In-service Degradation and Life Prediction of Coatings for Advanced Land-based Gas Turbine Buckets*

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In-service degradation mechanisms of over-aluminized MCrAlY duplex coatings have been determined by evaluating two long-term service-run blades. Cyclic oxidation tests were also conducted to characterize the degradation of the duplex coatings, GT29+ and GT33+. The results show that degradation of duplex coatings is manifested by the formation of oxide scale, the transformation of β -phase into γ , the coarsening of β -phase particles in the MCrAlY coating, and the enlargement of the interdiffusion zone. Considering all of the degradation mechanisms observed in these service-run coated buckets, a coating life prediction model, developed under an EPRI-funded program, was used to estimate the life of GT29+ and GT33+ coatings. A comparison of the model calculations and experimental data indicated that, conservatively, the useful life of duplex coatings can be predicted solely based on the Al content in the top aluminide coating. The predicted value of the coating life is increased by a factor of 1.4 to 2 if MCrAlY is included in the lifetime estimation.

Key Words: Combustion Turbine Coatings, Life Prediction Method, Degradation Mechanisms, Duplex Coatings, Coatlife, Oxidation Protection, GT29+, GT33+

1. Introduction

To improve the efficiency of land-based gas turbines, all of the major equipment manufacturers have been introducing advanced turbines that are designed utilizing improved design techniques/materials and coatings. These turbines are fired at higher firing temperatures and utilize optimum cooling of hot section components to increase efficiency of a turbine. As a result, these components experience higher operating temperatures. Because of the higher operating temperatures encountered in these designs, the performance and durability of the coating system have now become one of the prime life limiting factors of hot section components. Among these components, turbine blades are the most critical since reliability and availability of a gas turbine blade depends on the integrity and life of these blades. As the operating

metal temperature increases, the kinetics of the base material and the coating degradation increase with the metal temperature⁽¹⁾, which in turn lowers the coating service life.

In the mid 1960's, coatings were introduced in land-based turbines to provide hot corrosion protection of turbine blades. Both the blade alloys and the coatings are susceptible to hot corrosion (Type I or II) at operating temperatures ranging from 620°C to 930°C. The severity of hot corrosion increases with temperatures up to 870°C and then decreases with increasing temperatures above 870°C⁽²⁾. At temperatures above 925°C, oxidation supersedes hot corrosion. In addition, hot corrosion problems are normally encountered in turbines that are fired with contaminated fuels. Advanced turbines are fired with relatively clean natural gas and operate at a temperature range where oxidation supersedes hot corrosion^{(3),(4)}. Therefore, oxidation is the primary concern in these designs. To treat coating degradation under oxidizing conditions a COATLIFE model was developed and it was validated for Pt-Al coating against field data^{(5),(6)}.

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To provide oxidation protection, turbine blades are coated with overlay (MCoCrAlY) or diffusion type (aluminide or Pt-Al) coatings. However, an overlay (CoCrAlY or NiCoCrAlY) coating with or without a top aluminide is widely used on the first and second rows of turbine blades of modern turbines. Coatings provide protection by formation of a thin, adherent alumina (oxide scale) layer on the surface. The β -phase particles (CoAl or NiAl) in these coatings act as a reservoir for aluminum and supply aluminum to form the protective surface alumina layer. All of these coatings degrade during long-term service and the degradation of the coating adversely affects the durability and remaining service life of a turbine blade. Only limited studies have been published in the literature on the degradation of duplex coatings^{(3),(7),(8)}. The objectives of this study were to:

- identify the degradation mechanisms of duplex coatings,
- generate cyclic oxidation data for the duplex coatings, and
- calculate the life of duplex coatings using the COATLIFE model^{(5),(6)} developed under an EPRI-funded program and compare the calculated life with the experimental data.

2. Materials and Test Methods

2.1 Service run buckets

For this study, first stage blades from General Electric's (GE's) Frames 6001B and 9000FA were procured to identify the in-service degradation mechanisms for the duplex coatings. These blades were operated on gas fired engines. The 6001B blade had operated for about 25 800 hours and the other blade operated for approximately 17 200 hours. A transverse section was removed from the airfoil section at the 55% height location of each blade. For generating baseline data, a transverse section was also removed at the 10% height of the 6001B blade. The operating metal temperature at the 10% blade height is typically low and, as a result, the microstructure of the coating at this location is a good approximation of the initial, as-coated condition. The microstructure of the coating was characterized by optical and scanning electron microscopy. The extent of in-service coating degradation was determined by comparing the microstructures at the 10% and 55% blade height locations.

Both blades were made of a directionally solidified (DS) GTD-111 alloy and had an over-aluminized CoCrAlY coating. The nominal composition of the blade material is given elsewhere⁽⁹⁾. Typical compositions of the top aluminide and CoCrAlY coatings, as determined by Energy Dispersive Spectroscopy (EDS) of the coating at the 10%

blade height, are as follows, by wt. %:

Aluminide: 27.6% Al, 6.4% Cr, 2.8% Ni, and 63.3% Co

CoCrAlY Coating: 8.2% Al, 0.4% Ti, 6.8% Ni, 27.0% Cr, and 57.6% Co

2.2 Cyclic oxidation testing of coatings

Flat rectangular test specimens (30×16×1.5 mm) were machined from the shank sections of fully heat-treated GTD-111 blades using an electro-discharge machining process. The shank section operates at a low temperature and the microstructure of the base metal represent the original (virgin) condition. The specimens were subsequently ground, polished, and the corners were beveled on 400 and 600 grit Emory papers using standard metallographic procedures prior to application of either CoCrAlY or NiCoCrAlY using a Low Pressure Plasma Spray (LPPS) process. The standard metallographic procedures will not alter the microstructure of the specimens. The compositions of these CoCrAlY and NiCoCrAlY coatings, shown in Table 1, are comparable to the nominal chemistries of GE's proprietary coatings of GT29 and GT33, respectively. Following a vacuum diffusion heat-treatment (1120°C for 2 hours), the specimens were over-aluminized using a pack cementation process (at 1025°C for 4 hours). The specimens were packed in a mixture powders containing 20% chromium, 5–8% aluminum, and aluminum oxide (72–75%). Aluminum fluoride was used as an activator. Commercially available powders were used for the pack cementation process and no attempt was made to control sulfur contamination. Following application of coating, the specimens were given a diffusion treatment at 1080°C for either 2 or 4 hours. The compositions of the top aluminide, CoCrAlY, and NiCoCrAlY coatings, as determined by EDS, are shown in Table 1. The resulting over-aluminized CoCrAlY and NiCoCrAlY coatings will, hereafter, be referred to as GT29+ and GT33+, respectively. For GT29+, the top aluminide coating was about 30 μ m thick and the CoCrAlY was 150 μ m thick. For

Table 1 Chemical compositions of over-aluminized CoCrAlY (GT29+) and NiCoCrAlY (GT33+) used in this study (by wt.%)

Coating	Al	Cr	Co	Ni	Y
GT29+					
Top Aluminide	22.3	11.2	66.5	—	—
CoCrAlY	8.3	32.8	54.3	4.0	0.5
GT33+					
Top Aluminide	24.2	6.0	35.7	33.6	—
NiCoCrAlY	10.5	18.6	32.6	37.2	0.4

GT33+, the top coating thickness was 40 μm and the NiCoCrAlY was 160 μm .

Cyclic oxidation tests were conducted in a test facility consisting of a furnace, a forced air cooling system, a coated superalloy sample holder, and a computer-controlled transfer mechanism that moves the sample holder in and out of the furnace and to the cooling system. During the cyclic oxidation tests, the specimens were maintained in the furnace at a peak temperature of 1066°C or 1010°C and held for 55 minutes. They were then removed from the furnace and air cooled to 25°C in 5 minutes by forced air in the cooling system, and then reinserted into the furnace. The test was interrupted periodically to weigh the specimens. Cyclic oxidation tests were conducted on the GT29, GT29+, and GT33+ coated specimens. Selected specimens were sectioned and examined by scanning electron microscopy to characterize microstructural changes in the coating. Chemical compositions of individual phases in the coatings were determined using Energy Dispersive Spectroscopy (EDS). Quantitative metallography was used to measure the volume fraction of the β -phase.

2.3 Coating life modeling

The cyclic oxidation model developed by Chan⁽¹⁰⁾ was used for predicting the life of combustion turbine coatings. The computer code developed for this application is referred to as COATLIFE^{(6),(11)}, which has been used as a life-prediction tool for various combustion turbine coatings. The main features of the coating life model are: (1) oxidation kinetics, (2) spallation kinetics of oxides formed on the coating, (3) outward and inward diffusion, (4) overall kinetics of Al loss from the coating due to oxidation, spallation, and inward diffusion, and (5) a life prediction scheme based on a critical value of Al content that corresponds to the breakdown of a continuous alumina surface scale or the complete depletion of β in the microstructure. Since the coating life model has been published, the details of the model will not be repeated here but they are available in earlier publications (Chan⁽¹⁰⁾, Chan et al.^{(6),(11)}), including applications to aluminide, Pt-modified aluminide, and MCrAlY coatings.

The oxidation and spallation constants used in COATLIFE were evaluated for GT29+ and GT33+ coatings using the weight change data. This preliminary set of model constants was then used in conjunction with COATLIFE to predict the depletion of the Al content and β -phase as a function of thermal cycles. The values of the spallation constants were then fine-tuned by matching the calculated Al content and the volume fraction of β against experimental data for 1066°C. This adjustment was necessary

because there were discrepancies between the predicted and observed weight change response at 1066°C. After the spallation model constants were finalized, COATLIFE was then used to successfully predict the Al content and the volume fraction of the β -phase as a function of thermal cycles for other temperatures (1010°C and below). Because of space limitations, results for the lower temperatures will not be reported here. In the model calculations for the duplex coatings, the aluminide top coat was analyzed with COATLIFE by treating MCrAlY as the substrate. After the Al content in the top decreased to the Al level in the MCrAlY, both the top coat and the MCrAlY were treated as an MCrAlY coating and GTD-111 as the substrate.

3. Results

3.1 In-service degradation of coating

An examination of the transverse sections at the 55% height locations showed that the coating on both blades was degraded. The extent of degradation varied from location to location within a blade as well as between blades and, however, was less severe for the Frame 6001B blade than for the Frame 9000FA blade. Figure 1 shows the condition of the coating at the 10% and 55% height locations of the Frame 6001B blade. Below the protective surface oxide scale, a small continuous white layer, γ -phase, containing approximately 6 at.% aluminum was seen in the top aluminide coating at the 55% blade height. Comparison of coating microstructures at the 10% and 55% height locations also revealed that the long-term service exposure led to the reduction of the volume fraction and the coarsening of β -phase particles, and the enlargement of the interdiffusion zone below the CoCrAlY coating. The interdiffusion zone was wider at the trailing edge than at the leading edge. This suggests that the operating metal temperature of the trailing edge was higher than that of the leading edge.

Figure 2 shows the condition of the coating on the leading and the trailing edges at the 55% height location of the Frame 9000FA blade. The coating on the leading edge was severely degraded. The β -phase in the top aluminide coating decreased from 100% at the initial condition to approximately 25%. The β -phase in the CoCrAlY coating was almost consumed. In contrast to these observations, the coating on the trailing edge did not show any significant evidence of degradation and it was in good condition. The volume fraction of β -phase in the top aluminide and CoCrAlY coatings on the trailing edge was almost comparable to the amount that is normally seen in an undegraded coating. The interdiffusion zone width below the CoCrAlY coating on the trailing edge was

Fig. 1 Microstructure of the GT29+ coating on the Frame 6 blade: (a) the coating on the leading edge at the 10% blade height (undegraded), and ((b) and (c)) the degraded coating on the leading and trailing edges at the 55% blade height, respectively

Fig. 2 Microstructure of the GT29+ coating on the Frame 9FA blade: (a) and (b) coating on the leading and trailing edges at the 55% blade height, respectively

significantly smaller than at the leading edge (25 versus 115 μm). In contrast to the Frame 6001B blade results, the coating degradation results showed that the leading edge of the Frame 9000FA blade operated at a higher temperature than the trailing edge.

3.2 Life assessment model development and validation

Figure 3 compares the calculated weight change response against the experimental data for the GT29+ and GT33+ coatings at 1066°C. Both the GT29+ and GT33+ coatings behaved similarly and

Fig. 3 Calculated weight change results compared against experimental data for GT29+ and GT33+ coatings on GTD-111 at 1066°C

Fig. 4 Comparison of calculated and measured Al contents as a function of the thermal cycle for GT29+ and GT33+ coatings on GTD-111

were treated using the same approach. The comparison indicated that COATLIFE underpredicted the weight change of both coatings. For the calculations of the Al content and the volume fraction of the β -phase in the MCrAlY coatings, the model constants are required for both the CoCrAlY (GT29) and NiCoCrAlY (GT33). Cyclic oxidation data was generated for the GT29 coating in this program. Cyclic oxidation data was not generated for the GT33 coating. As a result, model constants for GT29 were used for GT33.

Comparisons of the calculated and measured results of the corresponding Al content and the volume fraction of the β -phase are shown in Figs. 4 and 5, respectively. The experimental data indicated that the Al content and the amount of β -phase in the top coat decreased with increasing thermal cycles. The rates of Al loss in the top aluminide coat shifted to those of MCrAlY when the Al content in the top coat and MCrAlY reached similar levels. This degradation

Fig. 5 Comparison of calculated and measured values of volume fraction of β as a function of the thermal cycle for GT29+ and GT33+ coatings on GTD-111

Fig. 6 The microstructure of GT29+ after 1938 thermal cycles at a peak temperature of 1066°C

behavior was accurately predicted by COATLIFE, as shown in Fig. 4.

The predicted coating life for the GT29+ coating was 1750 cycles, compared to about 2000 cycles experimentally. Figure 5 shows good agreement between the calculated and experimental values of the volume fraction of β , up to 1700 thermal cycles. Figure 6

Fig. 7 The microstructure of GT33+ after 1938 thermal cycles at a peak temperature of 1066°C

shows the microstructure of the GT29+ coating after 1938 one-hour thermal cycles at 1066°C. The amount of β -phase in the top aluminide and CoCrAlY coatings decreased from 100% at the initial condition to about 17% and from 50% to 7%, respectively.

A coating life of approximately 1700 thermal cycles is obtained using a critical Al content of 19 at.% for the aluminide top coat over the NiCoCrAlY (GT33) coating. The life can be extended to approximately 2300 cycles if credit is given to the NiCoCrAlY and a critical Al content of 7.7 at.% is used for this coating. As in the case of GT29+, the model calculation underpredicted the weight change response, but gave accurate predictions of the Al content and the volume fraction of β -phase (Fig. 5). The microstructure of GT33+ after 1938 thermal cycles at 1066°C is shown in Fig. 7. The amount of β -phase in the top aluminide and NiCoCrAlY coatings decreased from 100% in the as-coated condition to about 49% and from 50% to 17%, respectively. The GT33+ showed a higher Al content, a larger volume fraction of β -phase, and a longer coating life when compared to GT29+ after the same thermal cyclic exposure.

4. Discussion

The results of the service-run blades of Frame 6001B and Frame 9000FA turbines show that duplex coatings degrade during long term service. The extent of degradation varied from location to location and between the blades and it is sensitive to operating metal temperature⁽⁸⁾. It is well known that the metal temperature of a cooled blade varies from location to

location. The coating degradation is evidenced by the transformation of β -phase into γ in both the top aluminide and CoCrAlY coatings, and the enlargement of the interdiffusion zone below the MCrAlY coating. The transformation of β -phase into γ in the top aluminide coating is due to loss of aluminum resulting from spallation and reformation of the surface protective oxide scale during service. The aluminum content in the γ layer (Fig. 1) decreased from 55 at.%, in the initial condition, to approximately 6 at.%. Thus, the formation and spallation of the protective oxide scale promotes outward diffusion of aluminum.

The extent of the interdiffusion zone growth varied from location to location in both blades. The growth of this zone is due to the inward and outward diffusion of elements from the coating into the substrate and vice versa. Since the interdiffusion zone growth is a diffusion controlled process, the change in zone width is sensitive to the local metal temperature of a blade and it can be used to estimate the operating metal temperature of service-run blades^{(6),(12)}. The present results confirm that the mechanism of degradation of duplex coatings is due to the formation and exfoliation of protective oxide scale and the inward and outward diffusion of elements. The rate of aluminum loss during service due to inward and outward diffusion controls degradation of these coatings.

Considering all of these degradation mechanisms, a COATLIFE model^{(5),(6),(11)} life was developed. This model is used to calculate the useful life of duplex coatings (GT29+ and GT33+). For life calculations it is necessary to define the critical aluminum concentration for the top aluminide and MCrAlY coatings. Previous work indicated that the critical Al content for aluminide (NiAl) coating is 19 at. %^{(5),(6),(11)}. This is the minimum Al content required to form a continuous protective alumina scale on NiAl⁽¹²⁾. The same critical Al content is also applicable to an aluminide coating based on CoAl, since available data in the form of oxide maps showed the formation of alumina at this Al content or higher⁽¹³⁾. Furthermore, previous work also indicated that the critical Al content for CoCrAlY coatings is ≈ 7.7 at. %⁽⁶⁾, which is based on the depletion of β -phase in the microstructure. Comparison of the model calculation and experimental data for GT29+ and GT33+ at 1066°C indicates that, conservatively, the useful life of the duplex coating can be predicted solely based on the Al content in the top coat using a critical Al content of 19 at. %. A somewhat longer coating life is obtained if credit is given to MCrAlY and a critical Al content of 7.7 at. % is used. The MCrAlY's contribution to the overall life of the duplex coating is comparable to that of the top coat because the MCrAlY (150 - 160 μm) is consider-

ably thicker than the aluminide top coat (30 - 40 μm).

5. Conclusions

- Long-term service exposure at high temperatures leads to degradation of duplex coatings.
- The degradation of the top aluminide coating is evidenced by the transformation of β -phase into γ due to the spallation and reformation of protective surface oxide scale.
- The degradation of the MCrAlY coating is evidenced by the coarsening and the transformation of β -phase into γ , and the enlargement of the interdiffusion zone below the coating.
- The transformation of β -phase (CoAl) into γ in the aluminide coating, and the enlargement of the interdiffusion zone is due to inward and outward diffusion of aluminum during service.
- A COATLIFE model developed considering all of these degradation mechanisms, i.e., spallation, oxidation, and inward and outward diffusion of aluminum, can be used to predict the remaining service life of duplex (GT29+ and GT33+) coatings.
- The service life of duplex coatings can be conservatively predicted based on the aluminum content in the top aluminide coating. The useful life of duplex coatings is increased by a factor of 1.4 to 2 if MCrAlY is included in the lifetime calculation.

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