Development of Thermal Barrier Coating System with Superior Thermal Cyclic Properties with an Intermediate Layer Containing MoSi₂ *

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Abstract

The authors have developed a method of improving the thermal cyclic resistance of the thermal barrier coating system that is deposited on gas turbine components. A conventional thermal barrier coating consists of a duplex system: a top coating and a bond coating. The developed system has a protective intermediate layer of MoSi₂ which prevents oxidation of the bond coating. The conventional duplex plasma-sprayed coating was delaminated after 20 thermal cycles. On the other hand, the developed triple-layered coating system was not delaminated after 60 cycles. The reason for the enhanced resistance to thermal cycles of the developed triple-layered coating system is that the MoSi₂ layer between the top coating and the bond coating has a self-repairing property. MoSi₂ oxidizes to form SiO₂, which seals the cracks and pores formed between the top coating and the bond coating. Thus, the formation of a thermally grown oxide(TGO), which causes the delamination of the coating, is prevented and the thermal cyclic resistance is improved.

Key words: Thermal Barrier Coating, Oxidation, Thermal Cyclic Resistance, TGO, MoSi₂

1. Introduction

Nonutility power generation facilities are regularly used as co-generation systems, in which the waste heat produced from electricity generation is recycled as steam. Recently, gas turbines have been increasingly used instead of steam turbines, because of their superior characteristics such as compactness, light weight, and their clean waste gas.

Many approaches have been taken to increase the output and energy conversion efficiency of gas turbines and reduce their environmental load. One approach is to increase the operating temperature. The operating temperature of gas turbines can be increased by applying a thermal barrier coating (TBC) to the blades and vanes of the gas turbine ^{(1), (2)}. A conventional TBC usually consists of a ceramic-M(Co,Ni)CrAlY duplex coating. The ceramic top coating consists of partially stabilized zirconia (ZrO₂+8%Y₂O₃ : YSZ) which has low thermal conductivity. MCrAlY acts as a bond coating between the top ceramic coating and the superalloy substrate. A thermally grown oxide (TGO) is frequently formed between the bond coating and the top coating during the high- temperature operation of the gas turbine. Cracking tends to occur near the TGO surface, causing delamination of the

ceramic TBC⁽³⁾ as a result of the induced thermal stress. Therefore, the growth of the TGO reduces the thermal cyclic resistance of the TBC and eventually causes failure.

A triple-layered TBC system has been developed to enhance the thermal cyclic performance by introducing an intermediate layer of MoSi₂ between the top ceramic coating and the bond coating in the conventional TBC system. MoSi₂⁽⁴⁾ has a self-repairing characteristic owing to the formation of SiO₂ within cracks. The triple-layered coating is expected to prevent the formation of TGO on the MCrAlY coating surface by preventing oxidation of the bond coating subsequently increasing the thermal cyclic resistance of the TBC.

In this study, with the aim of applying the developed TBC to gas turbines, the properties of the developed TBC compared with the conventional TBC were investigated, and the mechanism by which thermal cyclic resistance is improved was considered.

2. Experimental procedures

2.1 Specimens

A cobalt-based superalloy of Co-25%Cr-10%Ni-7.5%W was used as a substrate. The bond coating was a NiCrAlY alloy with the nominal composition of Ni-21%Cr-8%Al-0.5%Y. A YSZ ceramic was used as the top coating material.

Table 1 Details of materials used in tests

Materials	Coating A	Coating B	Coating C (Conventional)	Coating D (Developed)	Coating E
Bond coating (150 μ m)	NiCrAlY (LPPS*)	NiCrAlY (LPPS)	NiCrAlY (LPPS)	NiCrAlY (LPPS)	NiCrAlY (LPPS)
Intermediate layer coating (100 μ m)	MoSi ₂ +YSZ (APS**)	MoSi ₂ (APS)	—	MoSi ₂ +NiCrAlY (LPPS)	—
Top coating (150 μ m)	YSZ (APS)	YSZ (APS)	YSZ (APS)	YSZ (APS)	YSZ +MoSi ₂ (APS)

* LPPS: Low-Pressure Plasma Spraying ** APS: Atmospheric-Pressure Plasma Spraying

The intermediate MoSi₂ layer was introduced between the bond coating and the top coating to enhance the oxidation resistance of the system.

2.2 Preparation of coatings

The substrate with dimensions of 100 × 40 × 5 mm was blasted with #24 alumina grit before spraying. For the duplex-layer TBC specimens, the NiCrAlY bond coating was deposited with a thickness of 150 μ m on the substrate before the deposition of the top coating. For the triple-layered TBC specimens, after the deposition of the bond coating on the substrate, the intermediate MoSi₂ layer was deposited with a thickness of 100 μ m on the bond coating surface, and then the top YSZ coating was sprayed on the MoSi₂ layer surface. All coatings were deposited either by atmospheric-pressure plasma spraying (APS) or by low-pressure plasma spraying (LPPS). The conditions of APS were as follows: power 35 V, current 800 A, working gas Ar at 0.35 MPa, auxiliary gas He at 0.28 MPa, and spraying distance 100 mm. The conditions of LPPS were as follows: power 35 V, current 700 A, working gas Ar at 0.35 MPa, auxiliary gas He at 0.28 MPa, spraying distance 200 mm,

Fig. 1 Cross-sectional SEM images of coatings used

and chamber pressure 50 torr for the five types of TBC specimens, which had different combinations of coatings. The constituents of all specimens are shown in Table 1. YSZ coatings were deposited by APS, and NiCrAlY coatings were deposited by LPPS to reduce alloy oxidation during spraying. Coating A shown in Table 1 consisted of an intermediate layer containing MoSi₂ and YSZ, which was deposited by APS using a mechanically blended composite powder of MoSi₂ and YSZ with a weight ratio of 3:7. Coating D in Table 1 contained the intermediate layer deposited by LPPS using a composite powder of MoSi₂ and NiCrAlY with a weight ratio of 7:3 to improve the ductility of the coating. The top

coating of coating E was deposited by APS using a composite powder mixture of MoSi_2 and YSZ with a weight ratio of 3:7. In the case of the coating sprayed by APS using a composite powder of MoSi_2 and YSZ, the microstructure becomes optimum at a weight ratio of 3:7, because the microstructure is most dense at this ratio. Therefore, a composite powder mixture of MoSi_2 and YSZ with a weight ratio of 3:7 was selected. In the case of the coating sprayed by LPPS using a composite powder of MoSi_2 and NiCrAlY, we found that the thermal cyclic property becomes optimum at a weight ratio of 7:3. Therefore, a composite powder mixture of MoSi_2 and NiCrAlY with a weight ratio of 7:3 was selected. Typical SEM images of coatings A-E are shown in Fig. 1. Deposited thicknesses of top coating, intermediate coating and bond coating were target values respectively.

2.3 Thermal cyclic tests

The dimensions of each specimen used for the thermal cyclic tests were $40 \times 40 \times 5$ mm. In the tests, the sample was heated in a furnace at 1273 K for 2 h, and then naturally cooled in ambient atmosphere for 10 min to induce thermal strain. The delamination characteristics of the coatings with increasing number of test cycles were examined.

The time at which delamination of over 10 mm^2 occurred on the surface of the coating was defined as the delamination lifetime on the basis of our previous experience. An example of the delamination of coating C is shown in Fig. 2.

2.4 Self-repairing tests on precracks

MoSi_2 exhibits a self-repair characteristic through the formation of SiO_2 during its oxidation⁽⁴⁾. This self-repair characteristic was investigated. A composite powder of MoSi_2 and NiCrAlY with a weight ratio of 7:3 was sprayed as the bond coating on substrates ($100 \times 40 \times 5$ mm) by LPPS.

(a) Delamination on the surface of thermally sprayed coating

(b) Delamination in thermally sprayed coating

Fig. 2 Example of delamination of thermally sprayed coating (coating C)

A microhardness indenter with a load of 98 N was used to form precracks as shown in Fig 3. The specimens were heated in a furnace to 1273 K then held at this temperature for 100 h to promote the oxidation of MoSi_2 so that we could examine the self-repair effect. The coating surface was examined by SEM, and X-ray diffraction analysis was used to identify the compounds formed near the precracks.

3. Results and discussion

3.1 Thermal cyclic resistance

The results for coating durability obtained by the thermal cyclic test are shown in Table 2.

For the conventional duplex TBC (coating C) with the NiCrAlY bond coating and YSZ top layer, delamination of the coating occurred after 20 thermal cycles. On the other hand, in coating D with an intermediate composite layer of MoSi₂ and NiCrAlY, no delamination occurred even after 60 thermal cycles. This observation indicates that the introduction of the composite layer of MoSi₂ and NiCrAlY between the bond coating and the YSZ layer in the conventional TBC system considerably improves the durability of TBCs. However, delamination was observed for coatings A, B and E after only one thermal cycle. In the case of coatings A and B, delamination occurred at the interface between the intermediate layer and the bond coating. Moreover, in the case of coating E, which has no intermediate layer, delamination took place at the interface between the top coating and the bond coating.

Fig. 3 Appearance of a precrack on a coated surface formed using an indenter under a load of 98 N

The thermal cyclic test results clearly indicated that coating D was more durable than the duplex coating. Furthermore, for coatings A and B, which has a porous microstructure prepared by APS, delamination occurred after one thermal cycle even though these coatings contained an intermediate composite layer of MoSi₂. Therefore, the preparation method for the intermediate composite layer significantly affects the durability of triple-layered TBCs. Accordingly, the morphology of the compounds resulting from the oxidation of MoSi₂ in both APS and LPPS composite coatings was examined. Both the APS coating and the LPPS coating were oxidized by heating to 1273 K and holding at this temperature for 72 h before being slowly cooled to room temperature. The phases resulting from the oxidation of the coating were identified by X-ray diffraction analysis.

Table 2 Fatigue test results

Materials	Coating A	Coating B	Coating C	Coating D	Coating E
Cycles to failure	1	1	20	60 (No failure)	1
Location of failure	Interface between the intermediate layer and the bond coating	Interface between the intermediate layer and the bond coating	Interface between the top coating and the bond coating	—	Interface between the top coating and the bond coating

The Formation of a Mo₅Si₃ phase was observed in the coating prepared by APS. The formation of Mo₅Si₃ possibly occurs through the oxidation of MoSi₂ during spraying by the reaction

Since the silicon content in Mo₅Si₃ is lower than that in MoSi₂, the amount of SiO₂ resulting from the oxidation of Mo₅Si₃ is very limited. As a result, only porous SiO₂ was present in the coating⁽⁵⁾. Therefore, when Mo₅Si₃ is formed during the deposition of the intermediate layer, a dense protective coating of SiO₂ cannot be formed within the cracks

resulting from the thermal strain. In this case, substantial amounts of oxygen diffuse through the intermediate layer and oxidize the bond coating. With the oxidation of the NiCrAlY bond coating, the TGO (Al_2O_3 layers) formed along the interface between the intermediate layer and the bond coating becomes thick. The formation of a thick TGO induces a volume increase⁽⁶⁾, which subsequently leads to coating delamination along the TGO. This is probably one of the reasons for the reduction in the resistance to thermal cycles of the coatings. Furthermore, the formed Mo_5Si_3 phase transforms from the β phase (a hexagonal phase) to the α phase (a cubic phase) at about 950 K during cooling in the thermal cyclic test. The phase transformation also leads to an increase in volume⁽⁷⁾. Therefore, the coating delamination after only one thermal cycle may have resulted from this phase transformation.

When LPPS is employed to deposit the intermediate composite layer, a uniform composite layer of MoSi_2 is obtained. Since LPPS is carried out in an inert atmosphere, the formation of Mo_5Si_3 due to oxidation during spraying is avoided. Dense SiO_2 is formed at above 800 K following the reaction given by equation (2). Because MoO_3 is evaporative, the resulting oxide consists of only of SiO_2 ⁽⁸⁾.

Therefore, for coating D, the cracks formed in the intermediate layer during the thermal cyclic test were sealed by a protective SiO_2 coating and the oxidation of the NiCrAlY bond coating was prevented. As a result, the thermal cyclic resistance was improved with the introduction of the LPPS intermediate layer. The parabolic oxidation rate constant of the MoSi_2 coating at 1773 K⁽⁷⁾ ranges from 10^{-10} to $10^{-11} \text{ kg}^2\text{m}^{-4} \text{ s}^{-1}$. This rate constant is comparable to that of alumina grown at 1300 K⁽⁷⁾. These results suggest that MoSi_2 has greater oxidation resistance at higher temperature.

3.2 Self-repair of the precracks

The above results suggest that it is possible for the SiO_2 resulting from the oxidation of MoSi_2 to seal cracks and pores. Figure 4 shows the surface morphology of the sample oxidized at 1273 K for 100 h. The precracks formed on the MoSi_2 coating surface are shown in Fig. 4(a). EPMA images of Mo and Si near the crack tips on the MoSi_2 coating surface are shown in Figs. 4(b) and 4(c), respectively. Mo is mainly present in the coating matrix and Si is mainly present in the open cracks. O is generally present because the MoSi_2 coating surface was oxidized.

The mechanism of coating delamination in the conventional duplex TBC (coating C) is schematically shown in Fig. 5. Oxygen atoms from the atmosphere penetrate YSZ mainly through cracks and pores to reach the bond coating and oxidize NiCrAlY at a high temperature. As a result, TGO (Al_2O_3 layers) is formed at the interface between the top coating and the bond coating. With the growth of TGO, the brittleness is increased and the thermal stress within the coating also increased. Accordingly, coating delamination occurs along the TGO⁽³⁾. A dense SiO_2 phase is formed as a result of the oxidation of MoSi_2 in the intermediate layer in the triple-layered TBCs. Some SiO_2 is formed at the interface between the top coating and the intermediate layer, but the majority is formed in spaces such as cracks and pores in the intermediate layer, which seals the cracks and pores in the coating. The self-repair mechanism is schematically shown in Fig. 6. Case I shows the morphology of the cracks initiated in the direction parallel to the interface between the bond coating and the intermediate layer⁽⁹⁾. The cracks are induced by compressive thermal stress resulting from the difference between the expansion coefficients of the bond coating and the intermediate layer.

Fig. 4 SEM image of open crack and results of EDX analysis of Mo and Si in the vicinity of open crack

Fig. 5 Schematic diagram of proposed delamination mechanism of conventional sprayed coatings (coating C)

Case II shows the propagation of existing longitudinal cracks toward the intermediate layer under the tensile stress induced by the thermal cycle⁽¹⁰⁾. In both cases, the reaction expressed by equation⁽²⁾ takes place in the intermediate layer at a high temperature, and a dense protective SiO_2 coating is formed through the oxidation of MoSi_2 . The SiO_2 coating is formed inside both cracks and pores and prevent oxygen diffusion from the atmosphere and penetration to the bond coating. Oxygen from the atmosphere can also penetrate through the coating matrix as well as through the cracks and pores. However, the flux of oxygen

Fig. 6 Schematic diagrams of proposed self-repair mechanism of sprayed coatings for cases I and II (coating D)

penetrating through the matrix is considered to be less than 1/10 of that through cracks and pores. Thus the majority of oxygen is through to penetrate to the bond coating through cracks and pores⁽¹¹⁾. Therefore, by sealing the cracks and pores with SiO₂ resulting from the oxidation of MoSi₂, the oxidation of the bond coating is prevented. The microstructure that prevents the bond coating from oxidation is shown in Fig. 7. The prevention of the bond coating from oxidation improves the thermal cyclic performance of the triple-layered TBCs. Also, the reduction of the gradient resulting from the difference between thermal expansion coefficients of the top coating and the bond coating upon introducing the intermediate layer improves the thermal cyclic performance.

Thermal barrier property of each specimen is same temperature level of about 100°C. It is noticed that thickness of coating has an effect on a delamination lifetime. And it is noticed that an oxidation occurs between the top coating and the intermediate layer.

4. Summary

A MoSi₂-containing composite was introduced as an intermediate layer in conventional duplex TBC systems to create triple-layered TBCs in order to clarify the possibility of preventing the oxidation of the MCrAlY bond coating and improve the thermal cyclic performance. The results obtained are summarized as follows.

- (1) The thermal cyclic performance of coating D with a LPPS-deposited MoSi₂ and NiCrAlY composite intermediate layer was superior to that of the conventional duplex TBC, coating C, under the test conditions employed in the present investigation.
- (2) The MoSi₂ phase in the intermediate layer of coating D formed SiO₂ after oxidation. The formed SiO₂ sealed the cracks and pores resulting from thermal stress during sprayed coating. The penetration of oxygen from the atmosphere mainly takes place through the cracks and pores, and the sealing of these cracks and pores by the formation of a SiO₂ coating prevents oxidation of the bond coating. Therefore, the formation of TGO is prevented, which leads to significant improvement of the thermal cyclic performance of coating D. Also, the reduction of the gradient resulting from the difference between the expansion coefficients of the top coating and the bond coating upon introducing the intermediate layer improves the thermal cyclic performance.

Fig. 7 Cross-sectional micrographs of the sprayed coating after oxidation test for 100 h

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