Mechanistic Understanding for Degraded Thermal Barrier Coatings*

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A two-layer plasma sprayed thermal barrier coating on Ni base superalloy substrate was characterized. The coating was comprised of an inner layer of MCrAlY bond coating and an outer layer of 8 wt% yttria stabilized zirconia (YSZ) thermal barrier coating (TBC). After aging, the thermally grown oxide (TGO) layer at interface between YSZ and MCrAlY was observed. The TGO layer had two different contrast layers in the SEM images. The black one was closer to MCrAlY and the gray one was closer to YSZ. The thickness of both layers increased with aging. Countless porosities at the gray layer and microcrack at YSZ were also observed. Most of the macrocrack grew through the porosities. From this point of view one may say that the mechanism of macrocrack formation is a deterioration of adhesion accompanied by an increase of number of the porosities or the microcrack.

Key Words: Crack Propagation, Laminated Construction, Ceramics, Thermal Stress, Thermal Barrier Coatings, Thermally Grown Oxide, Microcrack, Aging, Kirkendall Porosity

1. Introduction

In power generating gas turbine plants, increasing turbine inlet gas temperature (TIT) results in enhancement of turbine efficiency and energy saving. Accordingly, gas turbine plant product companies and electric power companies have studied and developed techniques of improvement of the operating temperature, actively. State-of-the-art gas turbine plants aiming at 50% turbine efficiency, have to operate at temperature above 1 500 deg.C^{(1),(2)}. Therefore, hot section parts such as turbine blades etc. are operated in severe environment. Consequently, the deposition

of thermal barrier coating (TBC) to the turbine blades is an indispensable technique for improvement of the turbine efficiency⁽³⁾⁻⁽⁵⁾. In the plant, the surface of 1st rotating blades is exposed to temperature over 1 000 deg.C. Accordingly, these harsh operational environments may result in degradation such as cracking, delamination, or spalling of TBC⁽⁶⁾. If the delamination and the spalling occur due to high temperature and long term of operation, serious accidents might break out. Thus, an analysis of the degradation mechanisms of TBC is important and indispensable in order to prolong service life time. As a result of the delamination or the spallation, Wu et al.⁽⁷⁾ suggested that the degradation mechanism is oxidation of the bond coating, coupled with unrelieved coefficient of thermal expansion mismatch stress caused by the pegging effect of protruded bond coating out-grown oxides growing into radial cracks of the top coating. Moreover, Wu and Chang⁽⁸⁾ described that NiO and Ni(Cr, Al)₂O₄ were observed on both the bottom of the spalled TBC top coating and the outer surface of the MCrAlY bond coating oxide scale after the TBC top coating had spalled on all the test specimens used in their study. This indicates that NiO or Ni(Cr, Al)₂O₄

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is the weakest link of the bond coating oxide scale, which might accelerate TBC failure. Bartlett and Maschio⁽⁹⁾ expressed that failure of TBC initiated in the thermally grown oxide (TGO) layer is caused by thermal expansion mismatch stresses associated with a nonplanar interface. Furthermore, they reported that crack propagation occurred in the YSZ top coating in all cases, due to the high fracture energy of the interface. Maier et al.⁽¹⁰⁾ proved that oxidation of the elements of YSZ and MCrAlY reduces the protective capacity of the bond coat and during thermal aging. Moreover, both severe degradation of the bond coating and large amounts of nickel oxide have been observed. This nickel oxide was shown to grow outward into the thermal barrier, which appears to result in increase of the stresses in the thermal barrier and contributed to its failure near the interface between TBC and MCrAlY. As indicated above, a significant amount of work has been done on the analysis of TBC degradation mechanisms. However, only few attempts have so far been made to investigate TBC degradation associated with TGO growth behavior.

In this study, a mechanistic analysis of TBC degradation was carried out concerning aged specimens at 1 000 deg.C for a long period of time. Particularly, kinetics of thermally grown oxide at interface between TBC and MCrAlY is investigated. Furthermore, initiation and propagation of the crack at TBC/MCrAlY interface was observed in detail.

2. Experimental Procedure

Ni base superalloy was used as a substrate material in this study. The substrate was initially grit blasted, and then positioned into a low-pressure plasma spray (LPPS) coating system for overlaying of MCrAlY (where M indicates Ni, Co, Fe or their combinations) bond coating (approximately 100 μm thickness). Furthermore, the substrate with MCrAlY bond coating was coated by 8wt% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ (Yttria Stabilized Zirconia : YSZ) TBC top coating (approximately 300 μm thickness) by an air plasma spraying (APS) coating system.

The specimens were uniformly aged at 1 000 deg.C by using high temperature furnace in the ambient air. The reason for the choice of 1 000 deg.C was to simulate the surface temperature of the first rotating blades of 1 500 deg.C class gas turbine plants. The coated specimens were aged at 1 000 deg.C for various lengths of time viz, 10, 50, 100, 500, 1 000 and 3 000 hours. The aged specimens were compared with as-received specimen due to investigation of an extent of degradation. The geometry of the tested specimens is shown in Fig. 1. Before aging, the TGO was identified

Fig. 1 The geometry of the tested specimen

at the TBC/MCrAlY interface. On the other hand, in case of the aged specimens, TGO formation was confirmed.

In order to understand the relationship between the aging time and the growth of TGO layer, cross-section of thermally aged specimens was characterized with use of scanning electron microscope (SEM). The thickness, porosity, and microcracks of TGO layer for the specimens were measured at over 50 points by using SEM. Furthermore, due to identification of chemical composition of the TGO, analyses were using energy dispersive X-ray spectroscopy (EDX) and electron probe micro analyzer (EPMA) performed.

3. Results and Discussion

3.1 Observations and identifications of thermally grown oxide

SEM observation gave information on the initial degradation such as microcracks, porosities, and TGO as well as microstructure. Typical SEM images of TBC of as-received and 3 000 hours thermally aged specimen are shown in Fig. 2. Moreover, typical SEM images of the cross-section around TBC/MCrAlY interface are displayed in Fig. 3. It is confirm that the TGO is formed at TBC/MCrAlY interface. Furthermore, the TGO layer has irregular shape and its thickness varies at the TBC/MCrAlY interface. This TGO layer contains at least two layers with different color contrasts on SEM images. There is black layer closer to the bond coating, and gray layer near YSZ. Observation of the TGO layer at higher magnification, Fig. 3, reveals that there are many porosities, especially in the gray layer.

Energy dispersive X-ray spectroscopy (EDX) analysis was performed in order to investigate the chemical composition of the black and the gray layers. The results of the EDX analysis are presented in Fig. 4. It turns out that the black layer in Fig. 3 contains only Al and O. Consequently, the black layer is identified as Al_2O_3 (Alumina). The EDX spectrum of the gray layer contains various peaks of Al, O, Co, Cr and Ni, suggesting that the layer can be a mixed oxide consisting of a combination of NiO , CoO , Cr_2O_3 ,

Fig. 2 Typical SEM images of the cross-section of TBC

Fig. 3 Typical SEM images of the cross-section around TBC/MCrAlY interface

Fig. 4 Results of EDX analysis

$\text{Ni}(\text{Cr}, \text{Al})_2\text{O}_4$ spinels. Since the composition of the gray layer is not well defined, it will be referred to as mixed oxide layer in this work.

In addition, EPMA elemental mapping was carried out due to identify the alumina and mixed oxide in detail. The result of EPMA analysis is shown in Fig. 5. In black layer, only O and Al are present as it was displayed in Fig. 2 and Fig. 3. Namely, the black layer was identified as Alumina. However, there is hardly any Al in MCrAlY bond coating. It is supposed that almost all Al in the MCrAlY is combined with

oxygen forming alumina at the interface.

In case of mixed oxide, Cr-rich layer was identified at outer of the oxide. On the other hand, Co and Ni-rich phase were found in inside of mixed oxide. As a result, it is thought that the outer of the mixed oxide is chromium oxide (Cr_2O_3), and the inner of the mixed oxide is CoO, NiO, or spinels.

3.2 Oxidation process of TGO

It is important to evaluate the oxidation behavior of TGO (alumina layer and mixed oxide layer) for prediction of remaining life time of TBC. Accordingly,

Fig. 5 EPMA analysis of the cross-section of TBC/MCrAlY interface

Fig. 6 Variation of thickness of each layer with aging time

we investigated thickness growth of alumina and mixed oxide layer in dependence on aging time. The relationship between average thickness of each layer and aging time is shown in Fig. 6. The YSZ layer as top coating has scarcely thickness variation in spite of increasing aging time. On the other hand, it is clearly visible that longer aged specimens contain thicker TGO layer, and the TGO layer gradually increases with aging time. For short aging time, the TGO is predominantly alumina rather than mixed oxide. However, when the thermal aging exceeds 1000

hours, the thickness of the mixed oxide layer becomes similar to that of the alumina layer due to significant increase of the thickness of the mixed oxide layer. Besides, it is determined that the growth of mixed oxide obeys parabolic law. Therefore, the mixed oxide is protective film in spite of having many porosities. On the other hand, the alumina thickness cannot be expressed in terms of a parabolic law in this study. Generally, it is known that alumina monolayer obeys parabolic law⁽¹¹⁾, however, the oxidation rate of alumina decreases as the thickness of mixed oxide increases due to the formation of protective mixed oxide over the alumina layer. It is thought that protective mixed oxide has an effect on penetration of oxygen or on reduction of oxygen potential. The oxidation rate constant k_A of alumina can be expressed as a function of the thickness of mixed oxide. At this time, a schematic diagram concerning the oxidation rate constant k_A is applied, Fig. 7. In our study, the thickness of the mixed oxide, x_M , and the alumina, x_A , can be expressed as follows:

Mixed oxide layer:

$$x_M = k_M \sqrt{T} = 0.125 \sqrt{T} \quad (1)$$

Alumina layer:

$$x_A = 1.29 T^{0.21} = k_A(x_M) \sqrt{T} = 0.388 x_M^{-0.588} \sqrt{T} \quad (2)$$

where T is aging time, k_M and k_A are oxidation rate constant of mixed oxide and alumina, respectively.

It is assumed in Eq. (2) that the alumina thick-

Fig. 7 Illustration of the change of the parabolic law constant k

Fig. 8 Relationship between oxide thickness and aging time

ness obeys anomalous parabolic law. The values calculated with use of Eq.(1) and Eq.(2), and the experimental values are compared. The result is shown in Fig. 8. The calculated value corresponded to the experimental value very well. Furthermore, it has been made clear that oxidation behavior of the mixed oxide layer obeys parabolic law, see Fig. 8. On the other hand, it is thought that the oxidation rate constant of the alumina is a function of thickness of mixed oxide.

3.3 Variation of microcracks and porosities for each layer

In case of formation of defects such as microcrack or porosity in the aged TBC specimen, these defects increase with stress in the vicinity of the tip. Accordingly, it is thought that macrocrack or delamination initiate from tip of these defects. There are some microcracks and porosities in the YSZ and TGO layer of aged specimens in this study. Consequently, the influence of increase in porosity and microcrack was investigated. The relationship between ratio of porosity and microcrack is displayed in Fig. 9. The porosities and the microcracks ratio are drastically increasing after more than 500 hours aging. The amount of the porosities and the microcracks in

Fig. 9 Time dependency of porosity and microcrack ratio

the each layer increased with aging time. Especially, the microcrack in the YSZ top layer is notably increased. Moreover, the porosities in the mixed oxide are remarkably formed. On the other hand, there is no remarkable increase in the porosities and the microcracks of the alumina layer. Normally, it is thought that YSZ layer decreases the porosity and the microcrack in inner of this layer due to sintering. However, countless porosity and microcrack in the YSZ layer are formed due to thermal expansion mismatch accompanied with formation and growth of TGO. Moreover, it is thought that formation of numerous porosities in the mixed oxide is caused by Kirkendall porosity⁽¹²⁾ due to difference in diffusion rates. The increasing porosities ratio is result of condensation of the porosities during thermal exposition.

3.4 Formation of the macrocracks

It is thought that the macrocracks and delamination in the YSZ were caused by the increasing amount of the porosity and microcrack. Correspondingly, the interface between TBC and MCrAlY was observed for the long-term aged specimen. The example of observation in the vicinity of the interface is shown in Fig. 10. In case of 500 and 1 000 hours aged specimens, there is almost no macrocrack in the vicinity of the interface. However, in case of 3 000 hours aged specimen, the macrocrack was detected at everywhere in the TGO. The macrocrack passed through the porosity of the mixed oxide or the microcrack of the YSZ. Furthermore, the macrocrack grew to vertical direction of the thickness. It is supposed that a reason for the formation of the macrocrack only in case of the long-term aged specimen is increase in thermal stress accompanied by thermal expansion mismatch due to increasing thickness of the alumina. This effect can be one of driving forces of delamination and macro-

Fig. 10 Microcracks in the vicinity of TBC/MCrAlY interface

Fig. 11 Degradation factors of TBC

crack formations. However, the driving force is not only thermal stress but also decreasing bond strength or formation of stress concentration site caused by formation of porosity or microcrack. Almost all macrocracks passed through the porosity in mixed oxide or microcrack in YSZ layer.

The microcracks were formed everywhere inside of YSZ. This means that there is some possibility of initiating macrocrack from the all of microcracks. However, almost all macrocracks were formed in the vicinity of the YSZ/MCrAlY interface, which is supposed to be caused by thermal expansion mismatch in the part close to interface.

Degradation factors leading to defects such as delamination or spalling are listed in Fig. 11. It is

thought that the delamination or the spalling is initiated and propagated due to an interaction of these degradation factors.

4. Conclusions

Mechanistic analysis of TBC degradation was performed. Particularly, kinetics of thermally grown oxide at interface between TBC and MCrAlY was investigated. Moreover, the driving force of macrocracks formation was suggested. The following conclusions are drawn:

1) During aging, TGO is formed at the TBC/MCrAlY interface. SEM and EDX analysis show that TGO contains two different oxide films. One is alumina closer to MCrAlY, and the other one is mixed oxide closer to TBC.

2) Thickness of both alumina and mixed oxide increased with aging time. On the other hand, YSZ layer as top coating has scarcely thickness variation in spite of increasing aging time.

3) The thickness of mixed oxide film obeys parabolic law, and the mixed oxide is protective film in spite of having many porosities. On the other hand, the alumina thickness cannot be expressed by parabolic law. The oxidation rate of alumina decreases, which is accompanied by increasing thickness of mixed oxide increases, due to the formation of protec-

tive mixed oxide over the alumina layer. Correspondingly, it is assumed that the alumina thickness obeys anomalous parabolic law.

4) In case of 500 and 1 000 hours aged specimens, there is no macrocrack in the vicinity of the interface. However, in case of 3 000 hours aged specimen, the macrocrack was identified everywhere in the TGO. This reason indicates that thermal expansion mismatch accompanied by formation and growth of alumina is one of the driving forces of macrocracks formation. However, the driving force is not only thermal stress but also decrease in adhesive force or formation of stress concentration site caused by formation of porosity or microcrack. Almost all macrocracks passed through the porosity in mixed oxide or microcrack in YSZ layer.

5) It is thought that the delamination or the spalling is initiated and propagated due to an interaction of these degradation factors such as thermal stress, initiation of stress concentration sites, and decreasing bond strength due to formation and growth of alumina, porosities and microcracks.

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