Effect of Water Vapor on the Spallation of Thermal Barrier Coating Systems During Laboratory Cyclic Oxidation Testing

V. Déneux · Y. Cadoret · S. Hervier · D. Monceau

Abstract The effect of water and water vapor on the lifetime of Ni-based superalloy samples coated with a typical thermal barrier coating system—β-(Ni,Pt)Al bond coat and yttria stabilized zirconia (YSZ) top coat deposited by electron beam physical vapor deposition (EB-PVD) was studied. Samples were thermally cycled to 1,150 °C and subjected to a water-drop test in order to elucidate the effect of water vapor on thermal barrier coating (TBC) spallation. It was shown that the addition of water promotes spallation of TBC samples after a given number of cycles at 1,150 °C. This threshold was found to be equal to 170 cycles for the present system. Systems based on β-NiAl bond coat or on Pt-rich γ/γ' bond coat were also sensitive to the water-drop test. Moreover, it was shown that water vapor in ambient air after minutes or hours at room temperature, promotes also TBC spallation once the critical number of cycles has been reached. This desktop spalling (DTS) can be prevented by locking up the cycled samples in a dry atmosphere box. These results for TBC systems confirm and document Smialek's theory about DTS and moisture induced delayed spalling (MIDS) being the same phenomenon. Finally, the mechanisms implying hydrogen embrittlement or surface tension modifications are discussed.

Keywords Thermal barrier coating · Water vapor · TBC spallation · Hydrogen embrittlement · Bond coat · Cyclic oxidation test · Thermally grown oxide

V. Déneux · Y. Cadoret · S. Hervier
SNECMA, Groupe SAFRAN, Site de Villaroche, Rond point René Ravaud, Moissy-Cramayel, France

D. Monceau (✉)
CNRS, Institut Carnot CIRIMAT, ENSIACET, 31077 Toulouse Cedex 4, France
e-mail: daniel.monceau@ensiacet.fr

Introduction

Thermal barrier coating (TBC) systems deposited on high-temperature blades in gas turbine applications are of high technological interest since they allow a higher combustion temperature. TBCs are known to fail because of a number of contributing factors such as stresses due to thermal expansion mismatch in this multilayered system upon cycling, stress concentration due to thermally grown oxide scales, impurities such as sulfur interfacial segregation leading to interfacial failure between the scale and the bond coat [1].

Moisture induced delayed spallation (MIDS) and desk top spallation (DTS) are modes of failure that may be very detrimental to the lifetime of alumina scale formers subjected to thermal cycling. Nevertheless, little data are available on TBC systems, and this cause of failure is generally not discussed in review articles about TBC life (e.g., [1]). Smialek proposed that MIDS and DTS have the same origin [2]. Moreover, it was shown that the amount of scale spallation increased when water vapor is added in the air of a testing furnace [3]. Hydrogen embrittlement due to the presence of water vapor is considered by many to be the root cause of the degradation [2, 4, 5]. The aim of this study is first to confirm the detrimental effect of water vapor on TBC spallation. Then experiments will be performed to determine if there is a critical threshold above which TBC systems are particularly sensitive to the water effect. The effects of water and of ambient air water vapor are compared. Finally, the mechanisms which can lead to this typical mode of failure are discussed.

Experimental Procedures

Materials

Experiments were conducted on disc-shaped samples 25 mm in diameter and 2 mm thick. They were composed of β-(Ni,Pt)Al bond coats grown on low sulfur (less than 0.5 wt ppm S) AM1 Ni-based superalloy single crystal substrates. The aluminide bond coats were processed in two steps. First, a layer of several micrometers of Pt was deposited. Secondly, the samples were aluminized by a low activity chemical vapor deposition process. This led to the formation of a single-phased β-(Ni,Pt)Al bond coat, whose thickness was close to 60 μm. The top coats of yttria stabilized zirconia (YSZ) were deposited using electron beam physical vapor deposition (EB-PVD). The top coat thickness was about 150 μm and this ceramic layer consisted of a standard EB-PVD columnar structure.

Experiments

Samples were subjected to thermal cycling in laboratory air in an automated rig at SNECMA laboratory. Each cycle consisted of a 15 min heat-up to 1,150 °C, a 45 min hold at 1,150 °C, and then a 15 min forced-air cooling to 80 °C.

Three experiments were performed:

(i) A set of 5 samples were oxidized at 1,150 °C for 200 cycles to exhibit the effect of water on TBC spallation. After thermal cycling, samples were cooled to room temperature and removed from the furnace. They were finally "water-drop tested". This operation consisted of applying a water-drop of 250 μL to the specimen surface as soon as specimens were cooled to room temperature. Sample spallation was recorded using a video camera.

(ii) A set of 15 samples was oxidized at 1,150 °C to determine if there was a threshold of thermal exposure from which TBC systems were systematically sensitive to water. Five cyclic exposure times were tested: 75 cycles, 160 cycles, 185 cycles, 225 cycles and 360 cycles at 1,150 °C (3 specimens for each duration). After each given number of cycles, samples were cooled to room temperature, removed from the furnace and immediately water-drop tested.

(iii) Finally, the influence of water vapor in the laboratory air at ambient temperature was tested. To do so, an original experiment was set up: 6 samples were oxidized for 200 thermal cycles at 1,150 °C, which exceeded the threshold over which water-drop produces early TBC spallation. After cooling to room temperature, specimens were subjected to three different atmospheres:

- two samples were *water-drop* tested;
- two samples were locked in a hermetically sealed box containing *ambient air*;
- two samples were put in another hermetically sealed box containing *dry air* during 48 h, and then placed out of the box for further observations.

Dry air was obtained by using a purge gas generator system from Balston[TM].

Microstructural Analysis

Samples surfaces and cross-sections were examined using a Philips XL40 FEG scanning electron microscope (SEM) operating at 15 kV.

Results

First Experiment: Water-Drop Effect on the TBC Resistance to Thermal Cycling

The first experiment was conducted to confirm the water effect on TBC spallation. After a high number of thermal cycles ($\sim$200 cycles) at 1,150 °C, five samples showed no spallation when cooling to room temperature. When a water-drop is placed on the ceramic top coat, spallation of the EB-PVD layer was systematically observed for the five samples after less than 1 min at room temperature. Figure 1 presents video sequences showing a complete delamination of the ceramic layer in 38 s. This shows clearly that TBC systems are highly sensitive to water after thermal cycling. SEM investigations of sample surfaces (Fig. 2a, b) demonstrate

T = 0 sec   T = 31 sec   T = 34 sec   T = 35 sec   T = 38 sec
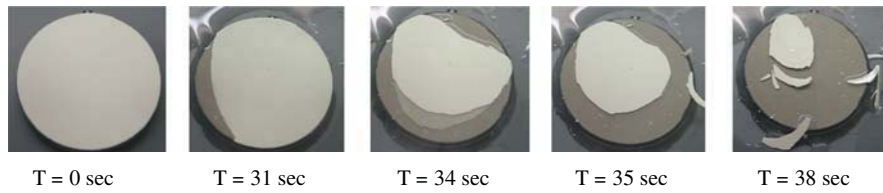
Fig. 1 Evolution of the TBC spallation as a function of time at room temperature in the presence of water. The specimen were previously exposed for 200 cycles at 1,150 °C
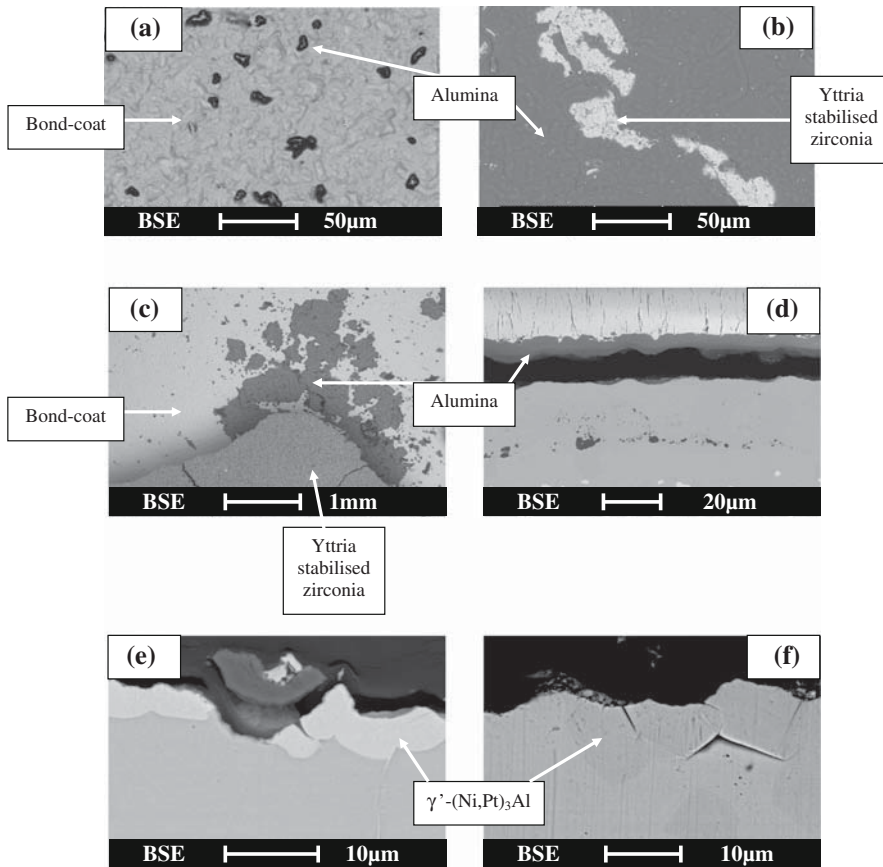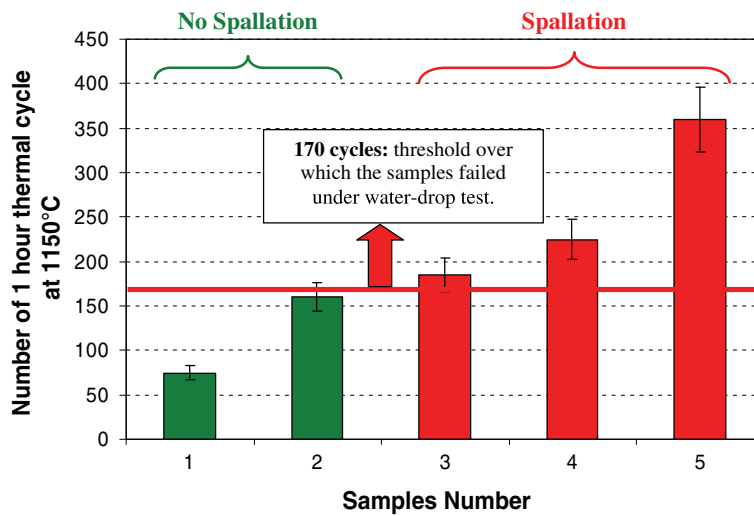

Fig. 2 SEM examinations of TBC system after 200 cycles at 1,150 °C. **a** SEM bond coat surface examination on spalled areas. **b** SEM surface examination of the inner part of the spalled ceramic. **c** SEM bond coat surface examination. **d** SEM cross-section examinations at the BC/TGO interface. **e** SEM cross-section examinations of the γ'-(Ni,Pt)$_3$Al phase in the BC. **f** SEM cross-section examinations of the γ'-(Ni,Pt)$_3$Al phase in the BC

that the failure always occurs at the bond coat/alumina scale interface. Figure 2c shows that the ceramic top coat is adherent where the alumina scale remains intact.

Table 1 Spallation of the ceramic topcoat as a function of high temperature cycles	Number of samples	Number of cycles performed at 1,150 °C	Water-drop test at room temperature
	3	75	No spallation
	3	160	
	3	185	Spallation
	7	200	
	3	225	
	3	360	

Fig. 3 Results of the second experiment reporting the effect of water-drop testing on samples after 5 durations of thermal cycling. Three specimens where tested for each duration

Figure 2d exhibits clearly the interface of failure, which is located in all cases at the BC/TGO interface.

Figure 2e and f further show that the γ'-(Ni,Pt)$_3$Al phase is also cracked after thermal cycling and the water-drop test. A previous study showed that environment could cause brittle grain boundary fracture in Ni$_3$Al [6]. This effect was explained by water vapor in the ambient air reacting with aluminum to form hydrogen and hydrogen embrittlement.

Second Experiment: Threshold in Thermal Cycling Sensitivity to Water-Drop

The aim of the second experiment was to determine if there is a threshold of high temperature exposure over which spallation of the ceramic layer is unavoidable and below which TBC systems are not sensitive to water.

Table 1 and Fig. 3 report the effect of water-drop testing on samples after five thermal cycles durations. Three specimens where tested for each duration. They all demonstrate the same behavior during the water-drop test carried out a few seconds

after cooling the specimens to room temperature. The first thing noted was that no spallation was observed right after the removal of the specimens from the furnace. When a water-drop was applied to specimens, spallation occurred systematically for the samples subjected to 185, 225 and 360 cycles. On the contrary, samples did not fail after 75 and 160 cycles. This shows that there is a critical threshold above which the samples fail consistently during the water-drop test (Fig. 3). It is noted, however, that the samples which did not fail during oxidation cycles above this limit are in a tenuous state, since they would fail immediately in contact of a water drop. The threshold was found to be about 170 one hour cycles at 1,150 °C (Fig. 3). This existence of a critical threshold is in good agreement with the data from Smialek et al. [2, 5] on alumina forming alloys.

Third Experiment: The Effect of Ambient Water Vapor

The third experiment consisted of exposing six TBC samples having a β-(Ni,Pt)Al bond coat for 200 one hour cycles at 1,150 °C, in laboratory air. This number of cycles is above the critical threshold defined in the previous experiment. After 200 cycles at 1,150 °C, all samples should fail when applying a water-drop on the top coat after cooling at room temperature.

In this new experiment, specimens were placed under three different atmospheres, right after the removal from the furnace. Two samples were subjected to the water-drop test, two samples were locked-up in a hermetically sealed box containing ambient air, and the two last samples are locked-up in a hermetically sealed box containing dry air. Results from these experiments are presented in Fig. 4 and Table 2. As expected, the two samples subjected to the water-drop test spalled quickly. This confirms that the TBC systems underwent a sufficient number of thermal cycles at high temperature to fail in presence of water. The two samples locked-up in the box containing ambient air failed as well after a short period of time. It is worth noting that this delay is about a few minutes. It is also interesting to note that the mode of failure was similar to the samples which failed during water-drop testing; that is to say, cracks propagation at the bond coat/TGO interface, leading to a complete spallation of the ceramic layer. The most demonstrative result was obtained with the two last samples, which were located in a hermetically sealed box containing dry air just after cooling. These samples never failed during the time
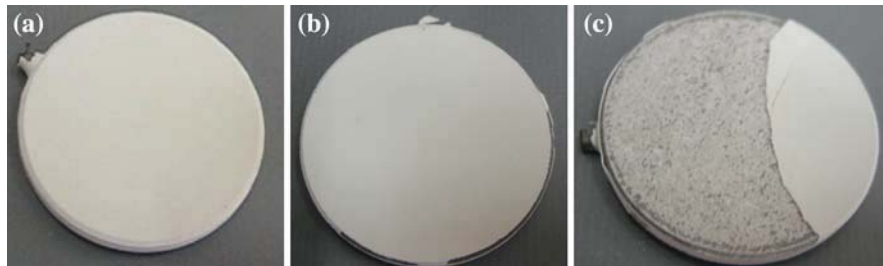
Fig. 4 Micrographs of sample at room temperature. **a** after 200 thermal cycles at 1,150 °C. **b** after 48 h in dry air. **c** after few minutes in ambient air (after removing from the hermetically sealed box)

Table 2 Spallation of the ceramic topcoat at room temperature under different atmospheres. The specimens were previously exposed for 200 cycles of 1 h at 1,150 °C in laboratory air

Atmosphere condition after 200 cycles at 1,150 °C	Results
Water-drop test (2 samples)	Spallation
Ambiant air (2 samples)	Spallation
Dry air (2 samples)	No spallation
Ambient air after 48 h in dry air (2 samples)	Spallation

of experiment, i.e., 48 h. However, they spalled very quickly once they were removed from the dry air box, i.e., in contact with ambient air. Figure 4 shows micrographs of these samples at different stages: (4a) after 200 thermal cycles at 1,150 °C; (4b) just after holding for 48 h in dry air; and (4c) few minutes after being removed from the hermetically sealed box. These results show clearly that water vapor at ambient temperature is responsible for the early TBC delamination. After spalling, all samples exhibited the same characteristic of a delamination at the BC/TGO interface. This experiment demonstrates that humidity present in the air is likely to be the root cause of early TBC spallation.

Discussion

This work confirms that water-dropping on samples after cooling can cause the accelerated spallation of the ceramic top coat [4, 5, 7]. This was shown with standard TBC systems based on (Ni,Pt)Al bond coats. In another study performed at SNECMA, three types of TBC systems based on different bond coats were tested in the same conditions: β-NiAl bond coat, β-(Ni,Pt)Al bond coat and Pt-rich γ/γ' bond coat usually named as "low cost bond coat" [8]. The results showed that after a high number of thermal cycles at 1,150 °C and under the water-drop test, the ceramic top coat is sensitive to the effect of water and leads systemically to earlier spallation of the system, whatever the nature of the BC. Any type of BC promoting the growth of an alumina scale at the BC/top coat interface were shown to be highly sensitive to water, no beneficial effect of Pt or of the nature of the phase under the alumina scale was observed.

In the present work, it is shown also that this event occurs when TBC samples have undergone a critical number of thermal cycles. It is also demonstrated that water vapor in ambient air can cause the same effect. The spalling process at room temperature requires seconds or minutes. Because of this delay, it is possible to prevent moisture-induced spalling (DTS or MIDS) by placing the samples after cooling in a dried air box, even if the critical number of cycles has been reached. When the samples are taken out of the dry box, they experience spalling because of water vapor in the ambient air. This proves that the water vapor effect occurs at room temperature after cooling and that reaction and/or diffusion steps with slow kinetics are involved in the failure mechanism.

The observed fact that samples do not fail before performing a critical number of oxidation cycles at high temperature shows that a critical level of stored elastic energy (which increases with TGO thickness) and/or a critical size of defects (micro-cracks) are required to observed DTS or MIDS. The slow growth of microcracks after cooling has been indirectly observed by acoustic emission in air plasma sprayed YSZ top coat/MCrAlY vacuum plasma sprayed bond coat system [4]. This threshold in cycle number could be viewed as the "real" lifetime of TBC systems during thermal cycling. It was 170 cycles at 1,150 °C in the present case whereas the average lifetime is about 350 cycles at 1,150 °C without water addition during cooling. The existance of a cycle threshold was previously observed for water-induced alumina spalling on PWA 1,480 superalloy (without TBC) [9]. Later, Janakiraman et al. [10] showed that the kinetics of spallation during cyclic oxidation in wet air were faster for alloy PWA1484 than for alloy PWA1480, whereas, these two alloys had similar oxidation kinetics in dry air. Then, the threshold for the effect of water on alumina spalling could depend on the oxide scale adherence on the substrate. This would need confirmation as the effect of water on the initiation of spalling would have to be differentiated from the effect on the extent of spalling after initiation, i.e., to interfacial crack propagation.

The combination of delay, water and high stress gradient caused Smialek to make an analogy with stress corrosion cracking involving hydrogen embrittlement [11]. Indeed, moisture-induced hydrogen embrittlement of intermetallics has been observed before for FeAl [12] and $L1_2$ intermetallic compounds [13]. Smialek proposed that the following reaction is relevant to explain the DTS and MIDS effects [11]:

$$Al_{alloy} + 3(H_2O)ads = Al(OH)_3 + 3H^+ + 3e^- \qquad (1)$$
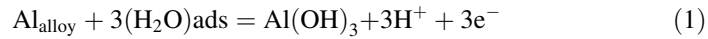
This reaction explains the hydrogen production. Interstitial hydrogen can then diffuse because of the electric field generated by released electrons or because of the stress gradient state toward the zones in tension, i.e., the metal below the alumina scale or at the tip of the metal/alumina interfacial crack. It is thought that this phenomenon occurs only near room temperature because hydrogen would diffuse out and escape from the system at a higher temperature.

In another study dealing with aluminum powder, Deng et al. [14–16] showed that water is in fact more reactive with the gamma alumina/aluminum system than with pure aluminum. It was shown that aluminum powder covered with cracked gamma alumina reacts with water to produce bohemite (AlOOH) and hydrogen gas, following the neutral reaction:

$$Al_{alloy} + 2(H_2O)ads = AlOOH(s) + 3/2\ H_2(g) \qquad (2)$$
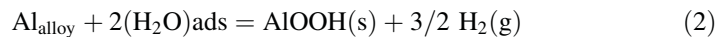
Both reactions (1 and 2) require a direct contact between water and the bond coat metal surface. It is likely that microspalling or cracks at the metal/alumina interface occurs during cooling at a temperature of a few hundred degrees where the metal can re-oxidize. At an intermediate temperature, formation of a very thin layer of gamma alumina may occur, leading to a system close to the one described by Deng et al. Some of the hydrogen gas formed by reaction (2) could diffuse in the metal and cause embrittlement, as it is known to occur for bulk alloys, including Ni_3Al

intermetallic [6], as reviewed by Chen and Liu [17]. It is interesting to note that interfacial crack propagation along both the alloy/alumina interface and the grain boundaries of bulk gamma prime (Fig. 2e, f) were observed in the present work.

Another explanation of the water effect could be the well-known effect of water on the delayed fracture of ceramics and glasses [18]. The delayed fracture of ceramics under tensile stress is due to the slow growth of microcracks below the critical flaw size for rupture. Water adsorbed at the surface of a fractured surface modifies the surface energy and thus the critical flaw size for failure. For a TBC system under thermal cycling, this mechanism would require that water or water vapor progresses in cracks from the outside of the top coat to the crack tip at the metal/TGO interface, at every cooling.

In order to determine the specific mechanism of the hydrogen effect, more observations would be needed in order to determine if an hydroxide is formed at the fractured bond coat surface ($Al(OH)_3$ or $AlOOH$) and if hydrogen is produced. Hydrogen has been detected by PIGE (Proton Induced Gamma Emission) below an alumina scale on pre-oxidized samples fractured in situ [19], but more data are needed in TBC systems.

All possible mechanisms are consistent with Smialek's idea that desktop spalling of a TBC [20–22] and moisture induced spalling of a TBC (MIDS) or water induced TBC spalling [4, 5, 8] are the same phenomenon. Our set of data with water-drop effect, as well as ambient air humidity effect on TBC delayed spallation at room temperature, confirm this idea.

It is worth noting that this phenomenon was never observed in service parts at the SNECMA laboratory, i.e., on TBC-coated parts which were cycled in a real engine until the end of coating life, prior to being "water-drop tested" in the laboratory. The explanation can be found through the observation of the alumina scale on such samples. Indeed, it was observed in a micro structural characterization conducted in parallel to the present study, that the thickness of the alumina scales formed in parts cycled in service was about 2 μm, i.e., much smaller than the thicknesses of the alumina scales formed on the samples tested in our experiments (more than 5 μm). With a flat EBPVD-YSZ/β-(Ni,Pt)Al/AM1 superalloy system, a critical TGO thickness of 5 μm was found to cause samples to be highly sensitive to water vapor and lead unavoidably to spallation of the ceramic top coat at the BC/TGO interface in presence of water. This critical value would need to be tested on industrial curved parts with different thermo-mechanical histories for industrial application.

Studies are in progress at SNECMA in order to improve understanding of the degradation mechanisms related to water vapor.

Conclusion

The detrimental effect of water (sprayed or ambient humidity) on the lifetime of standard TBC systems was clearly shown in this work. It was shown that the addition of water promotes significantly the spallation initiation and propagation of TBC systems after hundreds of thermal cycles. Several conclusions can be drawn from the three experiments performed in this study.

(i) The detrimental effect of water on TBC spallation was confirmed on a set of 15 samples oxidized for 200 one hour cycles at 1,150 °C. This phenomenon manifests as crack initiations and propagation at the BC/TGO interface leading to a complete delamination of the ceramic top coat. Several types of alumina-scale forming BCs were tested (β-NiAl, β-(Ni,Pt)Al, "Low Cost" γ/γ' BC). They all exhibited a high spallation sensitivity to water.

(ii) It was also demonstrated that a critical number of cycles is necessary to obtain spallation sensitivity to water-drop or water vapor. This observation confirms with TBCs what was known on alumina-scale forming superalloys.

(iii) The detrimental effect of water vapor was established for TBC systems by exposing the specimens in different atmospheres after cooling (ambient air, dry air). Spallation systematically occurred for samples stored in a box containing ambient air. However, no spallation occurred during 48 h in a hermetically sealed box containing dry air, in spite of more than 200 cycles spent at 1,150 °C. TBC samples spalled when they were taken out of the box and placed in contact with humidity of ambient air.

(iv) Brittle rupture at gamma-prime grain boundaries in the bond coat below the TGO was observed in conditions where the system was sensitive to water.

(v) It is proposed that the critical number of cycles (water sensitivity threshold: WST) could be used to define a lifetime to spallation. This will allow for shorter experiments and perhaps less dispersion in the lifetime results. In the present case, the threshold was found to be 170 cycles at 1,150 °C for standard TBC systems in contact of a water-drop after cooling. No spallation occurred below this critical threshold even in the presence of water on the surface of the TBC.

(vi) The observations are consistent with subcritical, slow flaw growth during and after cooling under the effects of high stress and stress gradient in the TBC system, and with water either increasing the crack velocity or decreasing the critical flaw size. More observations and experiments are needed to obtain direct evidence of the likely hydrogen embrittlement mechanism.

(vii) Such spallation is never observed on field returned parts because the TGO is not thick enough (<2 μm) to reach a critical level of stored elastic energy in the TGO. These industrial systems are not sensitive to the presence of water because they are deteriorated by other causes before being sensitive to water.

References

1. A. G. Evans, D. R. Mumm, J. W. Hutchinson, G. H. Meier, and F. S. Pettit, *Progress in Materials Science* **46**, 505 (2001).
2. J. L. Smialek, Report NASA/TM—2005-214030 (2005), pp. 36.
3. B. A. Pint, J. A. Haynes, Y. Zhang, K. L. More, and I. G. Wright, *Surface & Coating Technology* **201**, 3852 (2006).
4. M. Rudolphi, D. Renusch, and M. Schütze, *Scripta Materialia* **59**, 255 (2008).
5. J. L. Smialek, D. Zhu, and M. D. Cuy, *Scripta Materialia* **59**, 67 (2008).

6. E. P. George, C. T. Liu, H. Lin, and D. P. Pope, *Materials Science and Engineering* **A192/193**, 277 (1995).

7. J. L. Smialek, *Materials Science Forum* **595–598**, 191 (2008).

8. R. T. Wu, K. Kawagishi, H. Harada, and R. C. Reed, *Acta Materialia* **56**, 3622 (2008).

9. J. L. Smialek, Report NASA CP 10193, 1 (1997).

10. R. Janakiraman, G. H. Meier, and F. S. Pettit, *Metallurgical and Materials Transactions A* **30A**, 2905 (1999).

11. J. L. Smialek, *JOM* **1**, 29 (2006).

12. C. T. Liu, C. L. Fu, E. P. George, and G. S. Painter, *ISIJ International* **31**, 1192 (1991).

13. T. Takasugi, *ISIJ International* **143**, 128 (2003).

14. Z.-Y. Deng, Y.-F. Liu, Y. Tanaka, J. Ye, and Y. Sakka, *Journal of American Ceramic Society* **88**, 977 (2005).

15. Z.-Y. Deng, Y.-F. Liu, Y. Tanaka, H.-W. Zhang, J. Ye, and Y. Kagawa, *Journal of American Ceramic Society* **88**, 2975 (2005).

16. Z.-Y. Deng, J. M. F. Ferreira, Y. Tanaka, and J. Ye, *Journal of American Ceramic Society* **90**, 1521 (2007).

17. G. L. Chen and C. T. Liu, *International Materials Reviews* **46**, 253 (2001).

18. D. Francois, A. Pineau, and A. Zaoui, *Comportement mécanique des matériaux Tome 2: viscoplasticité, endommagement, rupture* (2° Ed.), ed. Hermes-Lavoisier, (1993), pp. 496.

19. H.-E. Zschau, M. Dietrich, D. Renusch, M. Schütze, J. Meijer, and H.-W. Becker, *Nuclear Instruments and Methods in Physics Research Section B* **249**, 2006 (381).

20. V. Sergo and D. R. Clarke, *Journal of American Ceramic Society* **81**, 3237 (1998).

21. V. Tolpygo and D. R. Clarke, *Materials Science and Engineering.* **A278**, 142 (2000).

22. D. Renusch, H. Echsler, and M. Schuetze, *Materials at High Temperature* **21**, 65 (2004).