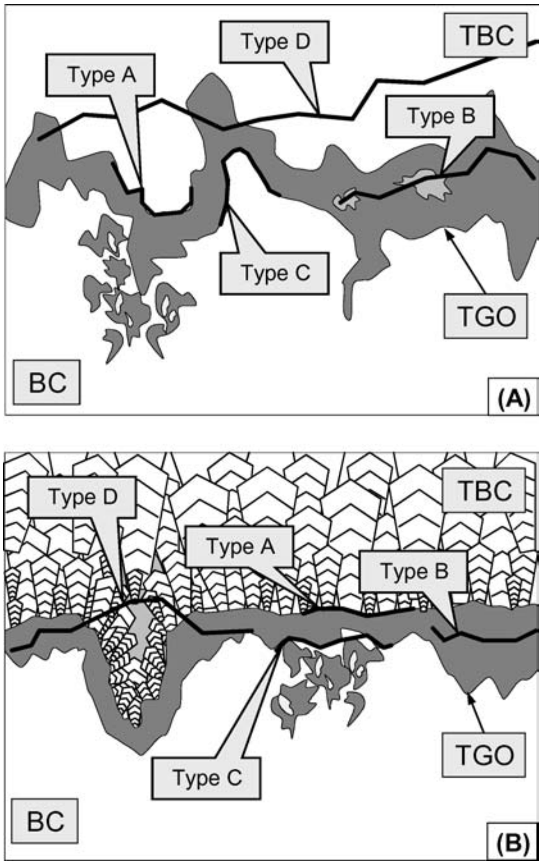

Figure 2 Schematic illustration defining various types of cracks in the TGO and its vicinity, (A): APS-system, (B): EB-PVD-system.

3. Results and discussion

In the following the results obtained during the isothermal oxidation tests will be discussed first.

Even without the superposition of repeated cyclic (thermal fatigue) loading TBC systems fail after a sufficiently long time at high temperature by spallation of the ceramic topcoat due to the oxidation of the bond coat. In the present study a temperature of 1050°C or higher was necessary to produce failure of the specimens within the maximum isothermal exposure time of 5000 h. Prior to final failure, damage in form of (micro-) cracking in the vicinity of the TGO can be observed in the metallographic cross sections. All these cracks are oriented parallel to the macroscopic BC/TGO/TBC interfaces and seem to start ($t < 300$ h) in the TGO or at its interface with the BC. For longer exposure times ($t > 300$ h) the longest cracks in case of APS topcoats were either located within the TGO (type B cracks) as given exemplarily in Fig. 3, or start in the TGO and subsequently penetrate into the ceramic topcoat (type D) (Fig. 4). For PVD coatings the cracks after exposure times of $t > 300$ h were mainly of type B (Fig. 5) and type C (Fig. 6). The latter means that these cracks are located at the BC/TGO interface and may cut inwardly growing oxide intrusions. In some cases shorter type A cracks can be observed in the vicinity of areas with a non-ideal bond coat surface

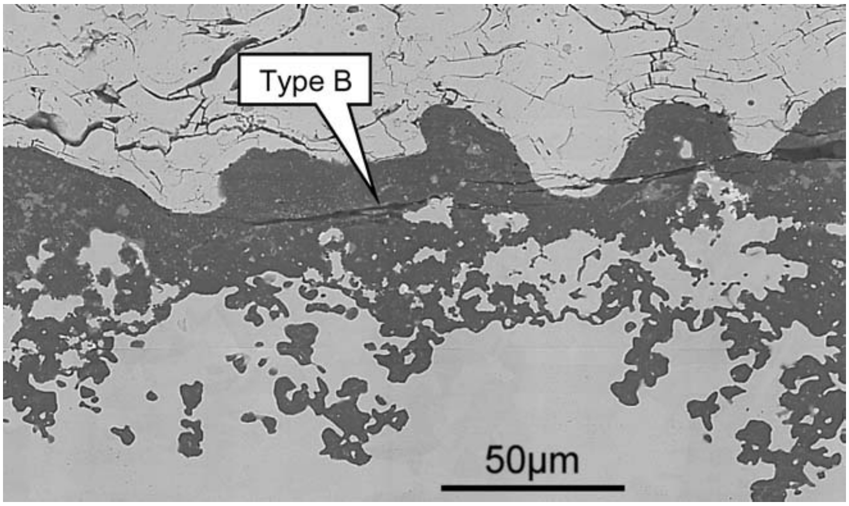

Figure 3 SEM-micrograph of a typical type B crack in APS specimen after isothermal exposure (1050°C, 3000 h).

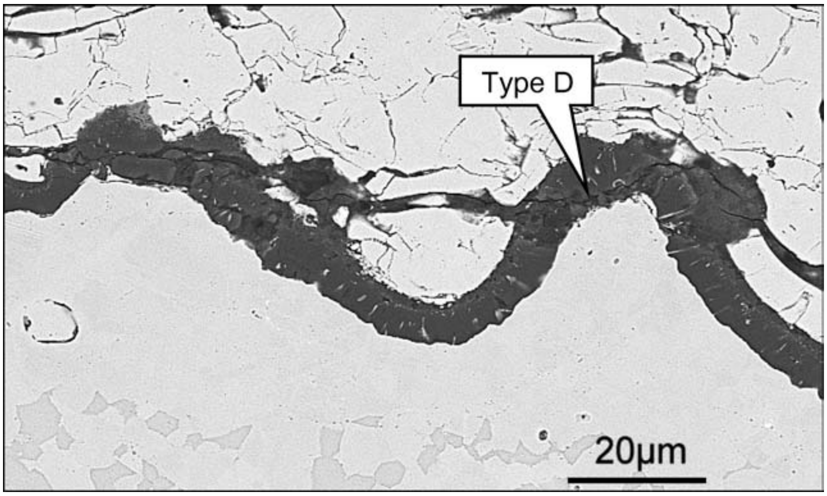

Figure 4 SEM-micrograph of a typical type D crack in APS specimen after isothermal exposure (1100°C, 300 h).

finishing. In all cases the measured crack length values increase with increasing temperature.

The specimens show a large variation in oxidation behaviour with respect to an inwardly growing "cauliflower like" oxide and, as a result, aluminium depletion indicated by the thickness of a β-phase depleted zone in the BC underneath the TGO. This behaviour was independent of the exposure temperature. Specimens showing mainly type B cracking, APS- as well as PVD-samples, have thicker TGO's and exhibit more severe attack by inwardly growing oxide. Most of the failed specimens (5 out of 6) show hardly any internally growing "caulyflower like" oxide but a "perfectly" appearing thin alumina scale. Details of all results obtained for the isothermally tested samples are given in [5, 8, 9].

After the cyclic oxidation tests a number of similarities with the observations after isothermal exposure can be found. Again, a large variation in the oxidation behaviour with respect to the amount of inwardly growing "cauliflower like" oxide (even on one sample) is visible. For APS-samples the longest cracks, as in case of the isothermal exposures, are of type B (Fig. 7) and type D (Fig. 8) whereby the latter seem to be relevant for initiation of the final TBC failure. For both exposure conditions the cracks prior to final failure in PVD systems are longer than those in the APS systems and other oxides than alumina, e.g. Cr_2O_3 or Ni- or Co-rich spinels, are more frequently observed in PVD systems. These other oxides are often found in the vicinity of areas of non-ideal bond coat surface finishing prior to top coating where the smoothening process of the originally rough surface was not satisfactory and locally a higher surface roughness remained (Fig. 9). In all studied cases PVD-systems failed at the BC/TGO interface.

The most remarkable differences of the crack formation and propagation during cyclic and isothermal exposure of APS systems are:

- During cyclic oxidation final failure appears by (macro-) delamination cracking starting from the

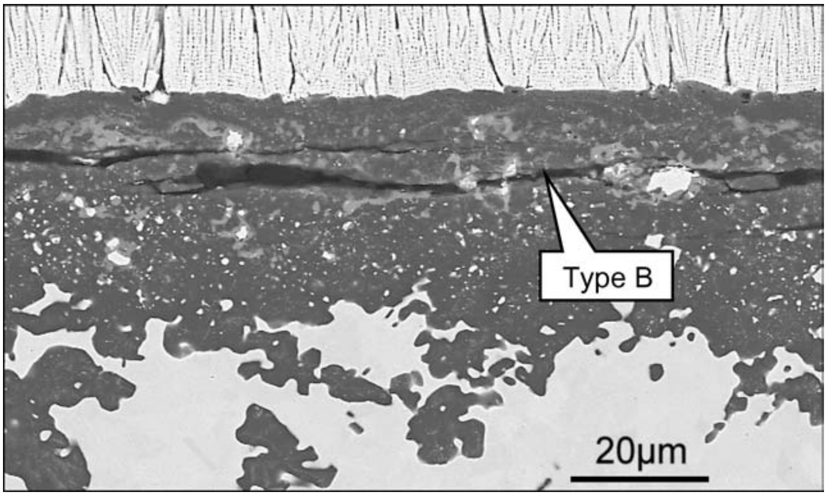

Figure 5 SEM-micrograph of a typical type B crack in PVD specimen after isothermal exposure (1000°C, 3000 h).

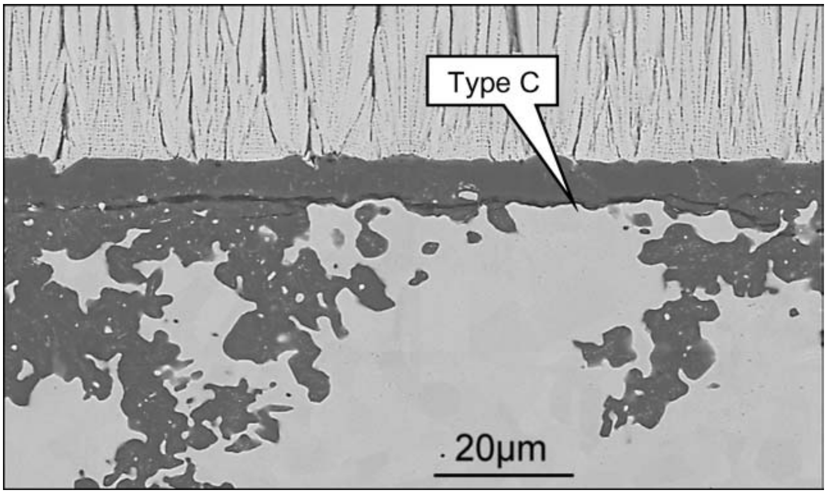

Figure 6 SEM-micrograph of a typical type C crack in PVD specimen after isothermal exposure (1050°C, 1000 h).

edges of the ceramic segment but large areas of the TBC are still adherent (Fig. 10). During isothermal treatment failure occurred by total spallation of the ceramic topcoat (Fig. 11).

- Cycling produces considerably longer type A cracks (Fig. 12) than occuring after isothermal oxidation. These type A cracks are located in the valleys of the BC roughness profile and seem to disappear for long exposure times ($t > 300$ h). Such type A cracks for the same coating system were also reported in case of isothermal LCF tests in Ref. [10] and TMF tests in Ref. [11], respectively.
- Cycled APS specimens show type C cracks (Fig. 13) at the apices of the BC roughness profile, especially during the 1050°C-exposure, and in areas with hardly any "cauliflower" type inwardly growing oxide.

For PVD specimens the differences imparted by cyclic and isothermal exposure are not as obvious as in the case of the APS-coatings:

- During cyclic exposure for times as short as 100 h mainly type B cracks are visible (Fig. 14) as observed during the isothermal tests. However, with increasing time these cracks seem to vanish towards the TBC/TGO interface (Fig. 15) and hence have in fact to be classified as type A cracks. At present it is not clear whether the latter are older ones and the vanishing is only an optical misinterpretation due to the inward growth direction of the TGO or whether these cracks are new ones, which are really formed slightly closer to the interface.
- During longer cyclic exposure times ($t > 1000$ h) new cracks are being formed, which are undoubtly type A cracks (Fig. 16). For PVD samples those type A cracks were also reported in Ref. [10, 11].
- Type C cracks in macroscopically intact specimens are less dominant than in case of the isothermal exposure (Fig. 17).

For both APS- and the PVD-coatings the following observations are valid:

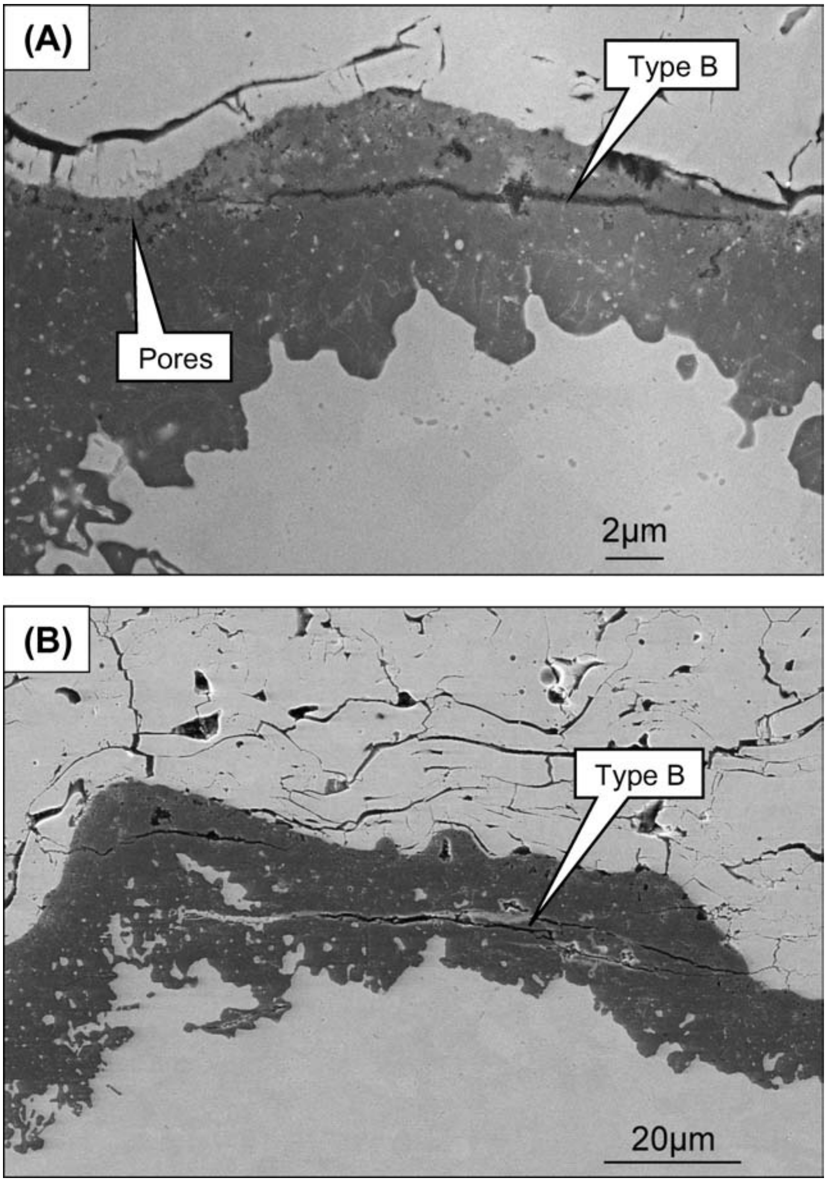

Figure 7 SEM-micrographs of typical type B crack in APS specimen after cyclic exposure (1000°C, 300 h).

- The life time of cycled TBC's is nearly in all cases (4 specimens out of 5) shorter than that of isothermally exposed specimens (Tables I and Tables II). For instance, at 1000°C for the APS-coating t_{fail}=1728 h compared to $t_{\mathrm{fail}} > 5000$ h for isothermal exposure. It should, however, be borne in mind that a comparison of the exact life times under isothermal and cyclic conditions is strictly spoken not possible. The measured life time under isothermal conditions is subjected to an "error bar" determined by the actualz life time and the exposure duration for the last intact specimen and the duration for the first failed one. In other words, the life time can per definition be only e.g. 300, 1000, 3000 or 5000 h, whereas during cyclic oxidation the failure can be detected after every 24 h of cycling.
- Cyclic exposure conditions in general produce longer cracks than isothermal exposure (Fig. 18). The longest cracks of macroscopically intact specimens after cyclic exposure are 3 times longer than those observed after isothermal treatment.
- During cycling more pronounced porosity is visible in the outer part of the TGO compared to isothermal exposure conditions (Figs 7a, 13 and 17).
- Samples forming a "perfectly" looking thin alumina scale show longer cracks than those exhibiting a certain amount of internally growing oxide.

Due to the various numbers of parameters (e.g. temperature, time at temperature, different types of topcoats and different exposure conditions) and different mechanisms like the non-uniform oxidation behaviour, a discussion of the results of the crack length measurements appears to be difficult. The following equation introduced by Schütze [6], which describes the onset or extension of interfacial damage or cracking by a critical compressive strain of

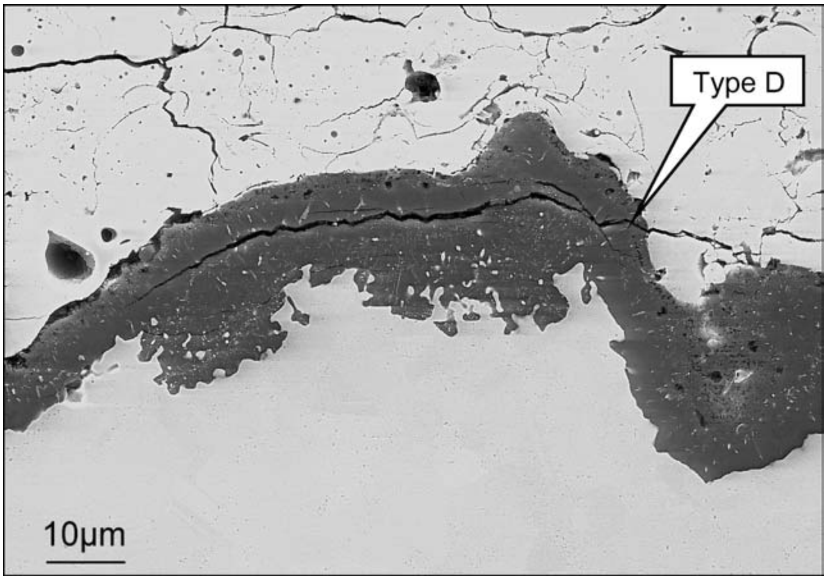

Figure 8 SEM-micrograph of a typical type D crack in APS specimen after cyclic exposure (1050°C, 1000 h).

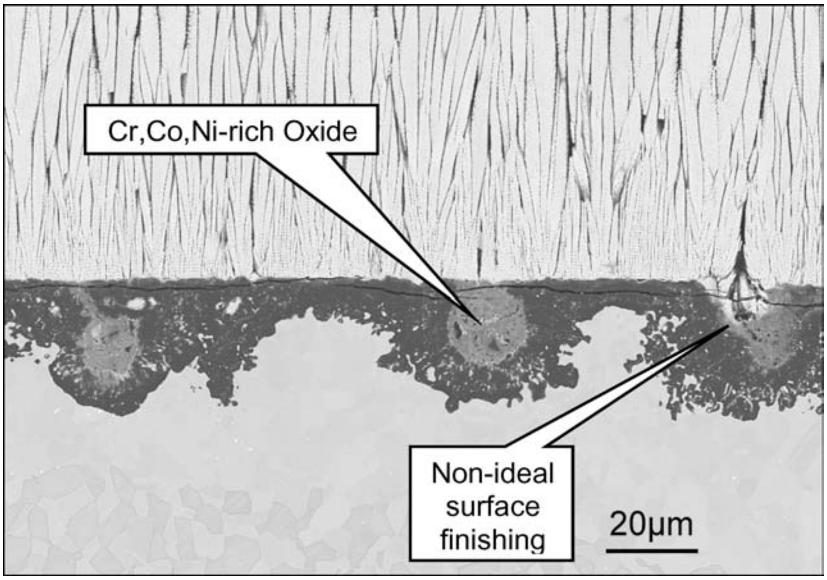

Figure 9 SEM-micrograph showing typical example of Cr, Ni and/or Co-rich oxides in case of a PVD-coated specimen (1000°C, 1000 h).

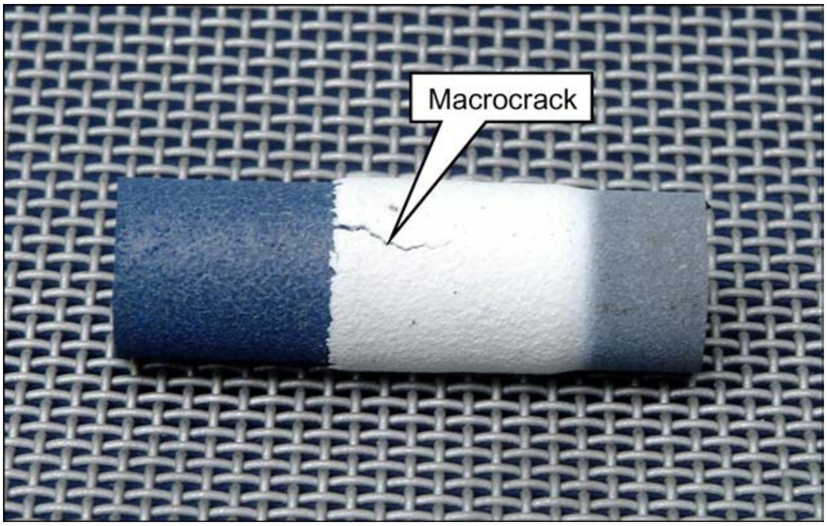

Figure 10 Macrograph of typical final failure of APS specimen after cyclic exposure (1050°C, 936 h).

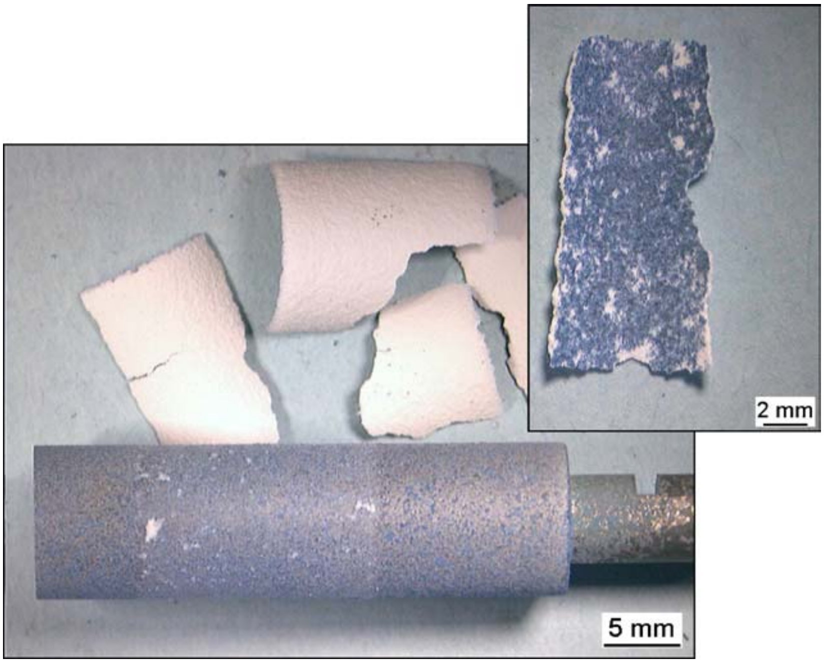

Figure 11 Macrograph of typical final failure of APS-specimen after isothermal exposure (1100°C, 1000 h).

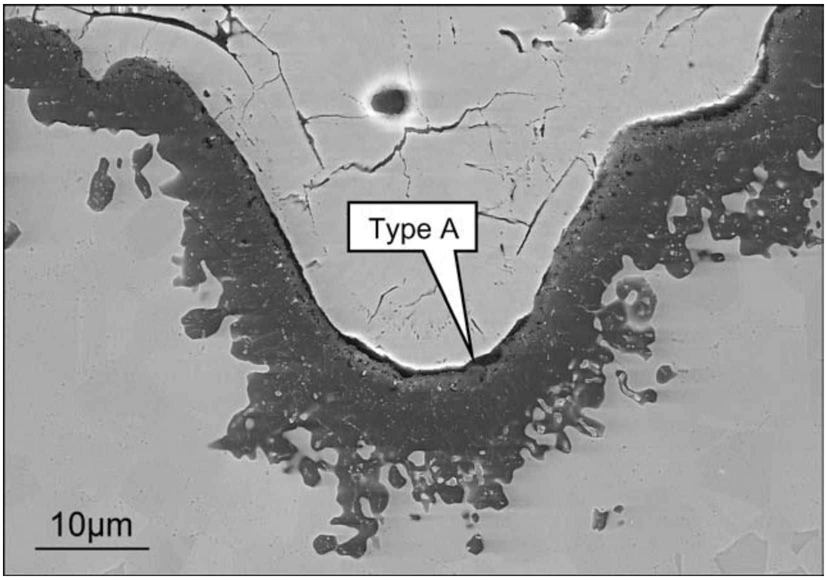

Figure 12 SEM-micrograph of a typical type A crack in APS specimen after cyclic exposure (1050°C, 300 h).

an oxide scale on a metallic material during cooling may serve as a starting point:

$$\varepsilon_{\text{tot}} \geq \varepsilon_{\text{c}} = \frac{K_{\text{Ic}}}{f \cdot E_{\text{ox}} \cdot \sqrt{\pi \cdot c}} \cdot \frac{(1 + r/d_{\text{ox}}) \cdot (1 + \nu_{\text{ox}})}{2} \qquad (1)$$

Here K_{Ic} denotes either the fracture toughness of the oxide/metal interface or the in-plane fracture toughness of the oxide scale, ε_{c} the critical strain for occurance of scale failure, E_{ox} the Young's modulus of the oxide, r the amplitude of the interfacial roughness, d_{ox} the oxide scale thickness, ν_{ox} the Poisson's ratio of the oxide, f a geometrical factor and c is half of the length of an embedded defect or the whole length of an interfacial defect. Strictly spoken this equation is only valid for a composite with a wavy interface as in the case of APS-coated systems but also the PVD-specimens show a certain interface roughness, although it is obviously smaller than in case of APS-systems. Cracking or damage of the scale occurs when the driving force in combination with the previously existing (micro-) defects exceeds the materials specific resistance against damaging. Hence, three different time dependent evolution paths, namely for K_{Ic}, c and ε_{tot}, exist that determine the damage behaviour in the respective area of the system.

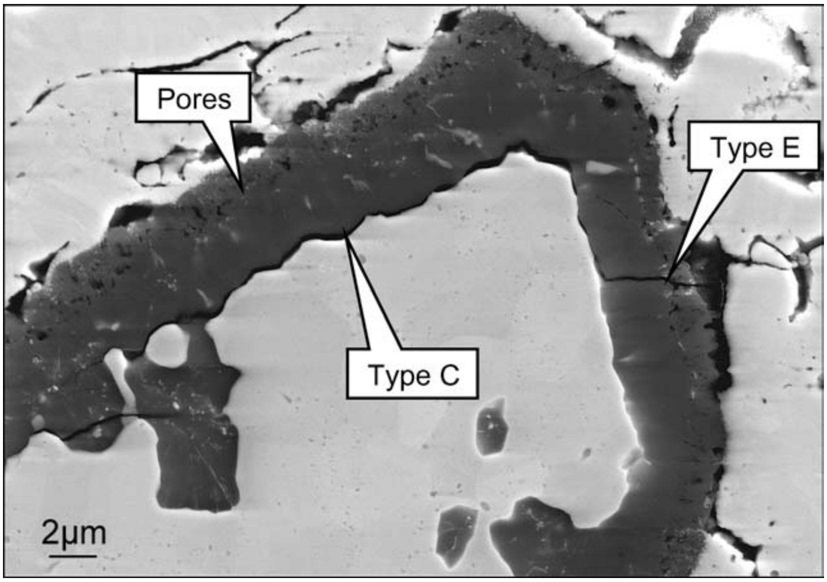

Figure 13 SEM-micrograph of a typical type C crack in APS specimen after cyclic exposure (1050°C, 300 h).

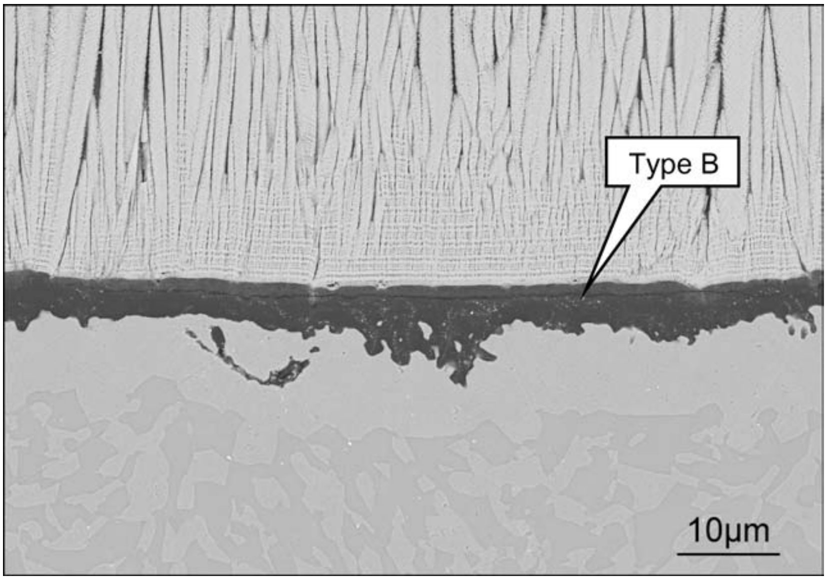

Figure 14 SEM-micrograph of a typical type B crack in PVD specimen after cyclic exposure (1000°C, 100 h).

First, a clear distinction between specimens with and without severe inwardly growing "cauliflower like" oxidation has to be made, because the oxide morphology apparently determines the dominant location of the cracks. With increasing internal oxidation attack the dominant type of cracks in the APS-systems changes from type D to type B for cyclically (Figs 7 and 13) as well as for isothermally oxidised specimens (Figs 3 and 4). At the same time the apparent interface roughness is decreased by the "cauliflower like" type of oxidation. According to Equation 1 a decrease of the roughness amplitude r reduces the critical strain for occurrence of damage ε_c. Furthermore, after sufficiently long exposure time the "cauliflower like" oxidation is accompanied by the formation of faster growing oxides containing Cr,Ni and/or Co within the pre-existing thick alumina scale. This likely may result in a reduction of the in-plane fracture toughness K_{Ic} of the oxide in Equation (1) by changing from a value for alumina to a value for the apparent oxide mixture. On the other hand type D cracks were more frequently observed after cooling from the highest testing temperatures (1050°C or 1100°C). The high temperatures increase the thermally induced strains or in other words the driving force for damage compared to lower temperatures where type B cracks are dominant. Sintering and hence stiffening effects of the TBC that result in an increase of the stored

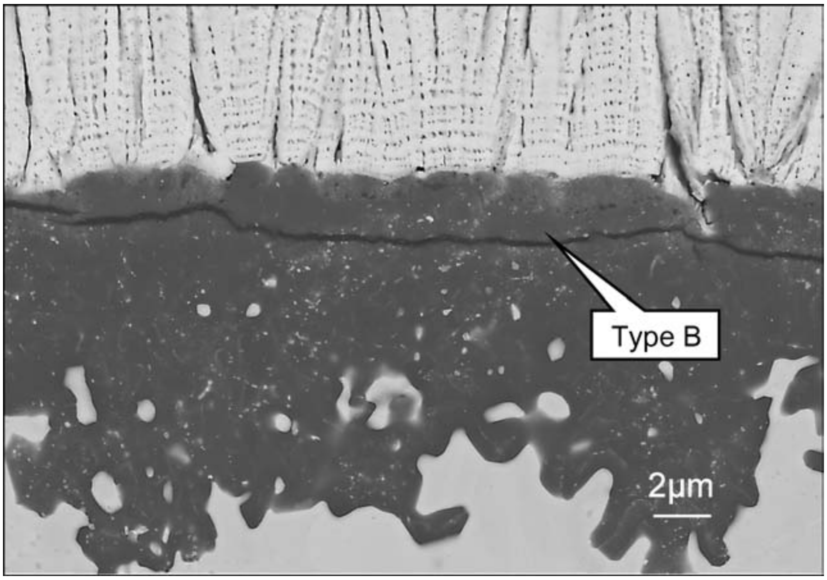

Figure 15 SEM-micrograph of a type B crack in the outer part of the TGO in PVD specimen after cyclic exposure (1050°C, 300 h).

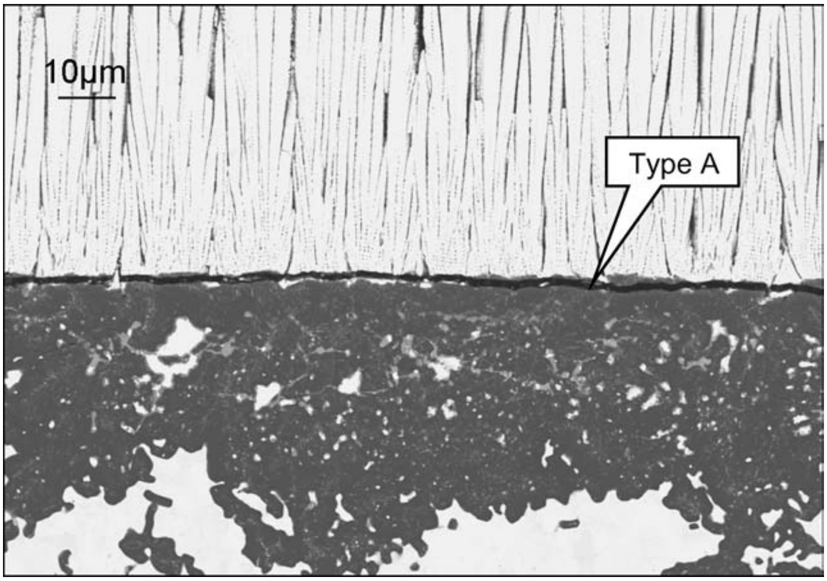

Figure 16 SEM-micrograph of a typical type A crack in PVD specimen after cyclic exposure (1000°C, 3000 h).

energy density in the TBC itself may also play a role at these higher temperatures. Cracks originally formed in the TGO can no longer be stopped at the TGO/TBC interface.

Also for PVD-systems the crack location vanishes from the BC/TGO interface towards the inside of the TGO with increasing extent of the "cauliflower like" oxidation. Even type A cracks at the TGO/TBC interface can be observed in the case of cycled PVD-specimens. Here, the BC/TGO interface, which is initially the weakest point of the TBC/BC interface region, is strengthened by the formation of inwardly growing oxide resulting in an increase of the interfacial roughness r in Equation (1) and hence an increase of the critical compressive strain. A possible counteracting reduction of the in-plane K_{Ic} value of the alumina by the formation of an oxide mixture seems to be less dominant. The occurrence of type A cracks and the significance for TBC failure in cycled PVD-specimens is at present not fully understood. However, the observed occurance of type A cracks, and the fact that all macroscopically failed PVD-specimens regardless of the exposure conditions show failure at the BC/TGO interface and hardly any inwardly growing oxide intrusions, again supports the beneficial effect of the "cauliflower like" oxidation on the interfacial fracture toughness for this particular TBC-system.

In any case macroscopically intact specimens after cyclic exposure show longer cracks than specimens after

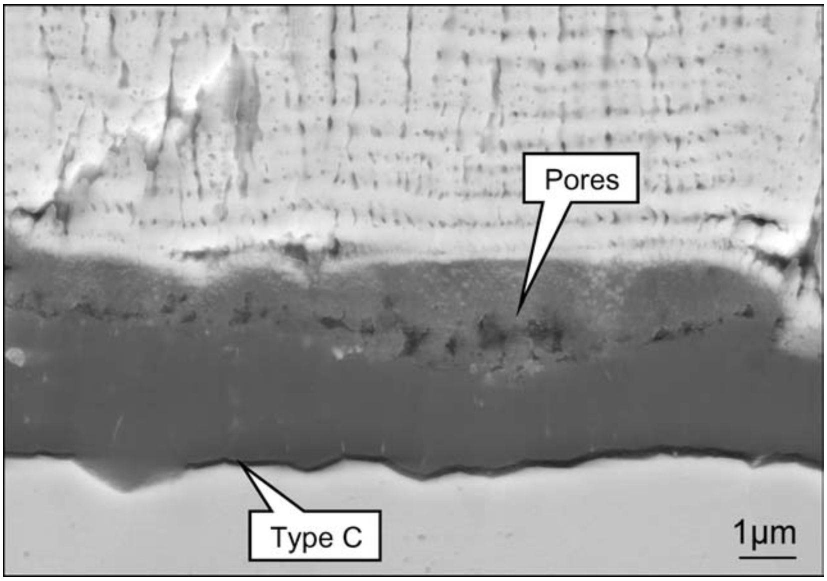

Figure 17 SEM-micrograph of a typical type C crack in PVD specimen after cyclic exposure (1000°C, 300 h).

isothermal exposure. Besides all the above mentioned that can be summarised as chemically weakening of the system with time there clearly exists a superposition of fatigue effects for the cycled specimens. Particular for the PVD-specimens showing a very thick and heterogenious TGO some indication exists that after similar oxidation time isothermal treatment produces shorter but a larger number of cracks than thermal cycling. A possible mechanism for the multiple crack formation in isothermally treated specimens may be the fact that they suffer only one cooling step where crack initiation and extension can occur. Due to the statistical character of the crack initiation, the stress relieve apparently occurs by the initiation of a large number of small cracks within the TGO and/or its vicinity. During cycling this multiple crack formation will always start during the very first cooling step. Due to the repeated thermocycling one particular crack, depending on location or orientation may grow with exposure time with each following cycle, respectively. This would thus result in fewer but longer cracks than observed during isothermal exposure.

TABLE I Test (failure) matrix of the isothermally oxidised specimens

	100 h	300 h	1000 h	3000 h	5000 h
950°C					
APS-150					
APS-300		I	I	I	I
PVD-150		I	I		I
PVD-300					
1000°C					
APS-150					
APS-300	I	I	I	I	I
PVD-150	I	I	I	I	I
PVD-300	I	I	I	I	I
1050°C					
APS-150					
APS-300	I	I	I	I	Failure
PVD-150	I	Failure	Failure	Failure	
PVD-300	I	I	I	I	
1100°C					
APS-150	I	I	Failure		
APS-300			Failure		
PVD-150					
PVD-300					

Numbers in second column (150 or 300) indicate TBC thickness in μm. Empty = not investigated, I = Intact, without macroscopic failure, Failure = Delamination of the topcoat.

TABLE II Test (failure) matrix of the cyclically oxidised specimens

	100 h	300 h	1000 h	3000 h	Failure
950°C					
APS-150					
APS-300					
PVD-150					
PVD-300					
1000°C					
APS-150	I	I	I	I	
APS-300	I	I	I		1728 h
PVD-150	I	I	I	I	
PVD-300	I	I	I	I	
1050°C					
APS-150					
APS-300	I	I	I		936 h
PVD-150					
PVD-300	I	I			288 h
1100°C					
APS-150					
APS-300	I				288 h
PVD-150					
PVD-300	I				612 h

Numbers in second column (150 or 300) indicate TBC thickness in μm. Empty = not investigated, I = Intact, without macroscopic failure, Number = Estimated life time with an error bar of max. 24 h.

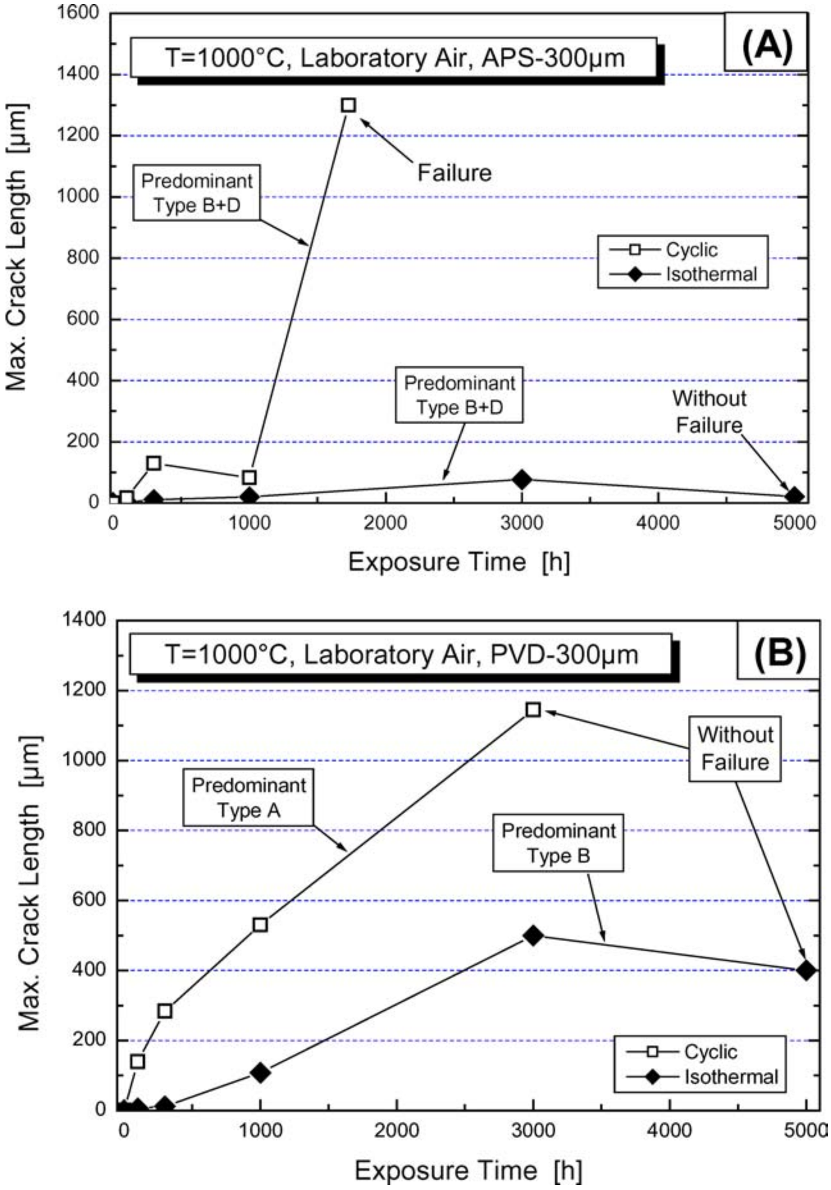

Figure 18 Maximum crack length data measured after various exposure times during isothermal and cyclic oxidation at 1000°C, (A): APS-system, (B): PVD-system.

4. Summary and conclusions

Fracture mechanical approaches can be useful for the further improvement of life time prediction models of TBC coatings and the presented cracks lengths in and/or in the vicinity of the TGO can serve as input data for modelling approaches. The present investigations show a number of similarities in respect to crack formation and growth occuring during isothermal and cyclic oxidation tests. Both types of testing exhibit unsystematic occurrence of inwardly growing, "cauliflower like" oxide. The most frequently occurring type of cracks in APS systems is practically independent of the type of exposure. Nevertheless, substantial differences concerning the final failure, oxide microstructure, crack growth behaviour and, finally life time of the component between isothermal and cyclic test conditions exist. A clear separation of the cycling effect appeared to be difficult because the investigated NiCoCrAlY-BC shows large variations in its oxidation behaviour and the apparent oxide microstructure. Indications were found, that presence of inwardly growing oxide intrusions hampers rapid crack propagation at the TGO/BC interface, frequently observed as major failure cause, especially in PVD coating systems.

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