Cyclic oxidation behavior of aluminide, platinum modified aluminide, and MCrAlY coatings on GTD-111

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ABSTRACT
Cyclic oxidation behavior of aluminide, platinum modified aluminide, and MCrAlY coatings has been investigated at three temperatures. Aluminide and platinum modified coatings were deposited on GTD 111 material using an outward diffusion process. CoCrAlY coating was applied on GTD-111 by Electron Beam Physical Vapor Deposition (EB-PVD). The oxidation behavior of these coatings is characterized by weight change measurements and by the variation of β phase present in the coating. The platinum modified aluminide coating exhibited the highest resistance to oxide scale spallation (weight loss) during cyclic oxidation testing. Metallographic techniques were used to determine the amount of β phase and the aluminum content in a coating as a function of cycles. Cyclic oxidation life of these coatings is discussed in terms of the residual β and aluminum content present in the coating after exposure. These results have been used to calibrate and validate a coating life model (COATLIFE) developed at the Material Center for Combustion Turbines (MCCT).

INTRODUCTION
The hot section components of advanced land based turbines operate at severe operating conditions—high thermal stresses and temperatures. Higher operating temperature play a dominant role in the material and coating degradation, which in turn adversely affects the service life of these components. The turbine blades are one of the most critical hot section components: thus, reliability and availability of a gas turbine depend on the blade life. Because of the higher operating temperatures encountered in these advanced turbines, the performance and durability of the coating system has now become one of the primary life limiting factors of coated blades.

In the mid 1960s, coatings were introduced in land based turbines to provide hot corrosion protection to superalloy (nickel and/or cobalt base alloy) blades and vanes. Nickel and cobalt base alloys are susceptible to hot corrosion (Type I and II) at the operating metal temperatures ranging from 1150°F to 1700°F (621°C to 927°C). The severity of hot corrosion increases with temperature up to 1600°F (871°C) and then decreases with temperature. Above 1700°F (927°C), oxidation supersedes hot corrosion. Furthermore, the source of corrodants is fuel and airborne salts carried by inlet air. However, airborne impurities can be prevented from entering into a turbine by effective use of air filters. As a result, hot corrosion problems are typically encountered in turbines that are fired with contaminated fuels. The advanced turbines are primarily fired with relatively clean natural gas and operate at higher temperatures. Degradation of coatings due to oxidation is the primary concern in these designs.

Coatings used on rows 1 and 2 turbine blades vary from one manufacturer to the other, but the generic types are similar and fall into three groups: aluminide, platinum modified aluminide (Pt-Al), and MCrAlY with or without an over aluminized layer. As part of an EPRI funded program, data on various coatings are being generated to calibrate and validate a coating life model developed at the MCCT (Chan, et al., 1997). The objective of this program is to use the COATLIFE model to determine the coating refurbishment intervals for turbine blades and vanes. The results generated on aluminide, Pt-Al, and CoCrAlY coatings are presented in this paper. Post-test metallurgical evaluations were also performed on the specimens to understand degradation of these coatings due to exposure to thermal cycles at different temperatures.

EXPERIMENTAL PROCEDURE
Specimen Geometry and Test Materials
Flat rectangular test specimens (30x15x1.5 mm) were machined from the shank section of a fully heat treated GTD-111 turbine blade using electro discharge machining process. The specimens were ground and polished to remove the recast layer.

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GTD-111 has a nominal composition by weight: C 0.1%, Cr 14.0%, W 3.8%, Co 9.5%, Mo 1.5%, Al 3.0%, Ti 4.9% and Ta 2.8%. The heat treatment for GTD-111 blades consists of a partial solution treatment at 2050°F (1121°C) for two hours followed by aging at 1550°F (843°C) for 24 hours (Embley and Kallianpur, 1985).

Coating Application
Aluminide and Pt-Al coatings were applied on the test specimens using an outward diffusion process. The process is described elsewhere (Shankar 1988, and Smith and Boone 1990). For Pt-Al coating application, the specimens were electroplated with approximately a 10 μm thick platinum plating prior to the aluminizing process. The CoCrAlY coating was applied using Electron Beam Physical Vapor Deposition (EB-PVD) process.

Cyclic Oxidation
Tests were performed using a facility designed and fabricated at SwRI. This test facility consists of a furnace, a forced air cooling system, and a computer controlled moving arm that transfers specimens in and out of the furnace and to the cooling system. For cyclic oxidation tests, the specimens were inserted in a furnace that was maintained at the temperature of interest, and held in that furnace at that temperature for 55 minutes prior to moving them to the cooling system. The specimens were then cooled by forced air for 5 minutes prior to re-inserting them into the furnace. The specimens took approximately four minutes to reach the test temperature and one minute to cool from the test temperature to room temperature. The tests were conducted at 1950°F (1065°C), 1850°F (1010°C), and 1750°F (954°C). Multiple specimens of each coating were run for 2000 cycles. The specimens then lost weight with increasing cycles, due to oxide spallation. The weight loss results show that Pt-Al offers slightly better resistance than aluminide coating. However the variation in weight loss results between the Pt-Al and aluminide coatings is not statistically significant. However, the CoCrAlY coating showed the least resistance among three coatings investigated.

Figure 2 shows weight change data of coatings as function of thermal cycles at 1850°F (1010°C). The aluminide and Pt-Al coated specimens gained weight; no evidence of protective oxide spallation was noted among the specimens in 1100 thermal cycles. Weight loss due to oxide spallation was observed in two of three CoCrAlY coated specimens. However, the weight change data for CoCrAlY coated specimens exhibited significant scatter. Weight change data of coatings as a function of thermal cycles at 1750°F (954°C) is illustrated in Figure 3. All three coatings predominantly gained weight. No evidence of weight loss due to oxide spallation was noted in these specimens which were run for 2200 cycles.

Coating Microstructure
As expected, exposure to thermal cycles led to degradation of microstructure of all three coatings. In aluminide and Pt-Al coatings, the coating degradation is manifested by transformation of β-NiAl phase into γ'. In CoCrAlY coating, degradation is manifested by the formation of β-CoAl phase depleted zones at the outer and the coating/substrate interface. The extent of degradation of coatings varied with the number of thermal cycles and the exposure temperature.

Aluminide and Pt-Al Coatings
Degradation of microstructure of aluminide and Pt-Al coatings after exposure to 400 and 1000 thermal cycles at 1950°F (1065°C) is illustrated in Figures 4 and 5. In both coatings, β-NiAl phase is partly transformed into γ'. The γ' phase was identified based on nickel and aluminum contents, as determined by EDS. Aluminium content in the γ' phase ranged from 8 wt.% to 10 wt.%. In both aluminide and Pt-Al, the β to γ' transformation was greater for the specimen exposed to 1000 cycles than for the one exposed to 400 cycles. Volume fraction of β phase in aluminide and Pt-Al coatings as a function of number of thermal cycles is presented in Figure 6. Little or no transformation was noted in the first two hundred cycles in both coatings. As the number of cycles increased, the amount of β phase decreased in both coatings. After 1000 cycles, the β phase content in the aluminide and Pt-Al coatings was reduced to 20% and 80%, respectively. For a given number of thermal cycles, the β to γ' transformation was more severe for aluminide coating than for Pt-Al. Since β phase acts as a reservoir for aluminium, cyclic oxidation life of a coating is directly related to the amount of β phase present in the coating and thickness of the coating. Hence, these results show that aluminide coating exhibits less cyclic oxidation resistance than Pt-

RESULTS
As-Coated Microstructure
A specimen from each coating was sectioned in the as-coated condition to determine microstructure and coating thickness. As expected, the aluminide and Pt-Al coated specimens exhibited a single phase (β-NiAl) structure, while the CoCrAlY coated specimen exhibited approximately 50% β (CoAl-precipitates) and 50% γ (matrix). The γ phase is a solid solution of primarily cobalt and chromium. Thickness of aluminide, Pt-Al, and CoCrAlY coatings ranged from 1.0 to 1.8 mils, 2.0 to 3 mils, and 9.0 to 10 mils, respectively. The chemistry of these coatings was determined at three locations on each specimen; the top, the middle, and the bottom of the layer of each coating. The average chemistry of the coatings in weight percent is as follows:
Aluminide: 29.5%Al, 2.8%Cr, 7.0%Co, 0.7%Ti, 57.5%Ni, 0.4%Mo, and 2.4%Ta.
Pt-Al: 19.9%Al, 4.1%Cr, 5.7%Co, 2.0%Ti, 51.2%Ni, 0.3%Mo, 2.9%Ta, and 15%Pt.
CoCrAlY: 9.9%Al, 24.5%Cr, 60.3%Co, and 2.5%Ni.

Cyclic Oxidation
Weight change of aluminide Pt-Al and CoCrAlY coated specimens as a function of thermal cycles at 1950°F (1065°C) is presented in Figure 1. As expected, all these specimens initially gained weight due to formation of a protective oxide scale with thermal cycles, up to approximately 400 cycles for aluminide and Pt-Al coatings, and 200 cycles for CoCrAlY. The specimens then lost weight with increasing cycles, due to oxide spallation. The weight loss results show that Pt-Al offers slightly better resistance than aluminide coating. However the variation in weight loss results between the Pt-Al and aluminide coatings is not statistically significant. However, the CoCrAlY coating showed the least resistance among three coatings investigated.

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The Pt-Al would be capable of providing oxidation protection for several thermal cycles at this temperature. Microstructure of aluminide and Pt-Al coatings after 1600 thermal cycles at 1750°F (954°C) is shown in Figure 7. Consistent with the weight change results presented in the previous section, both aluminide and Pt-Al coatings have shown little or no evidence of degradation.

**CoCrAlY Coating**

Thermal exposure at 1950°F (1065°C) resulted in formation of β phase depleted zones at the outer surface of the coating and at the coating/substrate interface (Figure 8). In addition, the width of the interdiffusion zone below the coating also increased due to inward diffusion of aluminum into the substrate during thermal exposure. The width of the β phase depleted zones increased with increasing number of cycles, and the β phase particles coarsened. As the number of cycles increased from 400 to 600, the volume fraction of the β phase decreased from 48.5% to 39.0%.

Similar coating degradation results were observed in the specimens exposed to 1850°F (1010°C) and 1750°F (954°C). However, the depleted zone widths were significantly smaller in these specimens.

**DISCUSSION**

It is well known that both diffusion (aluminide and Pt-Al) and overlay (CoCrAlY) type coatings protect the substrate blade alloy against oxidation and corrosion by forming a protective surface oxide layer. The β-NiAl or CoAl phase in these coatings acts as a reservoir, which provides aluminum for the formation of the protective oxide layer. As the protective oxide spalls during thermal cycling, aluminum in the coating diffuses outward to re-form the oxide layer at the surface. Aluminum also diffuses into the substrate alloy due to composition gradient between the coating and the substrate. As a result, the coatings degrade due to inward and outward diffusion of aluminum present in the coatings. Inward and outward diffusion of aluminum leads to transformation of the β-NiAl phase into γ' or γ phase in aluminide and Pt-Al coatings. The extent of transformation, however, depends on the test temperature and number of thermal cycles. The higher the test temperature and/or a larger the number of thermal cycles accelerates transformation.

The present test results show that the β-phase in both aluminide and Pt-Al coatings was partly transformed into γ as a result of thermal exposure. No evidence of γ phase was noted in the coating microstructure of the test specimens. However, Cheruvu and Leverant (1998) have reported that the β phase in the over-aluminized layer transformed into γ, containing 3 wt.% aluminum, in a service run GT29+ coated GTD-111 blade after 25,834 hours operation. A comparison of present results with the in-service degradation results suggests that long term tests will result in loss of aluminum in the γ phase, which will lead to transformation of γ into γ in these coatings. This suggests that even if the β phase completely transforms into γ, the latter phase will act as a reservoir for aluminum and will provide aluminum to reform the protective oxide layer.

CoCrAlY coatings also degrade due to inward and outward diffusion of elements. The diffusion of elements, in particular aluminum, results in dissolution of β phase particles at the outer surface of the coating and the coating/substrate interface, leading to the formation of β phase depleted zones in the coating (Daleo and Boone, 1997 and Srinivasan et al, 1995). As a result of exposure, nickel in the substrate also diffuses into the CoCrAlY coating. In addition to aluminum, cobalt and chromium in the coating also diffuse into the substrate. The outward diffusion of nickel from the base metal into the coating and inward diffusion of aluminum, cobalt, and chromium from the coating into the substrate results in coarsening of platelet precipitates in the interdiffusion zone and an increase in the width of this zone. Since diffusion is a thermally activated process, the widths of the depleted zones in the coating and the interdiffusion zone below the coating depend on the exposure temperature and time. The change in the width of the depleted zones and the interdiffusion zone are used to estimate operating temperature of service run blades (Srinivasan, et al. 1995 and Cheruvu and Leverant, 1998).

Though the weight change results showed an excessive weight loss after exposure to 600 thermal cycles at 1950°C (1065°C), only a small fraction of the original coating had degraded. The coating contained 39% β phase after exposure, suggesting that the cyclic oxidation life of the coating was not exhausted. The coating would be capable of surviving for many more thermal cycles at this temperature. For ranking coatings, consideration of weight change results alone may lead to an erroneous conclusion since these results are independent of coating thickness variations. Both weight change and post test metallurgical evaluation results need to be considered for ranking coatings. A more accurate indicator of coatings condition for its residual life estimation is either the aluminum content or the volume fraction of the β phase. The volume fraction of this phase is a better measure of the coating's ability to re-form a protective oxide layer.

**CONCLUSIONS**

The following conclusions can be drawn from the results of this investigation:

- Loss of aluminum due to spallation and reformation of a protective surface oxide layer during the cyclic oxidation testing led to transformation of β phase into γ' in both aluminide and Pt-Al coatings. The extent of transformation was temperature and cycle dependent.
- The β to γ' transformation was more severe for aluminide than for Pt-Al coating, suggesting that former coating was less resistant to oxidation.
- Degradation of CoCrAlY coating due to exposure to thermal cycles was evidenced by formation of β-phase depleted zones at the outer surface and at the coating/substrate interface, and by enlargement of interdiffusion zone.
- The volume fraction of the β phase in the coating decreased with an increasing number of thermal cycles and/or exposure temperature.
- Though weight change results showed an excessive weight loss after 600 thermal exposure cycles at 1950°F (1065°C), a significant portion of the CoCrAlY coating, containing 39% β phase, was in good condition, suggesting that the coating can survive a larger number of cycles.
- Weight change results alone should not be considered for ranking the coatings since these results are not a good measure of the coating's ability to re-form a protective oxide layer.
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Figure 1. Cyclic oxidation behavior of aluminide, Pt-Al and CoCrAlY coatings at 1950° F (1065° C).

Figure 2. Cyclic oxidation behavior of aluminide, Pt-Al, and CoCrAlY coatings at 1850° F (1010° C).

Figure 3. Cyclic oxidation behavior of aluminide, Pt-Al and CoCrAlY coatings at 1750° F (954° C).
Figure 4. β-phase variation in aluminide coating after exposure at 1950°F (1065°C) for a) 400 cycles and b) 1000 cycles.

Figure 5. β-phase variation in the Pt-Al coating after exposure at 1950°F (1065°C) for a) 400 cycles and b) 1000 cycles.

Figure 6. Volume fraction of β in the aluminide and Pt-Al coatings as function of thermal cycles at 1950°F (1065°C).
Figure 7. Microstructure of aluminide and Pt-Al coatings after 1600 cycles at 1750°F (954°C).

Figure 8. Influence of exposure to thermal cycles at 1950°F (1065°C) on the width of β depleted and interdiffusion zones in the CoCrAlY coating after a) 400 cycles and b) 1000 cycles.