

Protecting Gas Turbine Components

THE RELATIVE DURABILITY OF A CONVENTIONAL AND A PLATINUM-MODIFIED ALUMINIDE COATING

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One of the major maintenance problems for gas turbine engine operators is the degradation of high pressure turbine blades and vanes. The Australian Department of Defence was experiencing unacceptably high rejection rates of these components in one of its high performance engines as a result of severe hot corrosion attack. Accordingly a programme was initiated to find a more durable coating than the conventional aluminide coating supplied for the first-stage blades by the engine manufacturer. The coating chosen for the trial was a platinum-modified aluminide coating. Metallographic examination of both coating systems after 750 hours of service in an operational aircraft clearly established the superiority of the platinum-modified coating. This coating has now been adopted by the Australian Defence Force as the specified coating for first-stage blades in this engine.

A major problem facing operators of gas turbine engines is the high temperature degradation of the high pressure turbine (HPT) blades and stator vanes. In most engines these components determine the time-between-overhaul periods which, in turn, are a major factor in determining the cost of ownership of the engines. The Australian Defence Force has been experiencing unacceptably high rejection rates of HPT blades and vanes from one of its high performance gas-turbine engines. The major cause of this rejection was a phenomenon known as hot corrosion, which is defined as the combined attack of high temperature combustion exhaust gases (which are oxidising and commonly sulphur bearing) and condensed phases (which are commonly salts ingested with the intake air) on the surface of a component.

A component is rejected as unfit for further service when corrosion products have breached the protective surface coating and penetrated the underlying substrate alloy, degrading its mechanical behaviour. Hot corrosion is controlled, therefore, for as long as the protective coating is not breached.

The specified coating on the first-stage HPT blades was a conventional diffusion aluminide that was applied by a pack-cementation diffusion process. At full overhaul, after approximately 1000 hours of operation, at least 95 per cent of all first-stage blades were rejected because of unacceptable hot corrosion attack.

Accordingly, it was decided to try to identify an alternative coating with superior protective properties. A commercially available platinum-modified aluminide coating was chosen from a number of possibly suitable coatings to undergo engine trials to compare its performance with that of the original coating under identical conditions. Platinum-modified aluminide coatings were first developed in Germany in the early 1970s (1). Since then considerable efforts have been made to develop and test commercially viable platinum-modified aluminide coatings (2-5), although much of the work has not been reported in the open literature. Wing and McGill reviewed the development of such protective coatings and described in detail the particular platinum-modified aluminide coatings, JML-1 and JML-2, that resulted from a

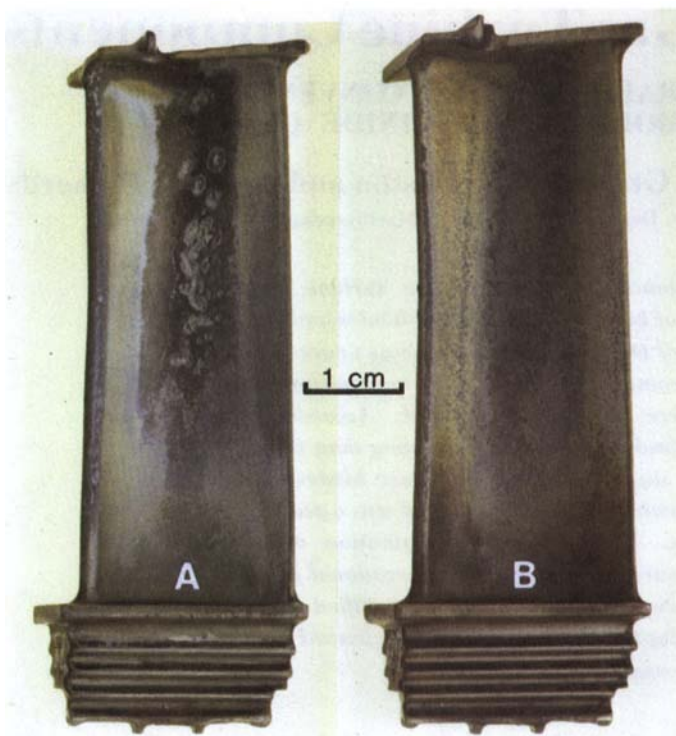


Fig. 1 First-stage turbine blades from the test engine after 750 hours. Blade A was coated with a diffusion aluminide and shows marked corrosive attack, while Blade B was coated with a platinum-modified diffusion aluminide and exhibits a significant improvement in the protection of the substrate alloy

collaborative exercise involving Rolls-Royce and Johnson Matthey (4).

The platinum-modified diffusion aluminide coating used in this trial was produced by electroplating a layer of platinum onto the aerofoil surfaces of the blades prior to a pack-diffusion aluminising process. The "test" wheel, with approximately half of the first-stage turbine blades coated with the original coating and the other half with the platinum-modified coating was fitted to an engine, which was then installed in an operating military aircraft for the trial. To the best of our knowledge, this was the first use of platinum-modified aluminides in a military gas turbine, although such coatings have been used by some commercial airline companies.

Both types of coated blades were removed from the wheel after approximately 520 hours and 750 hours of engine operation for metallographic examination and comparison. The results obtained from the 520 hours inspection have been reported elsewhere (6, 7); those

of the 750 hours examination are presented in this paper. A more complete description of the results obtained at this time is the subject of an Australian Department of Defence report (8).

Metallographic Examination of Blades

A marked difference in the appearance of each type of coating after both 520 hours and 750 hours of engine operation was clearly visible. An example of the appearance of the blades after 750 hours of engine operation is shown in Figure 1. The blades coated with the original diffusion aluminide exhibited marked corrosive attack of the leading edge and concave side of the aerofoil. Corrosion pits were evident along the centre of the concave side of the conventional diffusion aluminide coated blades, but not on the platinum-modified coated blades. The original diffusion aluminide coated blades showed extensive corrosion of the outer shrouds and some corrosion of the root platforms. The platinum-modified aluminide

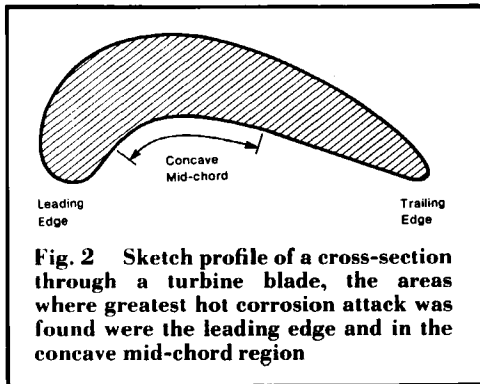


Fig. 2 Sketch profile of a cross-section through a turbine blade, the areas where greatest hot corrosion attack was found were the leading edge and in the concave mid-chord region

blades appeared to have experienced much less corrosion in these areas.

Blades with each type of coating were cut into ten cross-sections of approximately equal

thickness between, and parallel to, the root thick platforms and the shrouds. After nickel plating, to retain the surface oxide, the sections were then mounted and polished for metallographic examination.

As found previously (6, 7), extensive corrosion of the leading edges and concave mid-chord regions, delineated in Figure 2, of the original diffusion aluminide coated blades occurred. In these areas the products of hot corrosion were evident at considerable depths into the alloy beneath the coating, see Figure 3. The coating had been breached on each blade examined.

The blades coated with the platinum-modified aluminide similarly exhibited the most severe attack at the leading edge and concave

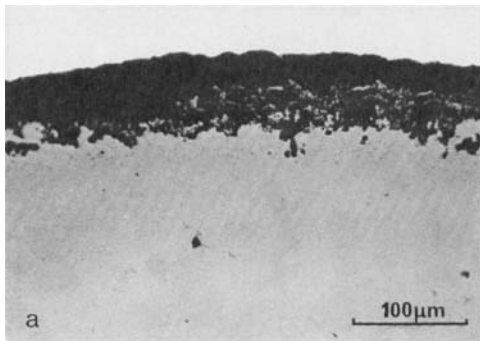


Fig. 3a This cross-section taken through the diffusion aluminide coating after 750 hours of operation shows the leading edge of the blade where no intact coating remains

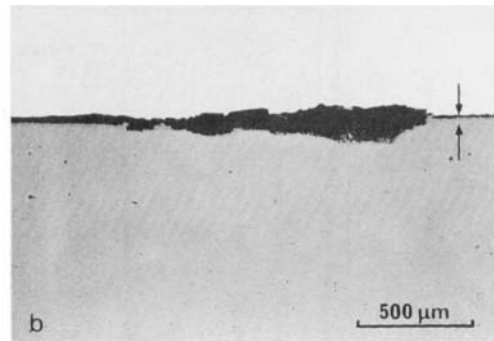


Fig. 3b This cross-section from the mid-chord region shows, between the arrows, an area where the diffusion aluminide coating is intact after 750 hours of operation

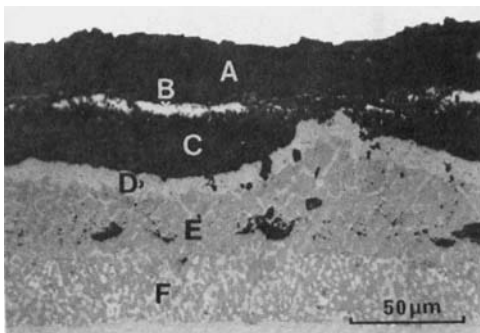


Fig. 4 Cross-section through a platinum-modified aluminide coating in the concave mid-chord region after 750 hours operation, areas marked A-F are referred to in the text

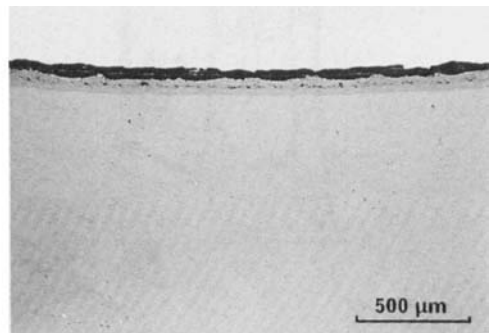


Fig. 5 The platinum-modified aluminide coating in the concave mid-chord region has corroded, after 750 hours forming a series of wide, shallow pits

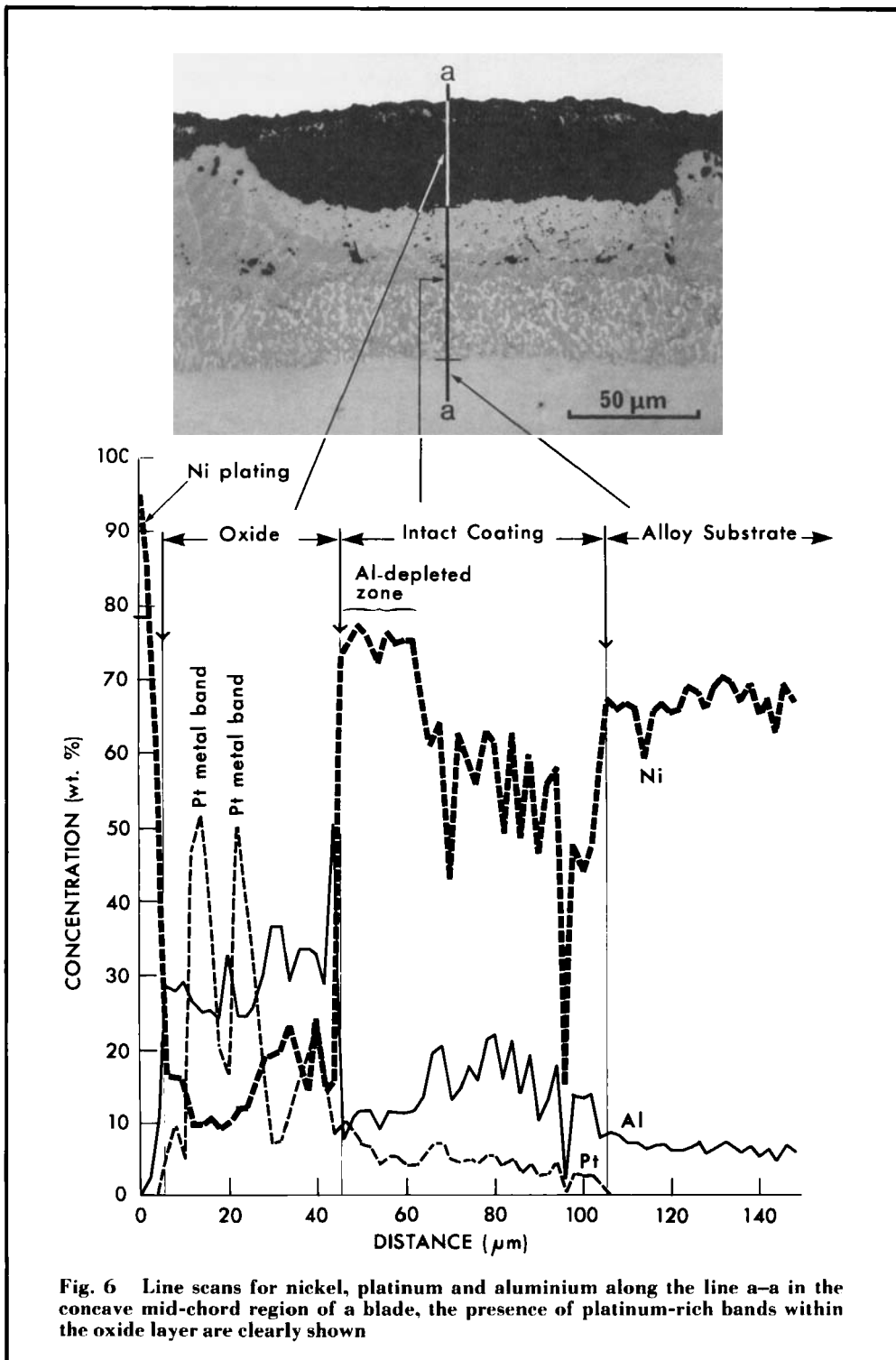


Fig. 6 Line scans for nickel, platinum and aluminium along the line a-a in the concave mid-chord region of a blade, the presence of platinum-rich bands within the oxide layer are clearly shown

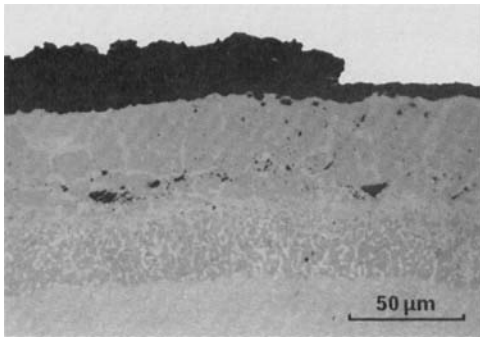


Fig. 7 This region of the leading edge of a blade coated with the platinum-modified aluminide shows an area where the coating is in good condition after 750 hours service. The oxide scale shows spallation and/or erosion

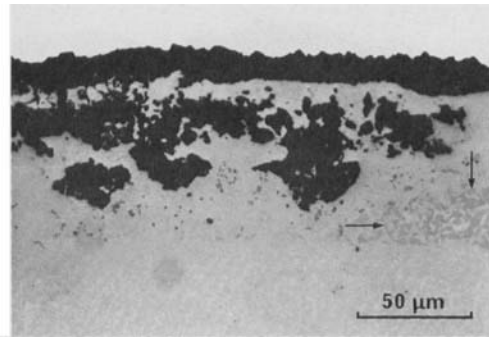


Fig. 8 Near the leading edge of a blade coated with the platinum-modified aluminide extensive internal oxide is present and the diffusion zone of the coating (arrowed) has partially disappeared

mid-chord regions. However, the coating remained intact over the length of the blade, with maximum attack occurring at approximately two-thirds of the aerofoil length up from the root platform. Even in the section where maximum attack of the concave face occurred, more than 50 per cent of the coating remained intact, as can be seen in Figure 4. The attack in this concave mid-chord region of the blades commonly formed a series of wide, shallow pits, as shown in Figure 5. Electron microprobe analyses of the areas marked in Figure 4 showed the presence of:

- (A) a continuous outer oxide rich in aluminium and oxygen
- (B) a metallic band, rich in nickel and platinum, which appeared to be near the position of the original surface of the coating
- (C) an oxide, which appeared to be porous, in the pit beneath the metallic band, and which was rich in aluminium and contained small amounts of nickel and platinum
- (D) a metallic coating zone, which was depleted in aluminium and had the approximate composition Ni_3Al
- (E) a coating zone, which resembled the original, intact, coating
- (F) a typical interdiffusion zone

The various zones of corrosion in the pits were further defined by simultaneous line scans

for platinum, nickel and aluminium, as shown in Figure 6. The line scans clearly define the presence of bands of platinum-rich metal within the oxide. In some areas the concentration of platinum was close to 70 weight per cent.

Again, in marked contrast to the original diffusion aluminide coating, the remaining thickness of the platinum-modified aluminide coating at the leading edge of the blades was greater than 50 per cent of the original thickness of the coating. The oxidation front, as defined by the oxide/metal interface, was uniform, in contrast to the pits found on the concave side of the blades. A microstructure typical of a position where the platinum-modified coating was in good condition, at the tip of the leading edge of a blade, is shown in Figure 7. A sharp variation in the thickness of the protective oxide scale, indicative of local spallation and/or erosion, is evident in this micrograph. Some areas of the coating in the vicinity of the leading edge contained extensive internal oxides, such as those shown in Figure 8. Area scans of a similar region, shown in Figure 9, clearly indicate the presence of alumina, both on the surface of the coating and within the coating, as well as the characteristic platinum-enrichment of the outer region of the coating. Quantitative analyses of the various phases present in the coating, marked in Figure 10, are given in the Table. These analyses show that the bulk of the coating surrounding these

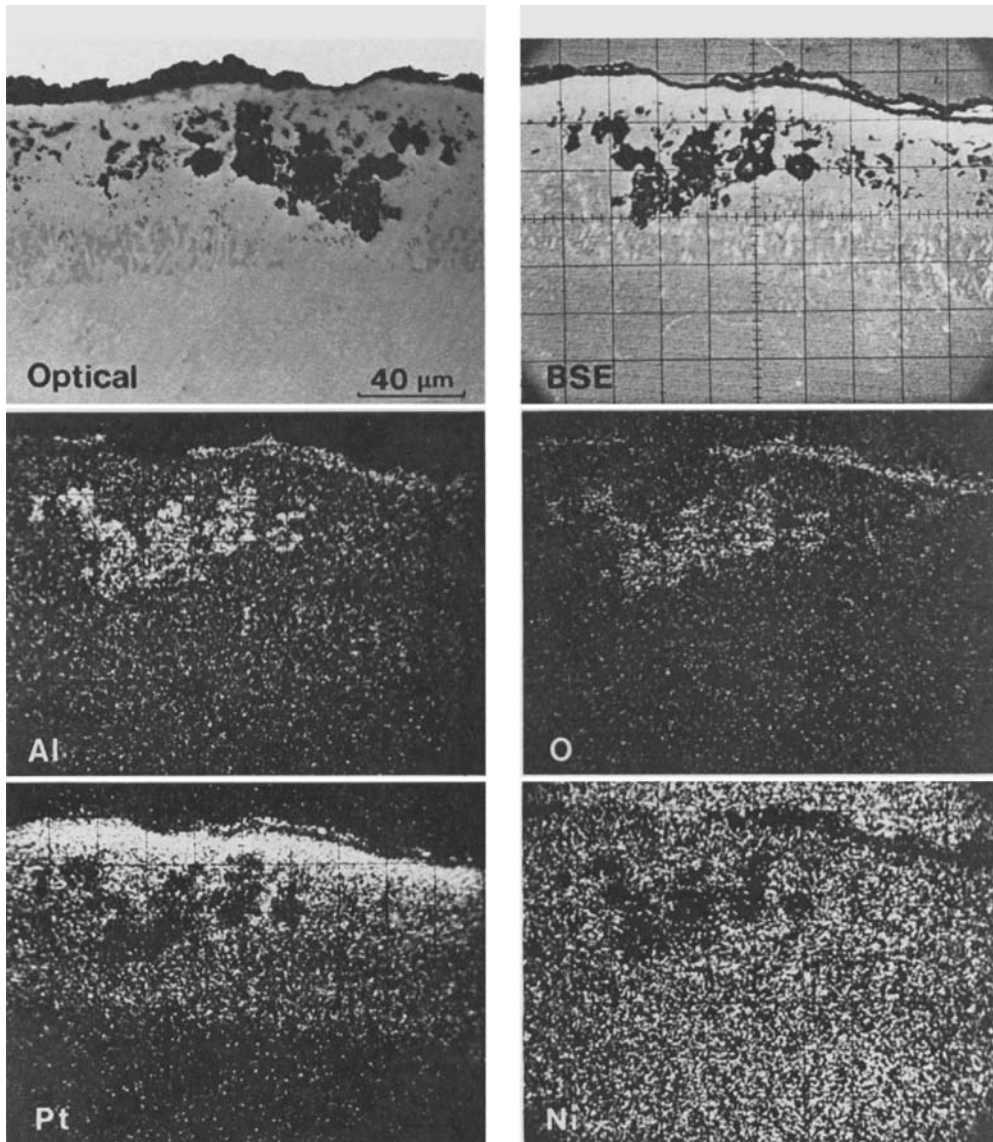


Fig. 9 Optical micrograph and electron probe microanalysis back-scattered electron (BSE) and element area scans for aluminium, oxygen, platinum and nickel of a region near the leading edge of a blade coated with the platinum-modified aluminide. The back-scattered electron image is a mirror image of the optical micrograph

internal oxides has been depleted of aluminium, producing a phase similar to area **D** of Figure 4. Interaction between the particles of oxides and the coating has resulted in the partial, or complete, removal of the β (NiAl) phase from the coating. Simultaneous line scans for platinum, nickel and aluminium through such an area of the coating are illustrated in Figure 11. Except

for the characteristic enrichment of platinum in the outer zone of the coating, there are no distinctive zones within the coating. The concentration of aluminium within the metallic part of the coating is uniformly low.

On the convex side of the blades coated with the platinum-modified aluminide there was only slight coating degradation and the coating

appeared to be in very good condition. A typical microstructure is shown as Figure 12.

Discussion

Examination and comparison of the platinum-modified aluminide and original diffusion aluminide coated blades from the test engine after approximately 520 hours of engine operation revealed significant differences in their protective capabilities (6, 7). This examination, after a further 230 hours of engine operation, further illustrates the significant difference in durability of the two types of coating.

The extensive attack of the conventional diffusion aluminide coating noted at 520 hours had steadily progressed so that, after 750 hours of operation, there was complete breaching of the coating at areas on the concave side of the blade and almost complete degradation and

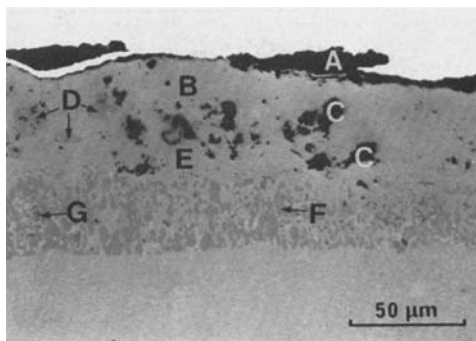


Fig. 10 These areas of the internal oxide, marked A-G, are referred to in the Table

consumption of the coating at the leading edge.

In marked contrast, the platinum-modified aluminide coating still provided a considerable degree of protection for the substrate alloy of the blade, in that less than 50 per cent of the coating was consumed in the vicinity of the

Quantitative Analyses of the Areas Labelled in Figure 10, in weight per cent										
Atomic percentages are given in round brackets										
Element wt. % (at. %)	Ni	Al	Pt	Cr	Co	Ti	Ta	O	C	Predominant Phase
A	2.6 (0.1)	42.9 (31.6)	Distributed as discrete particles within the oxide					43.3 (54.0)	8.7 (14.3)	Al ₂ O ₃
B	41.2 (53.5)	6.7 (18.6)	42.8 (16.5)	1.5 (2.1)	7.7 (9.3)	0.1 (0.1)				possibly (Pt _x Ni _{3-x})Al
C	An inhomogeneous oxide, the major phase present is Al ₂ O ₃									Al ₂ O ₃
D	48.9 (45.3)	20.8 (42.2)	22.2 (6.2)	1.9 (1.1)	6.1 (5.2)					NiAl
E	66.4 (64.8)	10.2 (21.6)	12.0 (3.1)	2.3 (2.1)	7.8 (7.2)	1.3 (1.1)				Ni ₃ Al
F	54.0 (44.9)	23.7 (42.8)	9.1 (2.0)	4.0 (3.1)	9.3 (7.2)					NiAl
G	14.8 (15.5)	2.0 (4.6)	0 (0)	1.4 (1.7)	2.3 (2.4)	10.1 (12.9)	61.2 (20.8)		present (41.9) (remainder)	carbide

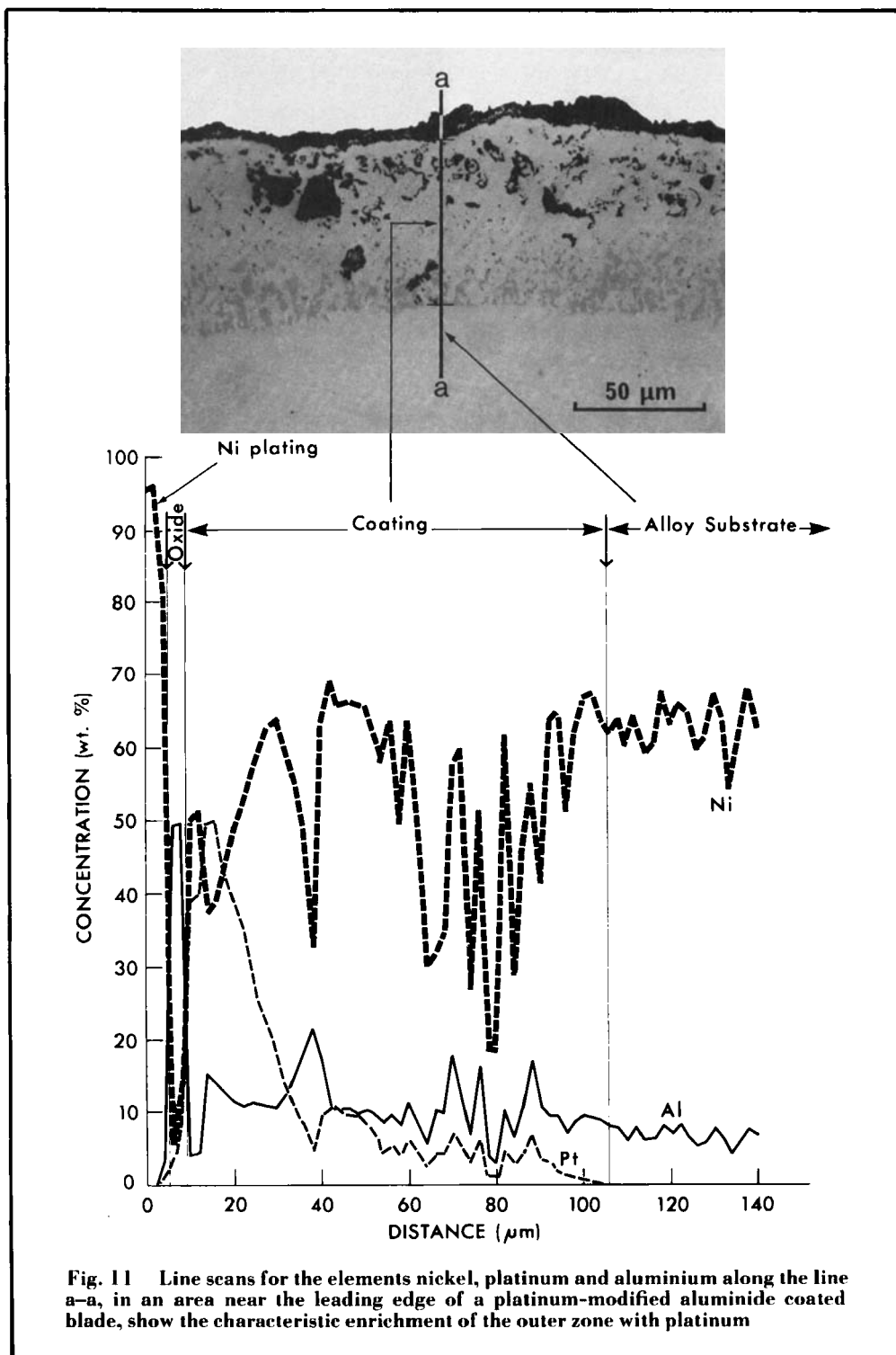


Fig. 11 Line scans for the elements nickel, platinum and aluminium along the line a-a, in an area near the leading edge of a platinum-modified aluminide coated blade, show the characteristic enrichment of the outer zone with platinum

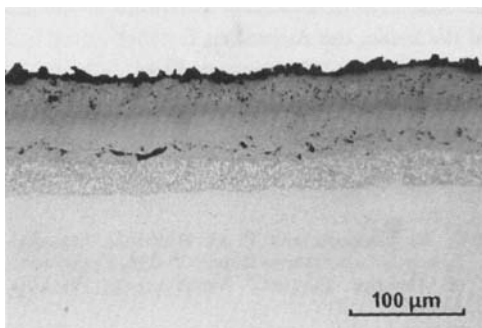


Fig. 12 On the convex side of a platinum-modified aluminide coated blade the coating appears to be in a very good condition

concave mid-chord and leading edge regions, that is at the points of greatest attack.

One feature of the corrosion attack that has not been reported before concerns the presence of alumina particles distributed through the platinum-modified coating, particularly in the vicinity of the leading edge. Such particles were also present after 520 hours of engine operation (6, 7) and the coating vendor proposed that they were alumina grit-blast particles which were entrained in the surface after the blades were cleaned, prior to the deposition of platinum and the subsequent aluminising process. However, the distribution and size of these particles is dependent on their position around the perimeter of the blade and they also appear to alter substantially with time in the engine. A large network of particles is present around the leading edge of the blades, suggesting that their growth is perhaps catalysed by the presence of mechanical stress, possibly as the result of erosive particles striking the blades in this region. The alloy adjacent to the alumina particles within the coating has become depleted in aluminium to such a large extent that, in some regions, the β (NiAl) phase which should be present, as it is in Figure 7 and area D in Figure 10, has been converted almost entirely to the γ' (Ni_3Al) phase, see Figures 8 and 10 and also the Table. This leads to the inference that aluminium within the coating reacts with oxygen ahead of the oxidation front (as defined by the surface oxide/metal interface) to increase the size of the internal alumina

particles and consequently deplete the metallic part of the coating of aluminium. One consequence of this mode of coating degradation is that although 50 per cent of the coating thickness remains, the reservoir of aluminium available to form the protective surface oxide has diminished by a larger factor.

It remains to be seen whether the platinum-modified aluminide coating will remain intact at the full overhaul life of 1000 hours of engine operation, but the present results indicate that a relatively low rejection rate is to be expected.

Conclusions

A platinum-modified aluminide coating has been shown to be superior to a conventional diffusion aluminide coating in the protection it imparts to first-stage turbine blades in a military gas turbine engine operating under conditions conducive to severe hot corrosion attack. After 520 hours of engine operation the original diffusion aluminide coating was breached in some areas whereas, in contrast, after 750 hours of engine operation the platinum-modified aluminide coating remained unbreached. In fact the latter coating still retained 50 per cent of its original thickness in the areas of greatest attack. Near the leading edge, alumina particles situated in the platinum-modified coating below the oxide scale/coating interface have grown substantially in size, presumably by aluminium in the coating reacting with inwardly diffusing oxygen ahead of the oxidation front. This internal oxidation has produced a substantial reduction in the concentration of metallic aluminium in the coating, decreasing the reservoir of aluminium that is available to form the protective alumina scale. These areas, adjacent to the leading edge, are likely sites for subsequent breakdown of the coating with further use.

In the concave mid-chord region of the platinum-modified aluminide, attack has occurred in the form of wide, shallow pits. A distinguishing feature of these corrosion pits is the distinctive metallic band, rich in platinum, which appeared to be at or near the position of the original surface of the coating.

The platinum-modified aluminide coated blades are fit for re-use after 750 hours of engine operation and there is a high probability that they will be fit for re-use at full overhaul, that is after 1000 hours of engine operation.

Because of this substantial extension to the life of the blade, the Australian Defence Force had adopted the platinum-modified aluminide coating as the specified coating on first-stage blades in this engine.

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An Effective Oxygen Evolution Catalyst

In order to expedite the efficient photocleavage of water into hydrogen and oxygen using solar energy, catalysts must be efficient, stable, specific and fast-acting towards the reduction and oxidation of water. A great deal of progress has been made in the design of hydrogen evolution catalysts using for example colloidal dispersions of platinum, but the search for oxygen generation catalysts has been less successful and results reported on the activity of hydrated ruthenium dioxide ($\text{RuO}_2 \cdot x\text{H}_2\text{O}$) in this regard have been inconsistent and difficult to repeat. Now, however, workers at University College, Swansea have reported that pretreatment of hydrated ruthenium dioxide at 144°C for five hours gives an active, stable reproducible catalyst (A. Mills, C. Lawrence and R. Enos, *J. Chem. Soc., Chem. Commun.*, 1984, (21), 1436-1438). Yields of 97 to 98 per cent oxygen were obtained from the test reaction represented by the equation:

$$4\text{Ce}^{4+} + 2\text{H}_2\text{O} \xrightarrow{\text{RuO}_2 \cdot x\text{H}_2\text{O}} 4\text{Ce}^{3+} + 4\text{H}^+ + \text{O}_2$$

Conversion of the RuO_2 to gaseous RuO_4 can compete with the oxygen evolution reaction resulting in loss of ruthenium and low oxygen yields. In a series of experiments Mills found that the oxygen yield was inversely related to ruthenium loss as RuO_4 and depended on the temperature previously used for the heat-treatment of the $\text{RuO}_2 \cdot x\text{H}_2\text{O}$. From experiments in which samples of the catalyst were preheated at temperatures from 60 to 900°C it was clear

that optimum yields of oxygen were obtained with the samples heated at about 140°C (97 to 98 per cent yield). With higher treatment temperatures, the catalytic activity of the samples decreased, probably due to a lowering of the surface area, but no conversion to RuO_4 took place. Thermal gravimetric analysis of commercial samples of hydrated ruthenium dioxide indicated water contents of 19 to 24 per cent, but after treatment at 144°C for five hours, the water content was 7 to 10 per cent.

Mills concludes that the ability to catalyse the oxidation of water and the instability to anodic corrosion (that is conversion to RuO_4) are both related to the amount of water weakly bound to the powder, and both reactions possibly involve the same reaction sites. The tendency to loss of RuO_4 can be removed by the heat treatment. Much of the controversy surrounding the use of hydrated ruthenium dioxide as an oxygen catalyst may therefore be rationalised in terms of the degree of hydration, which may vary from one sample to another but heat treatment at about 140°C for five hours does give a stable, active and reproducible oxygen release catalyst.

These results represent an important step along the pathway towards viable catalyst systems for the water-splitting reaction, and should help to clarify the significance of earlier reports on the use of ruthenium dioxide for oxygen generation.

D.T.T.