

MECHANICAL DEGRADATION OF COATING SYSTEMS IN HIGH TEMPERATURE CYCLIC OXIDATION

R.C. Pennefather* and D.H. Boone**

* CSIR, P.O. Box 395, Pretoria, South Africa

** Boone and Associates, Cascade Drive, Walnut Creek, USA

ABSTRACT

Cyclic oxidation tests were performed on a large variety of commercially available overlay coatings. The results of cyclic oxidation tests confirmed that the composition of the coating as well as the processing method of the coating can affect the life of the system. Coating life was determined by the time to coating penetration and initiation of substrate attack. As this work was part of a effort to evaluate the relative protectiveness of available coating systems for Industrial Gas Turbine applications at relatively high temperature, an extensive testing programme was undertaken. The different coatings were tested to visual failure. The results presented in this paper concentrate on the surface instability of the coating. Apart from usual oxidation of the coating an additional degradation mechanism was observed. A mechanical effect caused by the instability of the coating as a result of the difference in the thermal coefficient of expansion and mechanical properties between the substrate and coating. This effect, the so-called "rumpling" effect, resulted in a significant reduction in time to penetration and was in some systems the life controlling factor.

KEYWORDS

Overlay; coatings; mechanical properties; cyclic oxidation

INTRODUCTION

Protective coatings are required for the successful application and performance of critical airfoil components in Gas Turbines. The success of a coating in a high-temperature application is measured by its ability to remain in place, to resist oxidation, and to avoid cracking. In general, overlay coatings developed for intermediate temperature hot corrosion are often limited by oxidation behaviour, while diffusion coatings are more susceptible to thermal fatigue cracking in cyclic application¹. A review of some of the factors affecting the oxidation resistance of coating and their testing will be presented elsewhere. The main affects are summarized in Table 1. The mechanical properties of the coating are, however, also of importance in high temperature cyclic oxidation which is a point not often considered in coating section or life assessment.

Table 1: Factors affecting oxidation resistance of the coating.

Factors	Effect
Temperature of gas and metal	Amount of diffusion occurring at the alloy/coating interface. This results in the decrease of Al in the coating which is required for the formation of a protective coating.
Gas composition which can include contaminants	The composition can complicate the oxidation of the coating by introducing a corrosion parameter
Cyclic nature of temperature	Result in spalling of the protective alumina scale.

Since real-time evaluation of different coating parameters (ie composition, deposition techniques and substrate) is not often feasible in engines, laboratory tests have been developed for the screening and ranking of coatings. In the present effort a high temperature cyclic oxidation laboratory rig was used to determine the ranking of coatings for gas turbine application. However, often the ranking predicted by these tests are different from those observed when components are actually used in engines². This suggests that better laboratory tests are needed to more successfully predict coating performance in real-world applications by taking into account the different modes of failure observed during engine testing and the variations of engine operation environments. These failure modes include hot corrosion Type 1 and 2, oxidation and mechanical failure of the coating by brittle cracking or rumpling due to inadequate mechanical properties of the coating system. Figure 1 depicts an example of rumpling which occurred on a turbine blade after 12 000 hrs of service.

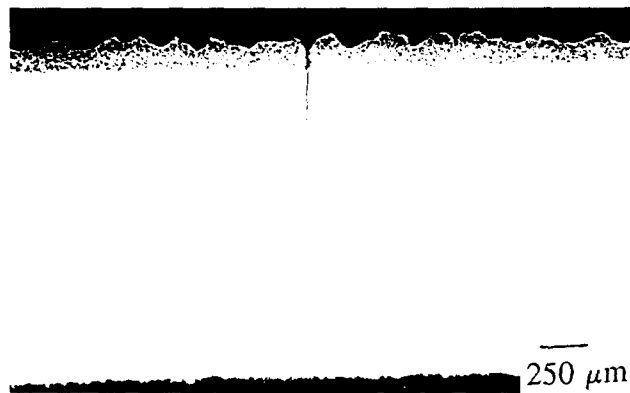


Fig. 1. Microstructure of a turbine blade after 12 000 hrs in service showing rumpling with crack initiation from a rumple.

The mechanical properties of coatings depend on its composition and the type of phase distribution. A high DBTT (ductile-brittle transition temperature) of any given coating is undesirable since the coating remains in the brittle mode to higher temperatures where tensile strains can occur as compared to a coating which has a lower DBTT. A low DBTT will place the coating substrate system into a ductile mode at lower operating temperature. Therefore the probability of cracking type failure for a low DBTT coating is much less than in high DBTT coating when turbine engine experienced various spectrum loading over a wide range of temperatures under hostile environments.

Frequent and rapid changes of engine power, particularly power reductions and trips from generating loads, lead to a significant thermal shock loading of turbine blades and their protective coatings. Thermally induced strains are generally largest at the surface of an airfoil. When the strains are severe, the protective barrier provided by the coating may be compromised by thinning or cracking. Additionally, fatigue crack propagation rates in the coating are a function of both strain intensity factor range (mechanical deformation at the crack tip), the coating structure, and the environment (the amount of the coating at the crack tip consumed by oxidation)³.

This thermal shock loading can lead to surface roughening of the more ductile coatings that do not fail by more brittle cracking. This surface roughening, referred to as "rumpling" is not new, and has been observed for a long time on thermal mechanical fatigue tested specimens. However, as service temperature and duration times have increased it is now an important consideration in the prediction of oxidation life as well. Strangman⁴ observed rumpling on MCrAlY overlay coatings subjected to intermediate temperature dwell periods during cyclic oxidation burner rig testing. The roughening was attributed to thermal expansion mismatch strain, between the coating layer and the substrate, which produce coating cyclic-reversed creep deformation. In some literature it has been suggested that rumpling observed in some tests may be the result of subcoating substrate melting. However, Manley⁵ found that while surface roughening can occur with coating affected substrate melting, it is on a much grosser scale and at significantly higher temperature (1200°C) than that of the surface rumpling observed during cyclic oxidation testing. As expected isothermally exposed specimens did not exhibit rumpling. He then showed that surface rumpling was dependent on the relative changes in strain that occur with thermal cycling.

Deb et al⁶ attributed the amount of rumpling observed to a number of possible effects including:

1. the coefficient of thermal expansion mismatch
2. thermal gradient across the coated specimen
3. the mechanical properties of the coating.
4. the strain and/or thermal cycle.

It was proposed that thermal expansion mismatch can produce either compressive or tensile strains within the coating during cycling depending upon the state of the CTE mismatch. If the CTE of coating α_c is greater than that of the substrate α_s during cooling (from a presumed neutral strain point), the coating will be in tension. If, however, the α_c is less than that of the α_s , the coating will experience a compressive strain during cooling. It was established that the case where the α_c value is less than the α_s value is true for coatings under going cyclic oxidation. The residual strain state at the start of the cooling cycle is also important as the low strength coating can relax to a zero strain state while the stronger substrate can maintain a significant strain level.

Thinner aluminide coatings were found by Deb et al⁶ to have a higher degree of rumpling irrespective of the initial coating structure and composition. The thicker coatings (with increasing aluminum and platinum level in the coating) tends to increase the thermal expansion mismatch induced strains, but with a postulated concomitant increase in coating strength. This increased strength apparently can serve to reduce the incidence of rumpling under cyclic oxidation testing. The higher coating strength and an increase in DBTT can result in a decrease in the ability of the coating to plastically relieve the higher strain build up which occurs during thermal cycling to elevated temperature. At some point these residual strains are relieved by crack initiation at the coating surface or within the coating and eventually propagate either in an inward or outward direction down the stress gradient in the coating.

Overlay coatings are composed of a more ductile, thicker two phase coating. The brittle β -phase Al reservoir is in a ductile matrix. The ductile matrix has a coefficient of thermal expansion which is greater than that of the β (NiAl) aluminide phase as well as the γ and γ' phase substrate. This increased ductility reduced the brittle cracking problem but is known to increase the amount of the "rumpling" in the coating.

In more recent work Peichl and Bettridge⁷ studied the effect of different MCrAlY coating compositions on rumpling during high temperature cyclic oxidation testing at 1050°C. The CoNiCrAlY coating was found to show pronounced rumpling and coating cracks developed after about 2500 cycles. A close relationship was found between crack propagation and oxidation. The NiCoCrAlY coating had a significantly longer life with more than 5000 cycles to cracking. The failure modes of the coating were similar to that of the CoNiCrAlY: rumpling, crack initiation at the coating surface, crack propagation through the coating into the substrate and Al-depletion. The NiCoCrAlY coating with Pt addition had an even higher thermal-fatigue resistance with more than 6000 cycles to cracking. Rumpling appeared to less pronounced and very low Al-depletion. The Re containing CoNiCrAlY coating proved to be the most rumpling resistant coating and did not crack within 8000 cycles. However, during this time the β -phase was totally consumed. Re is thus thought to strengthen the coating but apparently has no intrinsic effect on the oxidation resistance (oxide growth and oxide adherence) of the coating.

In the literature there are also reports of the effect of overaluminizing MCrAlY coatings on their oxidation resistance. Peichl and Bettridge⁷ observed an increase in the thermal fatigue resistance at high peak temperatures encountered at the leading edge of a turbine blade, but brittle cracks were found in the colder areas. Wood and Swede⁸ tested overaluminized MCrAlY blades in a rainbow test. These blades were found to have improved oxidation resistance which was especially evident in the hotter zones. Craze cracking was also observed on these blades. The cracks were blunted at the interface between the Al-rich outer layer and the more ductile MCrAlY inner layer. In both cases there was no noted evidence of rumpling emphasising the important role of the surface layer.

EXPERIMENTAL TECHNIQUES

In an attempt to study surface and structural changes occurring in MCrAlY coatings and their interactions with the substrate, high temperature cyclic oxidation tests were performed on a large variety of different overlay coatings. The coatings were chosen to allow comparison between deposition method and composition and the effect these parameters have on the protectivity and mechanical properties of the coating. The coatings tested are tabulated in Table 2.

High temperature cyclic oxidation testing was carried out at Liburdi Engineering Ltd, Canada. The maximum temperature was approximately 1125°C for approximately 30 minutes. The cooling period was 10 minutes during which time the coating test samples were removed from the cyclic oxidation rig furnace. The duration of each cycle was approximately 70 minutes.

During the testing of the coated samples, the samples were periodically removed and visually examined. Duplicates were removed periodically and metallographically prepared for microstructural examination. The average thickness of these samples was measured optically and the amount of β -phase in the coating was measured using an image analyzer. The amount of rumpling occurring was calculated by the distance between the rumples. The larger the distance of a rumple the less the frequency of rumpling.

Table 2: Properties of the coated test sample prior to testing

Designation	Deposition	Coating composition	Alloy	Thickness
CP0 A	LPPS	CoNiCrAlY	IN738	172
CP0 B	LPPS	CoCrAlY	IN738	152
CP0 C	LPPS	NiCoCrAlY + Si	IN738	166
CP0 D	LPPS	NiCoCrAlY + Si, Ta	IN738	134
CP0 E	LPPS	NiCrAlY + Si	IN738	166
CP0 F	LPPS	NiCoCrAlY	IN738	125
CP0 G	HVOF	NiCoCrAlY	IN738	261
CP0 F + TCC C19	LPPS and pack	NiCoCrAlY + Al	IN738	156

Analysis of interdiffusion and oxidation of the coatings will be presented elsewhere. This paper will concentrate on the surface instability of the coating.

RESULTS

The average thickness, the β -content and the amount of rumpling of the coatings removed after 500 cycles as well as the time to failure of the tested coating samples are given in Table 3. All microstructure of all the samples studied showed rumpling but the amount of β -phase was found to vary as indicated in Figures 2-5. In many cases no β -phase was observed after 500 cycles as can be seen from Table 3.

Table 3: Average thickness, β -phase content and amount of rumpling after approximately 500 cycles and number of cycles to failure of the coated test samples

Designation	Number of cycles	Average thickness	β -phase content	Rumpling	Cycles to failure
CP0 A	500	168	0	17.4	745
CP0 B	500	146	0	24.1	500
CP0 C	500	126	2	23.1	650
CP0 D	500	109	0	20.9	2018
CP0 E	500	126	0	12.1	915
CP0 F	500	85	2	17.3	1759
CP0 G	400	216	20	13.5	936
CP0 F + TCC C19	500	119	29	34.5	1759

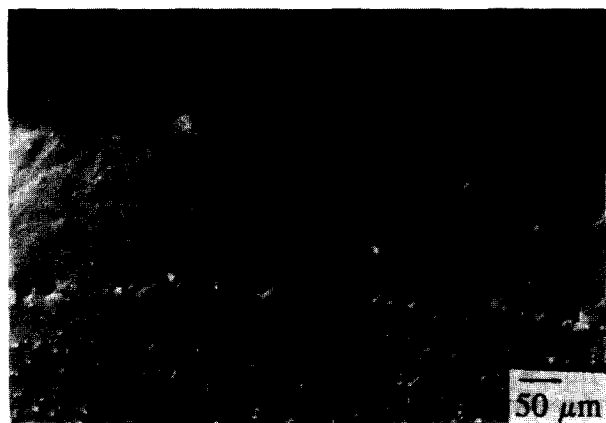


Fig. 2. Microstructure of the CP0 A coating after 500 cycles showing rumpling but no Al rich β -phase present.

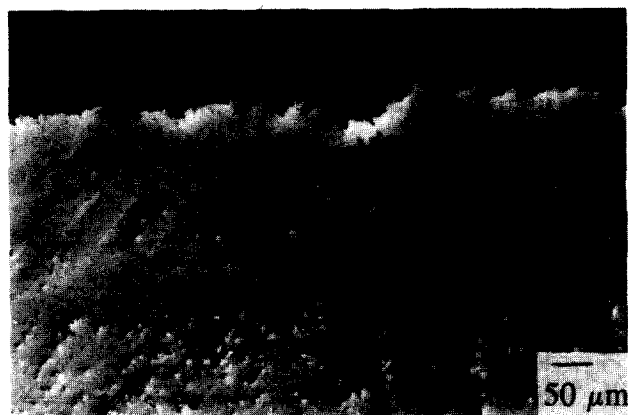


Fig. 3. Microstructure of sample CP0 E after only 208 cycles. The β -phase already appears to have disappeared and the coating is showing signs of rumpling



Fig. 3. Microstructure of the CP0 D coating after 208 cycles. There is still β -phase present in the coating. There is also evidence of crack initiation from the trough of a rumple.

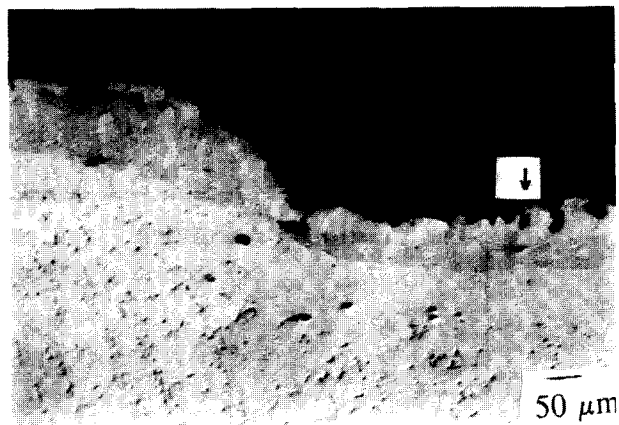


Fig. 5. The microstructure of the CP0 F overaluminized with TC C 73. There is still evidence of β -phase and the coating has begun to rumple. The arrow marks a region where the rumple is "falling over".

DISCUSSION

In high temperature cyclic oxidation the depletion of Al from the coating is often considered to be the rate controlling factor in the coating life. This generally occurs from the surface by oxide spalling. Ni and Co can also diffuse into the substrate causing a dilution in the Al concentration in the coating resulting in the β -phase going into solution. This dilution of Al in the coating can eventually result in a too low Al content for alumina to form. Once the situation has occurred where external alumina can no longer be formed internal oxidation of the coating occurs resulting in the more rapid oxidation penetration of the coating.

In this investigation some of the results suggested that depletion of Al is not the only controlling factor in the coating life. In the case of samples CP0 A and CP0 E (Figure 2 and 3) most of the overall Al (indicated by the amount of β -phase present in the coating) had been depleted by 500 cycles but the coating only failed after 745 and 915 cycles respectively. The cause of failure appeared to be a combination of internal oxidation and mechanical thinning of the coating. A reduction in coating thickness was observed in both samples suggesting that mechanical thinning as opposed to internal oxidation was the more predominant cause of failure.

In all the samples investigated a certain amount of rumpling was observed. Crack initiation at the troughs of the rumples was a common observation as depicted in Figures 4 and 5. These cracks are detrimental to coating as they increase the surface area of the coating exposed to oxidation. If the crack is sufficiently deep it can also provide an easy path for oxidation of the substrate and thus failure of the sample. In some cases the rumple peaks were found to "fall over". The arrow in Figure 5 shows the initiation of a rumple "fall over". This results in an oxidation site been formed in the coating. This internal oxidation of the coating then accelerates the failure of the coating.

As expected, the amount of rumpling occurring in the coatings investigated was found to be related to the composition of the coatings. From Table 3 it can be seen that for the MCrAlY coatings the samples the higher the Co content the more resistant the coating was to rumpling. (Sample CP0 B -CoCrAlY was more resistant to rumpling than CP0 E - a NiCrAlY coating). There maybe an apparent Si affect on the mechanical strength of the coating and thus the resistance of the coating to rumpling. The CP0 C and CP0 D coatings were NiCoCrAlY coatings containing Si and these were found to rumple less than the CP0 F coating which was a NiCoCrAlY coating with no Si. However, there is too little data at this stage to substantiate this effect. In the recent work by Peichl and Bettridge⁷ it appears that the addition of Re and Pt also improves the strength of MCrAlY coatings.

From Table 3 it can be seen that the addition of an overaluminized outer layer to the CP0 F coating reduced the frequency of rumpling. This is believed to be the result of the increased mechanical strength brought to the coating by the aluminide layer. However, as can be seen in Figure 6 brittle cracking of the outer aluminide coating occurred which appeared to stop at the MCrAlY interface. This resulted in the premature oxidation of the MCrAlY coating which accelerated the depletion of the Al reservoir.

CONCLUSIONS

1. Surprisingly, in the case of the MCrAlY coatings Al depletion was not always the controlling factor of the coatings resistance to high temperature cyclic oxidation.

2. The amount of rumpling was found to be dependant on the composition of the coating. Both Co and Si were found to improve the strength of the coating and thus reduce the amount of rumpling. As expected the overaluminizing of the MCrAlY coating also improved the strength of the coating.
3. The "new" degradation mode has to properly considered in any life acceptance effort. More studies in this field are required.

REFERENCES

1. Wood, J. H. & Goldman, E., Protective coatings. *Chapt 13. Superalloys II, Ed Sims, C. T., Stoloff, N. S. & Hagel, W.C.* (1987) 359-84.
2. Conner, J. A. & Connor, W. B., Ranking protective coatings: Laboratory vs. field experience. *JOM.* (1994)
3. Strangman, T. E. & Boone, D. H., Composition and processing considerations for the mechanical behaviour of coating-superalloy systems. *Proc 4th Conf. The behaviour of materials in marine environment.* (1979)
4. Strangman, T. E., Thermal fatigue of oxidation resistant overlay coatings for superalloys. *Ph.D. Thesis, University of Connecticut.* (1978)
5. Manley, T. F., Plastic instability of aluminide and platinum modified diffusion coatings during 1100°C cyclic testing. *Thesis ADA164506.* (1985)
6. Deb, P., Boone, D. H. & Manley, T.F., Surface instability of platinum modified aluminide coatings during 1100°C cyclic testing. *J. Vac. Sci. Technol. A5* (1987) 3366-3372
7. Wood, J. H. & Swede, S. T., Comparison of coating performance and degradation modes in heavy-duty land-based gas turbines. *Surface and Coatings Technology* 61 (1993) 1-5