Influence of High-Temperature Exposure on Interfacial Fracture Toughness of Thermal Barrier Coating*

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Abstract
In thermal barrier coating (TBC) sprayed on the surface of high-temperature components in a land-based gas turbine (GT), stress is induced thermally or mechanically in the coating with the start-steady-stop operation of the GT. The coating stress leads to a crack initiation at the coating interface, and consequentially to TBC spallation. Thus, it is necessary to ascertain TBC interfacial strength, in order to assess precisely TBC spallation life. The aim of this study is to present the interfacial fracture toughness of TBC by using a TBC specimen exposed under a high-temperature environment. For accomplishing this, the fracture test is conducted using a mixed-mode interfacial fracture test device that has been proposed by our group. Thermal grown oxide (TGO) formation at the interface and residual stress of TBC, which are known as the origins of a reduction of the interfacial strength of TBC, also are examined. The intrinsic interfacial fracture toughness of TBC, which was estimated with the residual stress energy stored in TBC by thermal spray process, is related with cohesion of splat boundary and pore characterizing microstructure of TBC, in order to make clear why the TBC interfacial fracture toughness varied with exposure condition.

Key words: Thermal Barrier Coating, Interface, Fracture Mechanics, High-Temperature Exposure, Thermally Grown Oxide

1. Introduction
Thermal barrier coating (TBC) is deposited on the surface of high-temperature components in a land-based gas turbine in order to protect the components from a high-temperature environment. In TBC specially sprayed by a thermal spraying process, stress is induced thermally or mechanically in the coating with the start-steady-stop operation of the GT. The compressive stress induced in TBC leads to crack initiation near the TBC interface by a local buckling loading (1)(2). If the compressive stress is enforced cyclically in the coating, TBC spallation damage could be brought consequentially, as shown in Fig 1. Figure 1 shows typical TBC spallation damage observed in TBC coated material subjected to a thermo-mechanical fatigue loading. The spallation leads to a reduction in the high-temperature fatigue life of the substrate material due to the forming of a localized hot spot. Thus it is necessary to ascertain TBC interfacial strength in order to assess TBC
spallation life precisely.

Many attempts have been made to measure TBC interfacial fracture toughness. Jordan et al. (3) have conducted a tensile fracture test using a sandwich-type chevron-notched TBC specimen and obtained TBC interfacial fracture toughness $G_c$. Yamazaki et al. (4) have applied a Charallambides-type four-point bending interfacial fracture test method to measure TBC interfacial fracture toughness. Examining the interfacial fracture toughness $G_c$ for a TBC specimen exposed at constant temperature 1273[K], they have shown that $G_c$ increases with the exposure time. Demarecaux et al. (5)(6) have estimated TBC interfacial fracture toughness $K_{IC}$ by measuring a crack length formed at the tip of the indenter mark induced by the Vickers indentation test. Evans's group (7)(8) has carried out a special TBC delamination test (they call it a wedge impression test) based on the shear loading formed by indenting the wedge with a tip at 90° angle on the TBC surface. This testing technique is quite simple and useful in engineering. However, the expression of $G_c$ has been obtained simply based on a classical beam model, in spite of the complex process of actual TBC delamination. Thus, the reliability of $G_c$ obtained by this method is doubtful. Now, it has been shown in this literature that $G_c$ obtained by a tensile-type fracture test takes 38[J/m$^2$] and $G_c$ by a shear-type test takes approximately 100[J/m$^2$]. Rabiei et al. (9) proposed that this difference in $G_c$ was caused by the existence of small-size defects included in the ceramic coating, such as open-pore and micro-crack defects. However, this difference can be explained through the following point by interfacial fracture mechanics: The tensile-type fracture test is method based on a tensile loading normal to the interface (Mode I-type loading). The Demarecaux-type fracture test also belongs to Mode-I type fracture tests. The Charallambides-type fracture test is one based on a shear loading along the interface (Mode II-type loading). It is found that the loading mode differs between the fracture tests, and the associated interfacial fracture toughness also varied with kinds of chosen fracture tests. To make clear how TBC interfacial fracture toughness varies with loading mode, we have proposed the mixed-mode interfacial fracture testing method (9) by a combination of compressive and slinging loads enforced to the coating beam and shown that TBC fracture toughness can be obtained in a wide range of loading phase angles ($\psi$) ahead of the tip of the interfacial crack. Also, we found that the interfacial fracture toughness increases with a loading phase angle, and the obtained values were almost the same as the values in the literature.

In this paper, TBC interfacial fracture toughness is shown by using a TBC specimen exposed under high-temperature conditions (973 and 1173[K]), in order to examine the influence of the high-temperature exposure on the interfacial fracture toughness. Here, the fracture toughness measured in this study is limited in mode-II loading (in the compressive-loading case only). The reason for this mode use is because a main mechanical factor for TBC spalling damage observed in a land-based gas turbine is caused with mode-II loading, and in order to have engineering data useful for estimating the spallation life of
2. Experimental Procedure

2.1 TBC specimen preparation

TBC material employed in this study is a partially stabilized zirconia (8wt%Y₂O₃-ZrO₂) as the ceramic coating, CoNiCrAlY as a metallic bond coating and cobalt-based superalloy (HA188 supplied by Mitsubishi Materials Corp.). This material combination is the same as with a TBC-coated GT combustor. The bond coating with thickness 0.1[mm] and then the ceramic coating with thickness 1.0[mm] are deposited by a thermal plasma spraying technique on the plate-type substrate with geometry of thickness 2.0[mm], width 100[mm] and length 100[mm]. TBC specimen with geometry of width \( w = 4.0 \text{[mm]} \) and length \( L = 40 \text{[mm]} \) for measuring the interfacial fracture toughness was cut from the TBC coated plate by a mechanical process. To examine the influence of the high-temperature exposure, an atmospheric high-temperature exposure test was performed under the following test conditions: exposure temperature 973[K] and 1173[K] for 500[hours] as a maximum exposure time. After this exposure treatment, a pre-crack was induced along the bond coating layer by a diamond cutter (the width of the cutter was 0.1[mm]). The appearance of the TBC specimen with the pre-crack is shown in Fig 2.

![Fig 2 TBC specimen used for measuring TBC interfacial fracture toughness using a mixed-mode interfacial fracture testing device developed by our group.](image)

![Fig 3 Mixed-mode interfacial fracture testing method by combination of compressive load applied by edge-flat punch and slinging load by thin tape hooked in coating beam.](image)
2.2 TBC interfacial fracture test

2.2.1 Outline of testing method

In this section, a brief explanation for the proposed mixed-mode interfacial fracture test is given. A schematic illustration of the proposed test is shown in Fig 3, and the appearance of the developed interfacial fracture test device is shown in Fig 4. The substrate in the TBC specimen is fixed by a rigid table as shown in Fig 4(b), and both compressive load $P$ and slinging load $Q$ at a distance $\xi$ from the tip of the interfacial crack are enforced individually to the ceramic coating beam in order to propagate the interfacial crack along the interface. Here, the substrate length is $L$, the thickness is $H$, the ceramic coating thickness is $h$, and the crack length is $a$. A feature of this fracture test method is the ability to change freely the loading phase angle $\psi$ under an arbitrary combination of $P$ and $Q$ loads. However, the loading mode in this study is limited in $P$ compressive load. As mentioning it in previous chapter, this mode limitation is because a TBC spallation damage is mainly caused with mode-II loading, and in order to have engineering data useful for estimating the spallation damage of TBC.

![Interfacial fracture test device developed by our group](image)

(a) Appearance of loading device

(b) Magnified photo of vicinity of loading component

Fig 4 Interfacial fracture test device developed by our group
As the peeling procedure conducted in this study, a compressive load $P$ was applied gradually to the coating edge. When it was observed by a digital microscope that the crack started to propagate along the interface, the compressive load was removed. Peak load $P_{\text{max}}$ obtained at that time was considered as critical load $P_c$. After this loading procedure, re-loading and un-loading processes were repeated continuously until the coating was spalled off.

### 2.2.2 Energy Release Rate and Associated Stress Intensity Factor

In this study, the TBC specimen was modeled as a bi-material structure without the metallic bond coating layer, because the material properties of bond coating are similar to those of the substrate and also the bond coating thickness is much thinner.

If the stress field ahead of the tip of the interfacial crack, which lays on the interface in a bi-material model, satisfies a small-scale yield condition, the tip-stress field can be characterized by a complex stress intensity factor $K = K_i + iK_\gamma$. Also, the associated energy release rate $G$ for our peeling problem is given as follows (9):

$$G = \frac{1-v_c}{2\mu_c} p^2 K \left( \frac{1-v_c}{4\mu_c} + \frac{P}{Q} \sqrt{\frac{a}{h}} \right) \left[ p^2 + 12 \left( \frac{Q}{h} \right)^2 + 4\sqrt{3} \cos \gamma \frac{PQ \xi}{h^2} \right]$$

(1)

where

$$p = \sqrt{1 - \beta^2} \sqrt{1 - \frac{\alpha}{\beta}}$$

$\alpha$ and $\beta$ are the Dundurs parameters, $P$ is the compressive load per unit of specimen width, $Q$ is the slinging load per unit of specimen width as shown in Fig 3. $v_c$ is Poisson’s ratio and $\mu_c$ is the shear modulus of the coating. $\xi$ is also given from an elementary beam theory consideration:

$$\xi = \frac{\xi(a - \xi)(2a - \xi)}{2a^3}$$

(2)

where $\gamma$ is a characteristic angle function with variables of a material combination and specimen geometry, and is given in Ref. (9).

A dimensional consideration gives us the following form for the complex stress intensity factor:

$$K = K_i + iK_\gamma = c_i \frac{P}{\sqrt{h}} + c_z \frac{Q \xi}{\sqrt{h}^3}$$

(3)

where $c_i$ denotes complex constants. Substituting Eq. (3) into Eq. (1), we can obtain the complex constants

$$c_i = \sqrt{2} a, c_z = \frac{\sqrt{3}}{p} e^{i(\phi + \gamma)}$$

(4)

where $\phi$ is also a characteristic angle function as well as $\gamma$.

Hence, substitution of Eq. (4) into Eq. (3) brings us to the following complete expression for the complex stress intensity factor:
\[ K = K_1 + iK_2 = \frac{1}{p} \left[ \frac{P}{\sqrt{2h} + \frac{b}{h^2} Q_0} \right] e^{\theta} \]  

(5)

Incidentally, individual expressions for the stress intensity factor \( K_1 \) and \( K_2 \) are given by

\[
\begin{align*}
K_1 &= \Re[K] \\
K_2 &= \Im[K]
\end{align*}
\]  

(6)

and also the related loading phase angle \( \psi \) becomes:

\[
\psi = \arg[K] = \tan^{-1} \left( \frac{\Im[K]}{\Re[K]} \right)
\]  

(7)

where \( \Re \) is the real part in the complex number \( K \) and \( \Im \) is the imaginary part.

### 2.3 Elastic modulus of ceramic coating

The elastic modulus of the ceramic coating would be changed with exposure conditions, because porosity in a ceramic coating is sintered by a high-temperature exposure \(^{10}\). Thus, the elastic modulus should be measured directly from the TBC specimen used in this test in order to evaluate precisely the interfacial fracture toughness.

The elastic modulus of ceramic coating was measured using a three-point bending test. The distance between supporting points was 10\([\text{mm}]\). A thin specimen, which attaches a strain gage on the surface of the ceramic coating spalled off, was employed in our bending test. The elastic modulus \( E_c \) was defined at a tangent in the stress-strain curve monitored in the three-point bending test.

### 2.4 Residual stress in TBC

The strain gage method was applied to measure residual stress in TBC. Strain gage was attached to the surface of TBC specimen. The strain gage and related lead wire were covered with a protector for preventing chemical damage. An electrolytic polishing process was performed for dissolving the substrate and bond coating. The electrolyte solution employed in this study had the following mixture ratio: 100\([\text{ml}]\) pure water, 5\([\text{ml}]\) hydrochloric acid and 10\([\text{g}]\) iron chloride (III). The voltage for conducting the electrolytic polishing was fixed at 6\([\text{V}]\). The strain was monitored continuously during the electrolytic polishing process and the residual strain \( \varepsilon_R \) after dissolving the bond coating and substrate was measured. The residual stress in TBC was obtained by following multiplication of the residual strain and elastic modulus \( E_c \).

\[
\sigma_x = -E_c \varepsilon_x
\]  

(8)

### 2.5 TGO observation

Thermally grown oxide (TGO) as shown in Fig 5 is formed at the TBC interface by following mechanism \(^{11}\): aluminum contained in a metallic bond coating and oxygen supplied from an outside environment reacts at the interface between the ceramic coating and the bond coating, and then the oxide grows with exposure time through a continuous reaction.

The importance of TGO formation in TBC for reducing TBC interface strength \(^{12}\) has been pointed out. Thus, in this study, TGO thickness was measured to relate with the TBC interfacial fracture toughness obtained in this study. To have TGO thickness, the polished cross section of TBC specimen after the interfacial fracture test was observed using a
scanning electron microscope (SEM). TGO thickness was obtained by dividing TGO area in a picture taken with a SEM by arc length along the TGO interface. Here, the area of TGO and associated length were extracted using a digital image analyzer (Micro Analyzer, JPD Co. Ltd.).

4. Experimental Results and Discussion

4.1 Test results

Figure 6 shows the measurement results of the elastic modulus of ceramic coating. The elastic modulus decreases until reaching the exposure time 100[hours] and then increases after that. The elastic modulus also increases with the exposure temperature.

Figure 7 shows variation of TBC interfacial fracture toughness $G_c$ with the exposure time. The interfacial fracture toughness shown in this graph indicates the average value for all data taken in the experiments. This result shows that $G_c$ increases with exposure time and then decreases after reaching 100[hours]. Equation (1) for evaluating the interfacial fracture toughness includes the elastic modulus of ceramic coating $E_c$ in the denominator. Thus, it was considered that the variation of the elastic modulus with the exposure time was directly reflected to variation of the TBC interfacial fracture toughness as shown in Fig 7.

Figure 8 shows TGO thickness against the exposure time. TGO does not form at the TBC interface in the exposure temperature 973[K]. In the more elevated temperature 1173[K], TGO grows monotonously with the exposure time. Previous study \(^{(9)}\) has asserted
that TGO formation leads to reduced TBC interfacial strength due to micro-cracking near an interface initiated with a stress concentration caused by a thermal expansion mismatch during the cooling process from an exposure temperature. However, our result shows that TGO formation cannot necessarily affect reduction of the TBC interfacial fracture toughness.

### 4.2 Intrinsic interfacial fracture toughness of TBC

TBC is usually deposited by a plasma spraying process, and the residual stress in the ceramic coating is induced by this high-temperature process. Thus, the energy release term for this residual stress must be considered into the evaluation of TBC interfacial fracture toughness. Figure 9 indicates the residual stress in TBC measured by the strain gage method. This graph shows that a tensile stress occurs in as-sprayed TBC material. This tensile residual stress was brought on by a quenching stress caused by rapid cooling when a coating powder was impacted onto the substrate. High-temperature exposure for as-sprayed TBC material leads to compressive shift.

In this study, evaluation of TBC intrinsic interfacial fracture toughness $G_{int}$ is attempted with consideration of the residual stress term. TBC problems including both an interfacial crack and residual stress in TBC are considered here: the problem treated in this study is how to solve for energy release rate in an interfacial cracked beam subjected to compressive load $P$, bending moment $M = Q \xi$ and constant residual stress $\sigma_n$ in
coating. The energy release rate solution originated by the residual stress can be obtained with considering superposition of following basic problems: a non-interfacial cracked problem including the residual stress in the coating as shown in Fig 10(a) and a problem subjected to axial loading $-\sigma_0 h$ at the edge of coating beam in the interfacial-cracked material as shown in Fig 10(b). However, the solution for the latter problem is necessary to obtain the energy release rate expression for the residual stress. Consequentially, replacing $P$ and $M$ with $hP_0 + \sigma_0 h$ and $2\sigma_0 h^2$, Equation (1) reduces to

$$G_{int} = G + G_R + G_{int}$$

(9)

where

$$G_R = \frac{1 - \nu_f}{2\mu_f} h \left(2 + \sqrt{3} \cos \gamma \right) \frac{\sigma_0 h}{2}$$

(10)

$$G_{int} = \frac{1 - \nu}{2\mu} \left[1 + \sqrt{3} \cos \gamma \right] M h + 2\left(3 + \sqrt{3} \cos \gamma \right) M \sigma_0 h$$

(11)

and $G_{int}$ is intrinsic interfacial fracture toughness, $G$ is the fracture toughness measured by the interfacial fracture test, $G_R$ is the residual stress term and $G_{int}$ is the interaction term between the residual stress field and the externally applied stress field. In this study, the bending moment $M$ takes zero.

Figure 11 shows the change in the residual stress term $G_R$ with exposure time. $G_R$ for the as-sprayed specimen has the highest value, and this value decreases with the exposure.
time up to 100 hours. After that, $G_R$ increases with time.

Figure 12 shows the relationship between intrinsic interfacial fracture toughness $G_{int}$ evaluated by Eq. (9) and the exposure time. It is found that $G_{int}$ for exposure temperature 973[K] decreases with the exposure time. On the other hand, $G_{int}$ for the exposure temperature 1173[K] is shown to take a constant value for the exposure time.

Here, we consider the reason why the trend as seen in Fig 12 has occurred. Firstly, the distance between the crack path and the interface between the ceramic coating and bond coating was examined from SEM pictures. Here, we call this distance the crack path distance. Figure 13 shows results of measurement of the crack path distance. It was found that the crack propagated within the ceramic coating near the interface. The graph also shows that the crack deflects to the ceramic coating side with higher exposure temperature. This deflection of the crack is caused by the microstructure change in increasing splat boundary cohesion or porosity by subjecting it to a high-temperature exposure. Thus, porosity was measured from SEM pictures. The porosity measurement revealed that the porosity obtained from an as-sprayed TBC specimen was 21[%], the porosity obtained from a TBC specimen exposed at 973[K] for 500[h] was 27[%] and the porosity in 1173[K] for 500[h] was 19[%]. Thus, it was found that the porosity in the 973[K]-exposure specimen had the highest value in spite of the fact that TGO was not formed at the interface, and this high porosity brought on reduction of TBC interfacial fracture toughness.

Here, we can claim by characterizing quantitatively the microstructure in ceramic coating that the crack observed in as-sprayed TBC material propagated along the
splat-boundary near an interface with the weakest cohesion. As is well known, the interface has larger roughness induced by a blasting treatment before thermal spraying. This roughness of the interface leads consequently to toughening for the interfacial fracture toughness due to a contact shielding mechanism \(^{(9)}\). For this toughening mechanism in as-sprayed TBC material, the exposure treatment at 973[K] gave an increase of pore in the ceramic coating. Thus, the crack deflected into the ceramic coating side and propagated along pores as defects in ceramic coating. This crack deflection into the ceramic coating led to reduction of the interfacial fracture toughness of TBC. On the other hand, 1173[K] exposure treatment gave stronger cohesion of splat boundary inside the ceramic coating as well as stronger cohesion near the interface. Thus, the fracture toughness was increased in comparison with 973[K].

5. Conclusion

This paper presented TBC interfacial fracture toughness \(G_c\) by using a TBC specimen exposed at a high temperature in order to examine the influence of the high-temperature exposure on TBC interface strength. Results obtained show that \(G_c\) increased with exposure.
time up to 100[hours] and then decreased with the exposure time. Also, $G_c$ had a strong dependency on exposure temperature: $G_c$ increased with the exposure temperature. It was found that the trend toward TBC interfacial fracture toughness changing with the exposure time can be characterized by the elastic modulus change of the ceramic coating. On the other hand, TGO growth cannot necessarily give an essential explanation of the relationship with the trend in $G_c$ observed in this study. Measurement results for the crack path distance between the crack path and interface implied that $G_c$ in as-sprayed TBC material had highest value due to a contact-shielding mechanism. Exposure temperature 973[K] brought about a diminution of TBC interfacial fracture toughness because of an increase in porosity in the ceramic coating. On the other hand, the higher exposure temperature 1173[K] led to stronger cohesion of splats, and thus higher interfacial fracture toughness in comparison with 973[K]. Table 1 shows a summary of TBC interfacial crack propagation mechanisms.

References


