The Protection of Gas Turbine Blades

A PLATINUM ALUMINIDE DIFFUSION COATING

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Turbine blades in gas turbine engines operate at elevated temperatures and in highly oxidising atmospheres that can be contaminated with fuel residues and sea water salts. These components, which are expensive to produce, are subjected to high stresses during operation but must be totally reliable during their design life. An economic way to maintain blade properties is to coat the base metal superalloy with a protective layer capable of resisting both high temperature oxidation and hot corrosion. Conventional aluminide coatings are widely used for this purpose but platinum aluminides offer improved corrosion resistance. A collaborative exercise involving Rolls-Royce and Johnson Matthey has now resulted in the development of a platinum aluminide diffusion coating that offers some advantages over the commercial systems.

The gas turbine engine was first developed some forty years ago and by the early 1950s it was a commonplace power unit for both military and civil aircraft. However, in more recent years the gas turbine has become the prime power unit in many diverse applications including military and commercial land transport and marine propulsion systems. It is in the latter role where the greatest number of corrosion problems occur, these being particularly severe within the turbine section of engines used in ships, hovercraft and helicopters. In each of these engine applications a high ingestion rate of salt laden air is inevitable and, although sophisticated air filtration systems are employed in most cases, sea water residues can always be detected downstream of the filtration devices; in the most arduous conditions, such as those encountered during helicopter rescue missions, sea water itself can be ingested into the working engine, see Figure 1.

The combination of high turbine operating temperatures and the presence of ingested sulphate and chloride salts, apart from fuel contaminants such as sulphur and vanadium, can lead to severe blade attack which often results in the premature rejection of very costly turbine components; this attack is termed hot corrosion or sulphidation.

The majority of gas turbines in current service rely upon the use of conventional nickel aluminide diffusion coatings to protect superalloy turbine components from both oxidation and hot corrosion, but in the more extreme environments, predicted turbine blade lives are not being achieved. This breakdown of the protective coating can result in severe metal loss from the blade alloy, as illustrated in Figure 2.

There are three solutions to this problem:
1. Improve the filtration system and use high quality, low contaminant fuels
2. Develop more corrosion resistant blade alloys (1, 2)
3. Develop improved coating systems.

All of these areas have and are being examined but it is the latter solution that
provides the most scope, and attention is specifically given to it in this article and particularly to the development of platinum aluminide coatings.

Although the development of more corrosion resistant blade alloys would appear to be an attractive alternative, the trend in recent years has been towards increased temperature capability but alloys designed for this purpose are inherently less corrosion resistant than their predecessors.

A General Background to Coating Technology

The conditions in which components operate in gas turbines are extreme, and the role of coatings is to protect turbine blades from the environment, ideally, for the design life of that part, whether it be creep or thermal fatigue that is seen as the limiting factor.

Currently, turbine entry temperatures range from approximately 650°C for industrial and marine engines to approximately 1300°C for the high performance aero engines, although in practice air cooling reduces the blade metal temperature, with 850 to 900°C being a realistic temperature range for the latter application. Additionally, in these days of rising costs, commercial operators require blades to last as long as possible with 5000 to 10,000 hours being typical for aero engines, and 100,000 hours for industrial turbines. It is against this background of blade metal temperatures and required life that coatings have been developed, but the effects of engine environment must also be considered.

The atmosphere in which turbine blades operate is generally highly oxidising with pressures of 10 to 20 atmospheres of oxygen, nitrogen, carbon dioxide and water vapour being seen in aero engines; additionally, fuel residues such as vanadium and sulphur, and ingested salts, can be present, with typical levels of 0.02 to 5 ppm of sea water salt being seen in
marine operation. Apart from the inherently corrosive nature of the turbine environment it can also be erosive when ingested dust is present or when carbon particles are released from the combustion chamber.

The prime role of a coating is to protect the blade substrate alloy against oxidation and hot corrosion (3, 4), but at the same time it must also possess some degree of erosion resistance and be able to tolerate minor impact damage. In addition it should withstand the mean blade stress due to the imposed centrifugal force (of the order of 150 MPa in some aero engines) and also resist the stresses caused by both thermal and mechanical fluctuations.

There are a variety of processing methods for producing turbine blade coatings but each must satisfy a number of essential requirements. The process must be able to produce uniform, controlled thickness coatings on complex geometry parts which are metallurgically bonded to the substrate alloy. Although gas turbine technology is inherently expensive, the cost of coating cannot be ignored and must be considered against the unit blade cost especially when coating small or solid blading.

The most widely used coating technique in current operation is that of pack cementation. This is generally considered a chemical vapour deposition process in which the element to be deposited is transferred to the surface of components by means of a volatile metal halide. The production of aluminide coatings by this method is one of the most economical and well proven process routes (5). An alternative technique for producing aluminide coatings is that of the slurry process, in which a slurry containing the required element is deposited onto the surface of the component; this is then dried and heat treated to achieve the required diffusion coating. However, this route has a number of disadvantages, a major area of concern being the handling of components during processing.

As well as the coatings that are formed by diffusion techniques, an important group of coatings, normally referred to as the MCrAlY overlays (M is cobalt or nickel), have been developed as corrosion resistant compositions and are applied to engine components by either physical vapour deposition (PVD) techniques or plasma spraying. Post coating processing is normally required to achieve metallurgical integrity of the coating.

Since current commercial coatings do not possess sufficient corrosion resistance, particularly when used in the more severe environments, coating technology is in a state of continual development. The areas of coating technology which are considered to offer the greatest potential for satisfying future engine demands are (i) constitutionally modified aluminides, (ii) platinum or platinum group metal aluminides (6, 7), (iii) constitutionally modified MCrAlY overlays (8-11) and (iv) platinum or platinum group metal modified MCrAlY overlays (12, 13).

At the present time interest is centred around further developments of MCrAlY overlay and platinum aluminide systems. Examples of each of these systems are commercially available, and have shown in both engine and burner rig tests to offer a significant improvement in corrosion resistance over the conventional nickel aluminide diffusion coatings currently in widespread use. Apart from improved corrosion resistance, engine testing has also identified a major difference between the two systems in that aluminide coatings can exhibit an inherent lack of ductility when subjected to either thermal or mechanical cycling.

It should be emphasised that the generally accepted brittle coatings as understood by microstructure type, can withstand cyclic conditions in the engine as long as the lower blade operating temperature lies above the brittle to ductile transition temperature (DBTT) of the coating.

The low aluminium β-NiAl phase of an aluminide diffusion coating for example, can accommodate an approximate 1 per cent tensile strain at 650°C with true deviation from brittle behaviour occurring at 540°C (14); the equivalent temperature for transition from brittle to ductile behaviour for the high aluminium β-NiAl phase is approximately 815°C. The various temperatures quoted will,
however, vary depending upon the actual constitution of nickel aluminate structures produced by different techniques. The DBTT for the MCrAlY overlays, however, generally lies between 350 and 500°C and hence these coatings can withstand a wider range of engine operating cyclic conditions.

Considerable evaluation of the MCrAlY and modified MCrAlY overlay coatings has taken place and a general understanding of the metallurgy of these systems is already known; the CoCrAlY overlays offer superior protection in hot corrosion environments while the NiCrAlY systems have the advantage in resisting high temperature oxidation. However, there is considerable impetus to develop these coatings further, and noble metal and other rare earth additions are being explored as alloying elements.

Although the overlay coatings are especially suited to military type engine applications where rapid and large temperature fluctuations can normally be expected, the modified aluminites and in particular the platinum aluminites are strong competitors in other engines where the reduced ductilities of these coatings can be tolerated. Platinum aluminites also show a real cost advantage when compared to the overlays for the same application. Further modification to improve the platinum aluminate system would appear to be a worthwhile objective.

**Platinum Aluminide Coating Systems**

The concept of the platinum aluminate coating system is historically attributed to Dr. Lehnert with the original British Patent being published in 1970 (15). The first commercial coating system, designated LDC–2, was developed jointly by Lehnert and Meinhardt (7) and marketed by a German company (Deutsche Edelstahlwerke Aktiengesellschaft); this first coating was produced by initially electrodepositing a platinum layer less than 10 microns thick onto a nickel base alloy and subsequently aluminitising the platinised component for several hours at approximately 1050°C. Since 1970 the process has been licenced by the American based companies, Chromalloy American Corporation and Howmet Turbine Components Corporation, and each has
produced its own commercial platinum aluminide coating, designated RT-22 and LDC-2A respectively.

As far as the authors are aware the commercial platinum aluminide coating systems have been developed on an empirical basis, and involve the use of a platinum electroplating technique prior to a high temperature pack aluminising process, which is essentially the original specification for LDC-2. Although some modifications to the aluminising cycle and pack composition may have been implemented more recently, platinum is still deposited by conventional electroplating.

The commercially available platinum aluminide coatings have now been extensively evaluated in burner rig trials and selected test engines by Rolls-Royce, other engine manufacturers and independent research organisations, and have shown a substantial improvement in hot corrosion and oxidation resistance compared to conventional aluminide coatings. Although systems such as LDC-2A and RT-22 generally perform well in the turbine environment, certain aspects of the total processing route could be improved to achieve a more consistent product.

The deposition of platinum by electroplating is a simple and well established process but deposits are usually hard, may be highly stressed and are particularly prone to porosity. Additionally, poor cleaning procedures prior to electroplating can cause entrapment of non-metallic deposits between the substrate and the platinum overlay, leading to poor adhesion and incomplete diffusion of aluminium and platinum during the aluminising process. A typical example of this type of defect is shown in Figure 3.

Potentially the most serious of these problems is that prolonged times at high temperatures during aluminising, with subsequent slow cooling from the process temperature, can affect the morphology of the \( \gamma'(\text{Ni},\text{Al}) \) ageing precipitate of the substrate alloy. In some of the more complex superalloys these changes appear to be non-recoverable, and subsequent heat treatments do not restore the original \( \gamma' \) morphology; testing has shown that some loss of creep strength can be associated with this effect.

**An Improved Platinum Aluminide Coating Designated JML-1**

Both Rolls-Royce and Johnson Matthey recognised the possibility of improving the existing process to produce more consistent high quality platinum aluminide coatings, and embarked upon a collaborative exercise which involved Johnson Matthey in the research and development of a fused salt platinum deposition process compatible with nickel based superalloys and which offered potential as a production process. Similarly Rolls-Royce had the task of developing an alumining process for platinum coated components that was compatible with retaining creep properties in blade alloys, and which produced a platinum aluminide coating that was equal or superior in corrosion resistance to those commercially available.

The technique of fused salt platinum plating was an obvious and attractive process to overcome the inherent problems of deposit adherence, porosity and hardness associated with an electroplating technique, and was consistent with the objective of developing a high quality platinum aluminide protective coating.
The process, refined and developed at the Johnson Matthey Group Research Centre for base metal cladding and electroforming (16), was developed further to achieve consistent high quality, even thickness platinum deposits on complex geometry superalloy substrates, an example of which is shown in Figure 4.

Additional effort was required during the early stages of development to establish an optimum substrate preparation and cleaning procedure which is now recognised as an essential part of the total fused salt deposition process. Having satisfied the initial requirements of the collaborative exercise, a critical examination of the post-platinising processes was undertaken by Rolls-Royce.

It was originally thought that a high temperature aluminising process would be needed to establish the characteristic platinum aluminide structure of the coating, but at the same time the process temperature should be kept below that at which irreversible changes occur to the ageing precipitate in the substrate alloy. Initial aluminising trials on platinum coated samples were carried out at 900°C but excessively thick platinum aluminide coatings were produced; similarly trials at 850°C and 800°C also produced thicker than required coatings. Subsequently, the use of a low temperature aluminising process successfully developed a platinum aluminide coating of the required thickness (50 microns).

The composition of the latter coating was considered inappropriate; this was later improved by a post-platinising high temperature vacuum diffusion treatment which was introduced prior to aluminising. This is a significant deviation from the accepted total processing route for commercial platinum aluminide systems, and rapid cool gas fan quenching from the diffusion temperature retains the existing $\gamma'$ morphology of the blade alloy.

Consequently Rolls-Royce was able to produce a platinum aluminide coating of consistent quality and microstructure, with no detriment to blade alloy properties. This development system was designated JML-1.

Further development work around the high temperature platinising diffusion treatment produced a second system with different element profiles, this being designated JML-2.

### The Structure of JML-1

Platinum aluminide coating systems that are developed on the surface of nickel based superalloys by diffusion processing can vary in their service performance, depending upon prior thermal and processing history. It has long been known that the degradation of any inherently protective coating is essentially a result of the natural response of the total substrate alloy/coating system attempting to establish thermodynamic stability. The degree to which this is achieved is obviously a function of service temperature and environment, and this has a direct influence upon the diffusivities of key elements within the total system.

The mechanism of degradation of conventional nickel aluminate coatings has been well established and involves the degeneration of protective $\text{NiAl}$ to lower aluminides by (a) the diffusion of aluminium inwards to the substrate alloy and (b) the diffusion of aluminium to the coating surface to form and maintain the protective oxide, $\text{Al}_2\text{O}_3$. The initial concept of using platinum in such a coating system can be attributed to the belief that it would form the basis of a diffusion barrier system that would overcome the
problem of aluminium migration to the substrate, and hence maintain the high activity of aluminium at the surface where it is essentially required. It is now known that platinum itself does not act as a diffusion barrier for aluminium but more as a diffusion medium which, during processing, allows aluminium to establish a nickel aluminate subsurface structure and simultaneously generate a platinum-aluminium intermetallic skin. A knowledge of the constitution and structure of platinum-nickel-aluminide coatings developed by diffusion processing is an important aspect of this type of coating technology but has had little attention over the last ten years (6).

The collaborative effort between Rolls-Royce and Johnson Matthey, which resulted in the development of JML–1 and JML–2, combined respective technologies in an attempt to overcome some of the process and environmental performance limitations that may occur with commercially available platinum aluminides. The aluminising process used to generate the JML–1 structure is essentially a high activity, low temperature pack treatment evolved out of the necessity to retain the inherent high temperature properties of the substrate alloy, and to develop a coating structure which was consistent with good hot corrosion/oxydation resistance, while retaining reasonable ductility throughout its possible service temperature excursions. Following pack cementation the coating and substrate alloy undergoes the accepted solutioning and ageing treatments.
associated with alloy requirements. The final structure of JML−1 is therefore dependent upon the integrity and thickness of the initial platinum deposit, the cementation process parameters and the alloy heat treatment schedule. A typical elemental profile through a JML−1 coating structure is shown in Figure 5.

The constitution of JML−1 is by no means simple but may be treated for convenience as a series of intermetallics associated with the nickel-aluminium-platinum ternary system. Although a more ideal system would be the quaternary nickel-aluminium-platinum-chromium, chromium can be considered as a solid solution constituent associated with one or more of the nickel-aluminium, aluminium-platinum or nickel-aluminium-platinum intermetallics. The photomicrograph shown as Figure 6 is typical of the JML−1 structure.

Within the total coating thickness of nominally 60 microns, the first 2 microns of surface structure consists of a continuous layer of Pt₂Al₃ which is gradually replaced by 12 microns of a duplex [PtNi]₂Al₃ + PtAl structured zone. The composition of the next 6 microns would indicate a duplex PtAl + [Ni(Pt)]Al zone. This top layer, with a combined thickness of 20 microns, generally shows no etching characteristics and can be easily identified.

The central portion of the JML−1 coating structure consists of the β-NiAl intermetallic occupying approximately 25 microns of the total coating thickness. The first 15 microns of this layer incorporates platinum as a solid solution component substituting for nickel in both the Al-rich hyperstoichiometric β-NiAl and the Ni-rich hypostoichiometric β-NiAl. The remaining 10 microns of this 25 micron central layer is virtually free of platinum and is essentially Ni-rich β-NiAl. The finger-like sub-structure (the diffusion zone) below β-NiAl occupying some 15 microns of the total coating is sequentially composed of β-NiAl + αCr and γ'(Ni₃Al) + αCr, together with intermetallics and carbides rich in the refractory elements. The coating finally terminates with the alloy microstructure of γ (solid solution matrix) + γ ′.

A number of important observations can be made regarding the diffusion of elements such as tungsten, molybdenum, titanium, cobalt, nickel and chromium within the total coating structure after complete processing. Titanium has greater diffusivity through platinum-aluminium intermetallics than the refractory elements tungsten and molybdenum. A similar behaviour is also apparent for cobalt. Although nickel can effectively diffuse throughout the β-NiAl structures, the intermetallic Pt₂Al₃ behaves as an effective diffusion barrier restricting the movement of nickel to the surface, thereby allowing unrestricted growth of protective Al₂O₃. The results of long-term high temperature stability tests on JML−1 would suggest that the latter situation is maintained, indicating that the stoichiometric intermetallics of platinum and aluminium are effective diffusion barrier materials when operating under hot corrosive gas conditions. The ability of titanium to establish a relatively high composition profile throughout the coating structure is undoubtedly beneficial to coating performance. Refractory elements such
as tungsten and molybdenum, although essential solid solution strengtheners, have an adverse effect upon resistance to hot corrosion and it is thought that the ability of the JML–1 system to restrict these refractory element mobilities gives rise to the improved performance over conventional aluminides.

The relatively high level of chromium throughout the platinum aluminide structure is considered an additional important benefit for the system, and is different to that of some commercial platinum aluminide coatings.

Within the platinum-aluminium binary system there are a number of intermetallic compounds. Due to the kinetics of the aluminising process, only the intermetallics PtAl$_2$, Pt$_3$Al, and PtAl are generally found in aluminised structures. Only the molecular volume of Pt$_3$Al shows any resemblance to the ‘ideal’ volume predicted by linear correlation between volume and composition. Aluminium-rich intermetallics form with considerable expansion; the platinum-rich with a contraction. Coating systems based upon the platinum-aluminium binary and which specifically generate PtAl$_2$ at the surface constituting a significant portion of the platinum aluminide layer, may undergo as much as 19 per cent surface volume contraction during service as a result of degeneration from PtAl$_2$ to PtAl. It is unlikely that such a volume change within an inherently brittle matrix could be accommodated without void formation or cracking. The JML–1 processing schedule develops a coating with a Pt$_3$Al$_x$ surface layer which, although undergoing a 9 per cent volume contraction during degeneration to PtAl, has shown little evidence for surface cracking.

Platinum aluminide systems in general may well have the potential for application in both hot corrosion and oxidation environments making them suitable as protective coatings for high strength alloys in industrial, marine and aero gas turbines. Similarly their resistance to sulphidation at high temperatures may well be a property that can be exploited in other industrial process environments normally considered corrosive to the best cast or wrought nickel based alloys. The key to the performance of platinum aluminides is, however, very much dependent upon achieving the optimum coating composition and structure through controlled processing. The development coating JML–1 is undoubtedly an advance in coating technology.

**Burner Rig Tests**

The gas turbine simulator, more frequently referred to as a ‘burner rig’, is generally used for hot corrosion studies and consequently sets out to simulate temperatures and atmosphere rather than specific dynamic parameters. Unfortunately, as a complete understanding of the important parameters in hot corrosion is limited at the moment, there is a wide variation in operation conditions to be found in various burner rigs operating throughout the world and indeed in the individual design from rig to rig; it is also difficult, at the present time, to accurately cross-correlate results from different rigs. The burner rig is, therefore, essentially a comparative corrosion test for evaluation of gas turbine alloys and coatings, but is a vital link between laboratory evaluation procedures and full engine testing.

The JML–1 platinum aluminide coating system has undergone exhaustive assessment in Rolls-Royce and in other independent burner rig trials, one of which was carried out at the Johnson Matthey Group Research Centre. The results from these trials have shown the JML–1 system to considerably outperform the conventional aluminide coatings.

The results of a burner rig trial carried out by Johnson Matthey are shown for example in Figure 7, and a schematic drawing of the burner rig is detailed in Figure 8.

The level of salt as residue passing through the combustion section was approximately 24 ppm by weight and the level of sulphur dioxide injected was 1.56 litres per hour. The rig is fuelled for convenience by a mixture of natural gas and air with an air : fuel ratio at the carousel section of approximately 30 : 1. Thermal cycling, from test to room temperature, was carried out once every hour.

Two commercial alloys, namely IN738 and
MAR–Mo02, were chosen as suitable and representative gas turbine alloy substrates to examine the performance of the JML–1 coating. Under burner rig conditions the total coated systems JML–1/IN738 and JML–1/MAR–Mo02 show obvious outstanding performance. The JML–2 system, a modification of the JML–1 system, designed to achieve a more even platinum distribution throughout the coating structure, clearly provides protection at higher temperature engine operation but has limitations as a system for lower temperature hot corrosion resistance.

It is also important to recognise the variation in coating performance as a function of alloy substrate. The coating and substrate are a single system, but the individual properties of each must be considered when matching the two. All elements in the substrate can, and usually do, diffuse into the coating and can influence oxidation and hot corrosion rates. Evaluation of similar coating systems must,
therefore, consider the effect of different substrates and care must be exercised in comparing results where different substrate alloys have been used.

**Engine Tests**

Apart from burner rig tests, platinum aluminide coatings have been widely evaluated in a variety of Rolls-Royce engines, and in all instances they have shown a significant improvement in corrosion resistance over conventional aluminides; a similar improvement is also shown by the MCrAlY overlay systems in this respect. Figure 9 shows the type of results obtained from a 500 hour engine test.

The JML-1 and JML-2 coatings have been evaluated principally in engines for marine applications; JML-1 in particular has been seen to perform as well as the commercial LDC-2 and RT-22 systems, and in some specific engines it has shown improved corrosion resistance. One reason that may explain the improved performance of the JML-1 system is that its compositional difference from the commercial platinum aluminides results in the production of an inherently more corrosion resistant coating. However, it is possible that other factors such as erosion resistance or ductility play a significant role in resisting coating degradation.

**Future Developments**

At the present time a number of industrial and marine engines in the United States of America are operating with blades coated with platinum aluminide systems as a standard production specification. A number of other countries including the United Kingdom are expected to follow suit as more and more engines are required to operate in aggressive marine environments with lower grade fuels. It is therefore important to further evaluate the most promising platinum aluminide coatings for the applications intended, and to examine ways of improving these systems.

Platinum aluminides are inherently less ductile than the MCrAlY overlays and cannot compete across the board with these systems, but further modification of the noble metal systems to overcome this problem could be a worthwhile task, and the potential rewards may be substantial.

Future developments in gas turbine technology will require even higher temperature capabilities from turbine blade materials in the search for higher performance.
and improved specific fuel consumption (SFC) (17). These goals will require new blade alloys such as single crystal, oxide dispersion strengthened and directional eutectic materials, and the introduction of these into engine operation will pose certain problems as to whether currently available coatings will provide adequate protection; there is still tremendous scope for further coating development.

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The alloy designation MAR-Moo2 is a trademark of the Martin Marietta Corporation and the alloy designation IN 738 is a trademark of Inco Ltd.

The platinum group metals in Society

A general concern about future supplies of industrially important materials was demonstrated in the interest shown in a recent London conference, entitled “Strategic Metals in the 1980s”. The internationally recognised authorities who spoke included Mr. D. R. Dumenil, an Executive Director of Johnson Matthey & Co Limited, who presented a paper on the platinum group metals.

Despite the relatively small quantities of platinum group metals that are available, the remarkable properties of these metals bring great benefits to industry, and to society in general. Due mainly to increased industrial use, but also to a growing interest in all things that are both rare and precious, the demand by Western World-including Japan-has increased four-fold over the past twenty years, with purchases of newly mined platinum, palladium and rhodium now being made at an annual rate of about 170 tonnes.

In addition to presenting an account of some of the many strategically important industrial processes that rely on the platinum group metals, most of which will be known to regular readers of this journal, reference was also made to the use of the metals as jewellery materials. Increasingly, jewellers and their customers are becoming aware that the colour of high-purity platinum enhances precious stones, while its strength enables the most delicate mounts to hold stones securely. Although platinum is the most important for this purpose, palladium is used as an alloying element, particularly in Japan, and electrodeposited rhodium is used to provide a brilliant protective surface on other metals.

In the foreseeable future, it is improbable that there can be any dramatic change in the world's dependence on South Africa and the Soviet Union for supplies of the platinum group metals, but in South Africa alone the reserves amount to over 300 years production. At present 10 tonnes of the Rustenburg ore yields little more than one and a half ounces troy of platinum metals, so a vast producer industry is already committed to satisfying the needs of the platinum users. Thus, providing there is a reasonable guarantee that consumption will continue at an adequate level, the underground reserves can be made available on the surface for a continuing expansion of use.

The authors wish to thank their colleagues who have directly or indirectly contributed to this paper.

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