ELSEVIER

Surface and Coatings Technology 76–77 (1995) 47–52

SURFACE & COATINGS TECHNOLOGY

Mechanical degradation of coating systems in high-temperature cyclic oxidation

R.C. Pennefather [a], D.H. Boone [b]

[a] *Division of Materials Science and Technology, CSIR, P.O. Box 395, Pretoria, South Africa*
[b] *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, which will be discussed elsewhere. Coating life was determined to be the time to coating penetration and initiation of substantial substrate attack. As this work was part of an effort to rank available coating systems for industrial gas turbine applications at relatively high temperature, an extensive testing programme was undertaken. During this test programme it was found that, in addition to the usual oxidation of the coating, another 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. While not a detailed study of the possible factors affecting "rumpling", the paper draws attention to its occurrence both in turbines and test rigs, and indicates that more attention must be given to its significant effects in coating evaluations and life assessments.

Keywords: Coatings; NCrAlY; Cyclic oxidation; High temperature

1. 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, avoid cracking and limit diffusion between the coating and substrate [1]. A review of some of the factors affecting the oxidation resistance of coatings and their testing will be presented elsewhere. The mechanical behaviour of the coating is, however, also of importance in high-temperature cyclic oxidation, which is a point not often considered in coating selection or life assessment.

Since real-time evaluation of different coating parameters (i.e. 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 is different from that observed when components are actually used in engines [2]. 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. Fig. 1 depicts an example of rumpling as a failure mode which occurred on a turbine blade after 12 000 h of service.

The mechanical properties of a coating depend on its

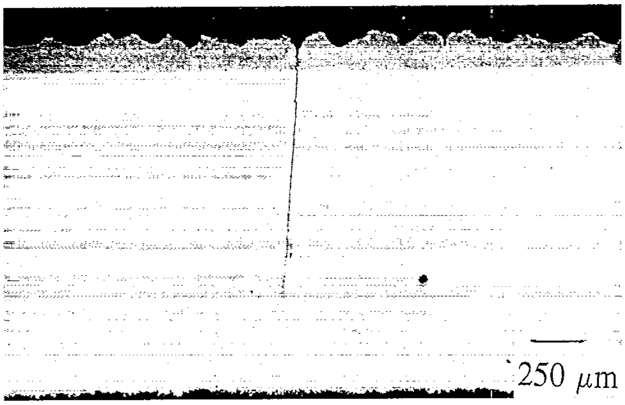

Fig. 1. Microstructure of a turbine blade after 12 000 h in service, showing rumpling with crack initiation from a rumple.

composition and the type of phase distribution. A high ductile–brittle transition temperature (DBTT) 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 coating substrate system with a low DBTT is placed into a ductile mode at lower operating temperature, reducing the probability of cracking-type failure.

Frequent and rapid changes of engine power, particularly power reductions and trips from generating loads, can lead to a significant tensile 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 spalling 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].

In addition, 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 a new phenomenon, and has been observed for a long time on thermal–mechanical fatigue-tested specimens. Strangman [4] included this surface-roughening phenomena in a thermal–mechanical fatigue life prediction model for coated superalloy turbine components. However, as service temperatures and duration times have increased, it is now a more important consideration in the prediction of oxidation life as well. Strangman [5] observed rumpling on MCrAlY overlay coatings subjected to intermediate temperature dwell periods during cyclic oxidation burner rig testing. In some literature it has been suggested that rumpling observed in some tests may be the result of sub-coating substrate melting. However, Manley [6] 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 al. [7] attributed the amount of rumpling observed to a number of possible effects. These include coefficient of thermal expansion (CTE) mismatch, the thermal gradient across the coated specimen, the mechanical properties of the coating and the strain and/or thermal cycle experienced by the coating. 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. It was established that for cyclic oxidation the CTE value for the coating is less than the CTE value for the substrate, and therefore the coating experiences compressive strain during cooling. The residual strain state at the start of the cooling cycle (and hence test hold time) 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 al. [7] to have a higher degree of rumpling irrespective of the initial coating structure and composition. The thicker coatings tended to increase the strains induced by thermal expansion mismatch, but with a postulated concomitant increase in aluminium content and presumably 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 structure. The brittle β-phase Al reservoir is in a more ductile γ-phase matrix. The ductile matrix has a CTE 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 under higher-temperature exposures and strains to increase the amount of the rumpling in the coating.

In more recent work, Peichl and Bettridge [8] studied the effect of different MCrAlY coating compositions on rumpling during high-temperature cyclic oxidation testing at 1050 °C. Both the CoNiCrAlY and the NiCoCrAlY coatings had similar failure modes: rumpling, crack initiation at the coating surface, crack propagation through the coating into the substrate with concomitant Al depletion. The NiCoCrAlY coating with Pt addition had an even higher thermal-fatigue resistance, and rumpling appeared to be less pronounced and little Al depletion was observed. The Re-containing CoNiCrAlY coating proved to be the most rumpling-resistant coating, and no cracks were observed in the test. 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 Bettridge [8] 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 Swede [9] tested over-aluminized 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, emphasizing the important role of the aluminide surface layer, whether by changing strength or CTE or both.

2. 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 overlay coatings. The coatings evaluated in that work were chosen to allow comparison between deposition methods as well as compositions, and the effect these parameters might have on the mechanical properties and the protective ability of the coating. As noted above, mechanical behaviour can play a strong role in this. The coatings tested are tabulated in Table 1. A platinum aluminide coating was also included for comparison purposes. All the coatings were deposited on to IN 738 pins of 7.5 mm diameter.

High-temperature cyclic oxidation testing was carried out in a laboratory rig. Fig. 2 graphically illustrates the heating/cooling profile of the furnace. An average of five samples were tested for each coating. During the testing, the samples were periodically removed and visually examined for substrate attack. Some samples were also removed at varying intervals and metallographically prepared for microstructural examination. At least two samples of each coating were tested to visual failure, which implies substantial observable substrate attack. The average cycles-to-failure figure of the coating was then recorded.

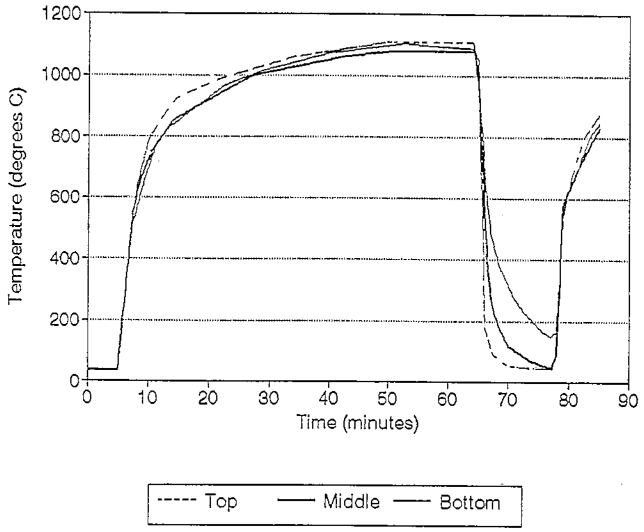

Fig. 2. Heating/cooling profile of the three zones in the cyclic oxidation furnace.

The average thickness of these samples was measured using an optical microscope using an average of 20 measurements. As part of a separate oxidation study, the amount of β-phase in the coating was determined using an image analyser. The percentage area of the darker β-phase in a set area of coating was measured. This was carried out in ten different regions of the coating. Quantifying the amount of rumpling occurring in the coating proved to be a difficult undertaking, as this effect was not isolated from other effects such as oxidation. The initial thickness of the coatings, an important factor, was not constant; thus no meaningful relationship between the amount of rumpling and the depth of the rumples could be made. For this reason, only the length of the rumples was used to qualitatively assess rumpling propensity.

Analysis of interdiffusion and oxidation of the coatings, which are also important degradation modes, will be presented elsewhere. This paper will concentrate on

Table 1
Properties of the coated test sample prior to testing

Designation	Deposition method	Coating composition (wt.%)	Thickness (μm)
CP0 Pt	Plate and pack	Pt-Al	110
CP0 A	LPPS	32%Co; 21%Cr; 8%Al; Y bal Ni	172
CP0 B	LPPS	29%Cr; 7%Al; Y bal Co	152
CP0 C	LPPS	32%Co; 28%Cr; 8%Al; Y; Si bal Ni	166
CP0 D	LPPS	23%Co; 18%Cr; 12.5%Al; Y; Si; Hf bal Ni	134
CP0 E	LPPS	25%Cr; 5%Al; Y; Ta; Si bal Ni	166
CP0 F	LPPS	23%Co; 18%Cr; 12.5%Al; Y bal Ni	125
CP0 G	HVOF	23%Co; 18%Cr; 12.5%Al; Y bal Ni	261
CP0 F + TCC C19	LPPS and pack	23%Co; 18%Cr; 12.5%Al; Y bal Ni + Al	156

Table 2
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 (μm)	β-phase content (%)	Rumpling length (μm)	Cycles to failure
CP0 Pt	500	115	61	132	635
CP0 A	500	168	0	174	745
CP0 B	500	146	0	241	500
CP0 C	500	126	2	231	650
CP0 D	500	109	0	209	2018
CP0 E	500	126	0	121	915
CP0 F	500	85	2	173	1759
CP0 G	400	216	20	135	936
CP0 F + TCC C19	500	119	29	345	1759

the surface instability of the coating observed and its effect on lifetime.

3. 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 2. Interestingly, all the coating combinations showed some degree of rumpling. The amount of β-phase was found to vary, as indicated in Figs. 3–5. In many cases no β-phase was observed after 500 cycles, as can be seen from Table 2. However, it should be noted that at these high temperatures the loss of β-phase does not necessarily mean a loss of ability to form a protective layer. The failure modes observed in these coatings were always a combination of oxide spalling, Al depletion and mechanical thinning as a result of the surface instability. This prevented any direct correlation being made between the amount of rumpling or β-phase present and the number of cycles to failure. Only inferences could be made from these results.

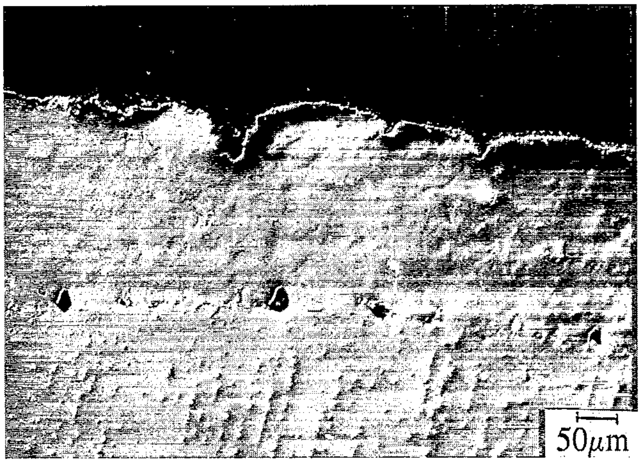

Fig. 3. Microstructure of the CP0 A coating after 500 cycles, showing rumpling but no Al-rich β-phase present.

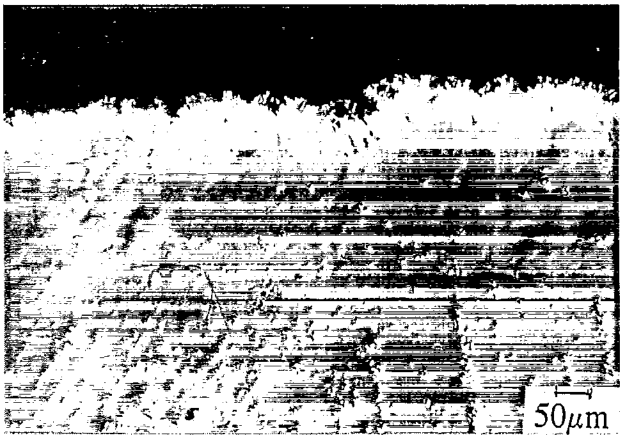

Fig. 4. Microstructure of the CP0 E coating after 208 cycles. The β-phase has been depleted and the coating is showing signs of rumpling.

Fig. 5. 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.

4. 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. Elements including Ni and Co can also diffuse from 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 too low an Al content for alumina to form, because of the presence of other elements which form competing and detrimental oxides, e.g. TiO_2. 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. This was observed to a certain degree in all the coatings studied.

However, in this investigation some of the results suggested that the depletion of Al was not the only controlling factor in the coating life. In the case of samples CP0 A and CP0 E (Figs. 3 and 4), most of the overall Al (indicated by the amount of β-phase present in the coating) had been depleted at 500 cycles, but the coating failed only after 745 and 915 cycles respectively. The cause of failure appeared to be a combination of internal oxidation of the coating and mechanical thinning of the coating. A significant reduction in coating thickness was observed in both samples, suggesting that mechanical thinning as opposed to simple oxidation degradation was the more predominant cause of failure.

As previously mentioned, a certain amount of rumpling was observed in all the coatings investigated. The more the coating rumples, the larger the surface area of the coating which will be exposed to oxidation, hence the faster the coating would be expected to degrade. It is thus suggested that rumpling combined with other degradation modes can result in accelerated failure of the coatings. In most life prediction work on very-high-temperature oxidation, this rumpling effect is not considered, which may result in incorrect predictions.

Crack initiation at the troughs of the rumples was also observed, as depicted in Fig. 5. These cracks are detrimental to the coating, as they once again increase the surface area of the coating exposed to oxidation and may further accelerate crack propagation. If the crack is sufficiently deep it can also provide an easy path for “short-circuit” oxidation of the substrate or the often vulnerable interdiffusion zone depleted by outward Ni diffusion, thus resulting in failure of the sample. The coating illustrated in Fig. 5 also shows evidence of the β-phase still being present. This suggests that rumpling-induced cracking may occur alongside Al depletion in the degradation 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. When considering coatings CP0 B, CP0 A and CP0 F, the apparent decrease in Co content (64%, 32% and 22%, respectively) resulted in the decrease of the rumple length from 241 μm to 135 μm. An increase in rumple length (or reduction in the frequency of rumpling) implies a decrease in the amount of rumpling.

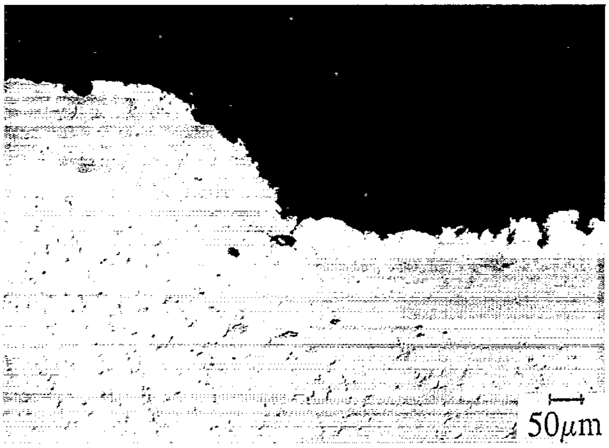

Fig. 6. Microstructure of the CP0 F coating, over-aluminized with a pack coating.

When comparing the length of the rumples for coating CP0 C (166 μm) and CP0 F (125 μm), it appears as though Si may also improve the rumpling resistance of the coating, although it is not readily clear why this should occur. However, data are insufficient at this stage to substantiate this effect. In the recent work by Peichl and Bettridge [8] it appears that the addition of Re and Pt also improves the strength of MCrAlY coatings and hence rumpling resistance.

An increase in the length of the rumples, hence an increase in rumpling resistance, was observed with the addition of an over-aluminized outer layer to the CP0 F coating (a rumple length of 345 μm as opposed to 173 μm for the CP0 F coating). This is believed to be the result of the reduced CTE difference with the substrate and/or increased mechanical strength brought to the coating by the aluminide layer. However, as can be seen in Fig. 6, brittle cracking of the outer aluminide coating occurred, which appeared to stop at the MCrAlY interface, as has been seen elsewhere. This resulted in the premature oxidation of the MCrAlY coating, which in turn accelerated the depletion of the Al reservoir.

5. Conclusions

1. In the case of the MCrAlY coatings, simple Al depletion was not always the controlling factor of the coating's resistance to high-temperature cyclic oxidation.
2. The amount of rumpling was found to be dependent on the composition of the coating. Both Co and Si were found in this investigation to improve the

strength of the coating and thus reduce the amount of rumpling. As expected, the over-aluminizing of the MCrAlY coating also improved the strength of the coating.

3. The results of this investigation suggest that rumpling enhances other modes of coating degradation. For this reason rumpling should be considered in any life prediction effort. More studies in this field are required.

Acknowledgements

The authors wish to thank Les Chapman of Liburdi Engineering Ltd., Canada for the cyclic oxidation testing.

References

[1] J.H. Wood and E. Goldman, in C.T. Sims, N.S. Stolloff and W.C. Hagel (eds.), *Superalloys II*, Wiley, New York, 1987, Chapter 13, p. 359.

[2] J.A. Conner and W.B. Connor, Ranking protective coatings: Laboratory vs. field experience, *J. Mater., 46* (12) (1994) 35.

[3] T.E. Strangman and D.H. Boone, Composition and processing considerations for the mechanical behaviour of coating–superalloy systems, paper presented at *4th Conf. The Behaviour of Materials in Marine Environment*, 1979.

[4] T.E. Strangman, Thermal–mechanical fatigue life model for coated superalloy turbine components, *Superalloys 92*, Minerals, Metal and Materials Society, Warrendale, PA, 1992.

[5] T.E. Strangman, Thermal fatigue of oxidation resistant overlay coatings for superalloys, *Ph.D. Thesis*, University of Connecticut, 1978.

[6] T.F. Manley, Plastic instability of aluminide and platinum modified diffusion coatings during 1100 °C cyclic testing, *Master's Thesis*, Naval Postgraduate School, Monterey, CA, ADA164506, 1985.

[7] P. Deb, D.H. Boone and T.F. Manley, Surface instability of platinum modified aluminide coatings during 1100 °C cyclic testing, *J. Vac. Sci. Technol. A, 5* (1987) 3366.

[8] L. Peichl and D.F. Bettridge, Overlay and diffusion coatings for aero gas turbines, in D. Coutsouradis (ed.), *Materials for Advanced Power Engineering, Part 1*, Kluwer, Dordrecht, p. 717.

[9] J.H. Wood and S.T. Swede, Comparison of coating performance and degradation modes in heavy-duty land-based gas turbines, *Surf. Coat. Technol., 61* (1993) 1.