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Al-rich Precipitation in CoNiCrAlY Bondcoat at High Temperature

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A thermal barrier coating (TBC) is applied on a surface of a gas turbine blade to provide a thermal barrier and oxidation resistant properties for the components. The ability to resist oxidation of the coating arises from the self-healing, protective Al_2O_3 scale on top of the bondcoat, which is formed during service. However, if Al depletion occurs within the bondcoat, the protective scale will lose its self-healing ability, and hence, its oxidation-resistant property. This paper investigated the depletion of Al within the bondcoat by studying the microstructure of the bondcoat on a gas turbine blade after it has been in 4000 h service at 1200 °C. The results showed that Al depletion had occurred at different levels throughout the turbine blade. In the area where Al depletion had not yet occurred, precipitation of an Al-rich phase was detected. Most of the Al was contained within this phase, leaving only small amount of Al in the surrounding matrix. A well-defined boundary was observed between the depleted and non-depleted regions.

Keywords Al-depletion, bondcoat precipitation, thermal barrier coating, thermally grown oxide

1. Introduction

The high-pressure gas turbine section in a land-based industrial gas turbine engine is subjected to a high temperature, high-pressure environment. Component materials must, therefore, possess good chemical and physical properties at high temperature to withstand such aggressive conditions. Thermal barrier coating (TBC) is often employed to protect these parts from the severe environment in order to increase the engine efficiency or to extend the service life of the gas turbine components (Ref 1, 2).

A typical TBC consists of two layers of coating, an MCrAlY bondcoat (M is Ni and/or Co) and an Y_2O_3 partially or fully stabilized ZrO_2 topcoat (Ref 3); both can be applied onto the components using an air plasma spraying technique (Ref 4). The ZrO_2 topcoat acts as a thermal insulator, working together with a cooling system within the turbine blade to reduce the temperature to which the component and the bondcoat are subjected (Ref 5). The intermediate MCrAlY bondcoat is a bonding layer for the ceramic topcoat and an oxidation resistant coating for the underlying component (Ref 6). This coating will selectively form a dense and protective aluminium oxide film at the bondcoat/topcoat interface. This oxide film will slow down further oxidation of the bondcoat.

However, the self-repairing Al_2O_3 film requires a constant supply of Al from the bondcoat to maintain its protective property since the film may get damaged locally. If Al depletion occurs within the bondcoat, which results in insufficient Al being supplied to the oxide film, secondary oxides may form on top of the Al_2O_3 film (Ref 7, 8). The secondary oxides are formed by other elements within the bondcoat, such as Ni, Co, or Cr, diffusing to the bondcoat/topcoat interface to form oxides (Ref 9, 10). Since the secondary oxides are often not protective in nature, if the protective Al_2O_3 scale is damaged, the bondcoat will no longer be oxidation resistant, which will affect the lifetime of the components. It has also been found that cracks may originate from defects contained within these secondary oxide scales (Ref 11). These cracks may propagate into the ceramic topcoat, toward the outer coating surface, leading to spallation of TBC.

This work was, therefore, carried out to study the Al depletion and the microstructural changes in the bondcoat after long-term service at high temperature.

2. Experimental Procedure

The investigation was performed on a first-stage high-pressure turbine blade from a gas turbine engine model Mitsubishi 701F, Gas Turbine WN-C 102 (Mitsubishi Heavy Industry, Japan), which was obtained from the Electricity Generating Authority of Thailand (EGAT). The turbine blade was produced from IN738LC and was air plasma-sprayed with TBC. The TBC consists of Co-32Ni-21Cr-8Al-0.5Y (wt.%) bondcoat with a thickness of 150-200 μm and ZrO_2-20 wt.% Y_2O_3 topcoat with a thickness of 300-400 μm. The turbine blade has been operating isothermally for 4000 h in the gas turbine engine at a service temperature of about 1200 °C and a gas pressure between 127.5 and 137 MPa.

Sample segments from various areas on the turbine blade were cross sectioned through the TBC coating and polished for microstructural observation. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and quantitative energy dispersive x-ray (EDX) techniques were employed for the microstructural study and for the investigation of the Al depletion within the bondcoat.

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3. Results and Discussion

Spallation of the ceramic topcoat was observed in the leading and trailing edge regions. Examination using SEM revealed a large number of macroscopic cracks parallel to the bondcoat/ topcoat interface, traveling at a small angle towards the outer surface, as shown in Fig 1. These cracks were found mainly in the leading edge and trailing edge regions of the turbine blade. Further propagation of these cracks may lead to spallation of the topcoat.

A protective Al_2O_3 scale was formed at the interface throughout the turbine blade, but the secondary oxide layer was observed only in some areas; in particular, the leading and trailing edges of the blade (Fig. 2). Since the presence of the secondary oxide can lead to crack initiation in the ceramic topcoat, this observation agrees with the cracked structure found in Fig. 1. Formation of the secondary oxide scale also indicates an insufficient Al within the bondcoat to continue formation of the protective Al_2O_3 scale.

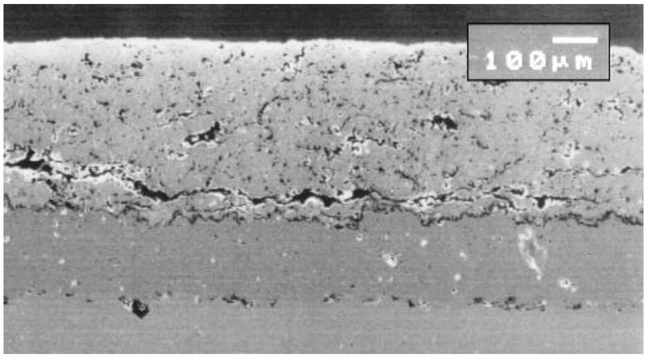

Fig. 1 Microstructure of TBC on the leading edge of the turbine blade showing a large crack within the topcoat after 4000 h at 1200 °C

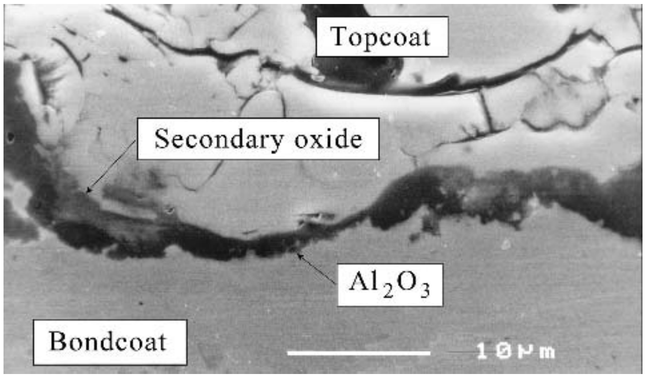

Fig. 2 Microstructure of the bondcoat/topcoat interface showing thermally grown oxide scales

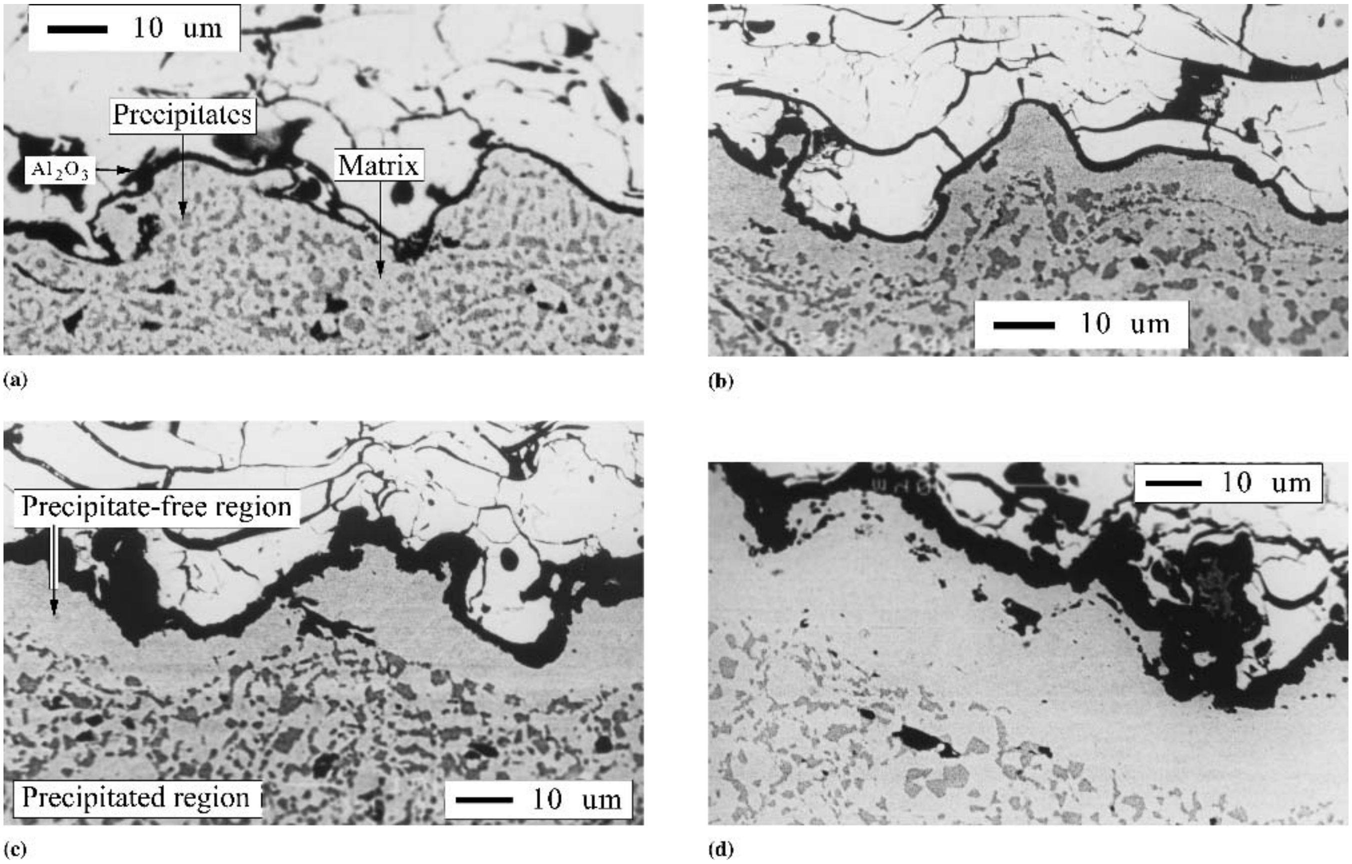

Fig. 3 SEM micrographs of the bondcoat/topcoat interface showing the second phase precipitated within the bondcoat: (a) convex region, (b) concave region, near the leading edge, (c) convex region, near the trailing edge, (d) concave region, near the trailing edge

On examining the microstructure of the bondcoat, it was found that sintering of the bondcoat had occurred throughout the blade. This is identified by the disappearance of the splat boundaries (Fig. 1). Some splat boundaries were still evident mostly on the convex side of the blade, possibly due to the lower operating temperature and gas pressure on this side. Vague outlines of the splat boundaries are still visible in Fig. 3(a) and (b). These are less evident in Fig. 3(d).

One other major change in the bondcoat was the precipitation of a second phase as a dark colored precipitation (Fig. 3). Although these precipitates were observed scattered throughout the bondcoat, some areas adjacent to the oxide scale were found to be free of these precipitates. Similar findings were observed in a work done by Teratani, et al., where samples, coated with low pressure plasma sprayed MCrAlY, were oxidized isothermally for short periods of time (Ref 12). It was found that an “Al-lacking layer” was formed within the bondcoat adjacent to the thermally grown oxide between the bondcoat and the topcoat. The thickness of the Al-lacking layer was dependent on the testing time and temperature. For the TBC studied in this experiment, it was found that the width of the precipitate-free region varies from one location to another. The well-defined boundary between the precipitate-free region and the precipitated region may have followed the splat boundary; however, this is not clearly evidenced in the micrographs shown in Fig. 3.

The total oxide scale thickness, which is the combination of the Al_2O_3 scale and the secondary oxide scale, is largest around the leading and the trailing edges due to the increasing thickness of the secondary oxide in these regions. The total oxide thickness increases with increasing thickness of the precipitate-free layer. This trend can be seen in Fig. 3, but no specific relationship was found. Previous work suggested that the region on the blade with thicker precipitate-free layer would have suffered a higher service temperature (Ref 12).

EDX mapping (Fig. 4) shows that the precipitates consist mostly of Ni and Al, represented by the high concentration of white specks. The lighter colored matrix is, in turn, made up mainly of Ni, Co, and Cr. The quantitative TEM-EDX analysis (Tables 1 and 2) confirms the darker phase to be rich in Al in comparison to the matrix.

Table 1 Composition results of the precipitates from quantitative TEM-EDX analysis

	Composition of the precipitate, wt.%				
	Al	Ti	Cr	Co	Ni
1	60.7	3.9	3.0	3.9	28.5
2	61.2	3.9	3.0	3.8	28.1
Average	61.0	3.9	3.0	3.8	28.3

Table 2 Composition results of the matrix from quantitative TEM-EDX analysis

	Composition of the matrix, wt.%					
	Al	Ti	Cr	Co	Ni	Y
1	3.7	2.3	9.0	15.5	66.7	2.8
2	4.4	1.4	5.7	17.0	69.2	2.3
Average	4.05	1.85	7.35	16.25	67.95	2.55

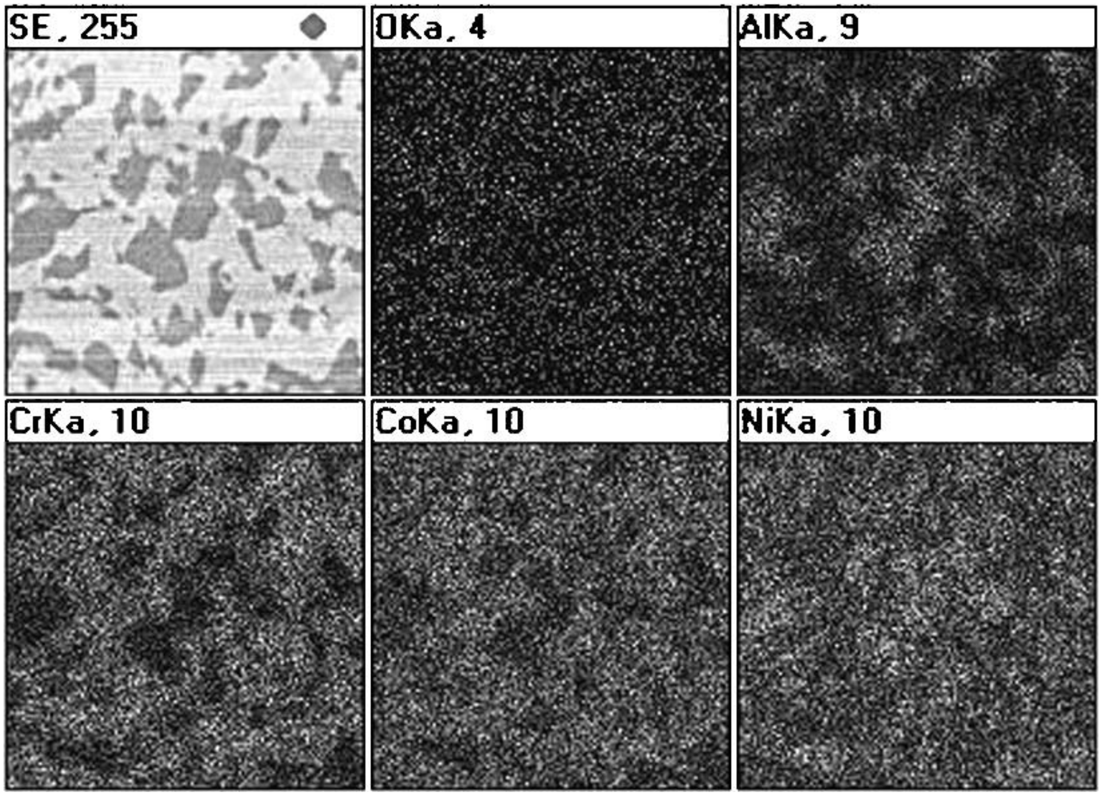

Fig. 4 EDX mapping showing the concentration of each element in the precipitated region in the bondcoat. EDX analysis was carried out at the convex region, near the trailing edge (Fig. 3c), at the midpoint along the thickness of the bondcoats

In some areas, particularly in the coating on the trailing edge where a large amount of secondary oxide was found, the precipitates were not present in the bondcoat adjacent to the protective oxide but were found about 10-20 μm lower, existing all the way to the bondcoat/substrate interface (Fig. 3c and d). Since the matrix of the precipitated region and the precipitate-free region are the same phase, it can, therefore, be concluded that the precipitate-free region has been exhausted of Al because no Al-rich precipitate has formed.

As discussed previously, the precipitation boundary appears to follow the splat boundary, which would suggest that Al depletion occurs only in the upper splats near the topcoat, while the next lower splats could still have sufficient Al to form oxide scale. The Al in the lower splat should then diffuse upward along the concentration gradient, but this does not occur. This could be due to the diffusion path being blocked by inter-splat oxide or porosity. The Al diffusion behavior is yet to be investigated.

Evans and Taylor proposed a concept of a "diffusion cell," which concerned the individual splat particles of the MCrAlX bondcoat being diffusionally isolated from the bulk of the coating, affecting the oxidation behaviour of the TBC (Ref 13). This concept will help explain the observation in this work, where a sharp boundary between the near-interface Al-depleted region and the undepleted region was found. If the splats are isolated from one another, Al cannot diffuse across the splat boundary. Therefore, only the Al contained within the splats near the bondcoat/topcoat interface can diffuse to the interface and only these splats will become depleted of Al. However, the internal intersplat oxide responsible for the creation of the diffusion cell was not evidenced in the turbine blade coating. This may be because the blade coating was subjected to higher operating temperature and much higher pressure than the specimen tested by Evans and Taylor, resulting in a faster growth of the interfacial protective Al_2O_3 scale (Ref 13). Once the protective scale becomes continuous along the bondcoat/topcoat interface blocking the lateral porosity between the splat particles, the oxygen molecular transport into the bondcoat is greatly reduced if not eliminated; thus, internal oxidation is not detected, as demonstrated previously (Ref 14). The diffusion cell can still take place if there is a wide enough gap to stop the Al diffusion, caused by the inter-splat porosity characteristic of an air plasma sprayed coating, which may be the case in this turbine blade coating under investigation. Sintering of the bondcoat could then take place later on in service resulting in the disappearance of the splat boundary and the gradual departure from the concept of the diffusion cell. However, further investigation is required to support such speculation.

4. Conclusions

From the microstructural study of the air plasma-sprayed TBC on the first stage high-pressure gas turbine blade, which underwent an operation at a service temperature of 1200 °C for 4000 h, conclusions can be drawn as follows.

Al depletion adjacent to the protective oxide layer and formation of the secondary oxide scale occurred within the bondcoat, particularly in the coating near/on the leading and the trailing edges.

Some Al in the bondcoat was consumed to form a protective oxide scale, but a larger amount reacted with Ni to form small Al-rich precipitates, which scattered throughout the bondcoat.

The precipitates were not present in the area where Al depletion occurs, most likely because there was not enough Al left in the bondcoat to form an Al-rich precipitate.

A clearly defined boundary was observed between the depleted and undepleted regions, suggesting an Al diffusion channel blockage. The concept of a "diffusion cell" may apply.

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