

APPLICATION OF DIFFUSION AND Pt MODIFIED DIFFUSION COATINGS FOR ENVIRONMENTAL PROTECTION - PAST, PRESENT AND FUTURE

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INTRODUCTION

Historically, the aerospace industry has been producing diffusion coatings since the mid 1950's and noble metal modified diffusion coatings since the early 1970's. These coatings were developed to provide more resistance for turbine components against environmental degradation due to the high temperature and chemically harsh environment to which they are typically exposed. The environmental damage that gas turbines are subjected to can be described as follows:

- Dust / Sand -----> Erosion
- Salt Spray -----> Galvanic Corrosion
- Salt & Sulfur -----> Sulfidation
- Air & Heat -----> Oxidation

While many turbine alloy diffusion coatings have been developed over the past few decades - these protection systems are still undergoing further refinement. Most of these diffusion coatings have been based on the surface enrichment of Aluminum and Chromium and have been applied using a wide variety of application techniques including pack cementation, slurry aluminizing, CVD and "above the pack" gas phase coatings. Each process has its own positives and negatives. These techniques can be used as the method to produce "stand-alone" aluminized components, as the aluminide diffusion formers for precious metal plated components and also as underlayers for the subsequent deposition of overlay coatings such as EBPVD and / or LPPS. It is expected that future developments will be centered on the addition of elements such as hafnium, yttrium, silicon, etc, improved processing methods and the use of diffusion coatings as improved underlayer "bond" coatings.

Coating Selection Factors

When a specific coating type is applied to a component, we need to thoroughly understand some of the requirements of a tailored coating / substrate system. Our basic goal is to obtain a coating that produces a stable surface oxide with a low rate of scale formation - that is also ductile and adherent.

Some of those properties can be detailed as follows:

Coating Property	Requirement
Oxidation / Corrosion Resistance	Low rate of scale formation
	Uniform Surface Attack
	Thermodynamically stable surface oxide
	Ductile/Adherent Surface Scales
Interface Stability	High Concentration of scale forming elements within the coating to act as a reserve for scale repair.
	Low rate of diffusion across interface at operating temperature
	Limited compositional change across interface.
Good Adhesion	Absence of embrittling phase formation during service.
	Optimum surface conditions before coating
	Minimization of growth stresses during coating formation
Mechanical Strength	Matched coating and substrate properties to minimize coating mismatch and stress generation of coating substrate interface.
	Coating must withstand all stress (creep, fatigue and impact loading) generated at component surface during service.

Well matched thermal expansion coefficients between coating and substrate to minimize thermal stressing and fatigue.
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Thus, it is noted that the principal function of a diffusion or modified diffusion coating is to facilitate the formation of a suitable protective oxide and the marriage of the correct coating property with the substrate - looking at the oxide structure formed. The environmental resistance afforded by a surface coating results from the ability to produce and maintain the necessary oxide scale which forms a barrier between the environment and the coated component. Plainly then the role of the coating is to provide a large reservoir of scale forming elements such that rapid repair of surface oxides can occur. For newer coating systems, the diffusion coating can also be used as a type of "bond" coating which can help improve adherence of an outer overlay coating.

CORROSION FACTORS

The hot corrosion experienced in most turbine components is plainly a form of accelerated oxidation caused by impurities in the combustion gases. The most common form of hot corrosion in turbines burning distillates and residual fuels is due to the deposition of alkali sulfates on the metal surface. The aluminide diffusion coatings serve to retard the accelerated oxidation and has been the traditional coating which satisfies at least 50% of the current world market for protecting turbine components under aero, marine and industrial service.

These coatings involve the formation of high temperature intermetallic compounds with either nickel or cobalt. and provide protection by formation of an external aluminum oxide (alumina) layer which is stabilized by the aluminum content of the intermetallic compound.

Methods of evaluating the corrosion resistance of coatings range from simple laboratory tests to burner rig and engine evaluations. Over the 750 - 900 deg. C. temp range, platinum modified aluminides performed exceptionally well. Of the other diffusion coatings, chromized and chrome aluminized coatings generally fared worse than the conventional aluminides although it is understood that chromium rich coatings have shown improved performance over the simple aluminides in certain industrial turbine environments. In general, the thermal stability of coatings tends to decrease as the temperature increases and interdiffusion rates become higher. In aluminide coatings the degradation results in the breakdown of the outer beta NiAl phase by the formation of the gamma Ni₃Al network which, after extended exposure time, can completely penetrate the beta phase. These gamma leaders behave as a short circuit corrosion path which cause rapid coating failure. The addition of Platinum greatly improves the thermal stability of the beta NiAl and is a prime reason why it has found such great acceptance.

Techniques for diffusion coatings

Application methods for aluminizing depends on the structure of the coating, method of transporting the aluminum, coating thickness and subsequent post coating heat treatment needed to achieve the properties desired. The techniques used - mainly involving variations of CVD - Chemical Vapor Deposition - used in pack and above the pack coating. have seen many improvements with both processing equipment and control improvements over the last few years - mainly through improved equipment and Platinum plating processing.

At high temperatures, Al reacts with either the nickel or cobalt bases substrate through the following possibilities:

- 1) By the halide vapor phase (CVD)*
- 2) Through a metallic vapor phase (unactivated pack)*
- 3) through solid state diffusion (contact with the component)*
- 4) By inclusion of metal particles (outward growing coating)*

5) *By molten metal dipping, migration, wetting and capillary action*

At low temperatures - pure elements deposited followed by reaction (melting) at higher temperatures:

- 1) *Organo-metallic deposition*
- 2) *Ion-vapor deposition (IVD) Ionizing - Sputter Ion Plating)*
- 3) *Electrophoretic deposition*

Principally, diffusion coatings can be classified as one of two types. Inward - low temperature high activity (where aluminum or chromium diffuse inwards) - or inward/outward - high temperature low activity diffusion coatings where the temperature is high enough to permit outward diffusion of nickel or cobalt from the substrate. These coatings are essentially tailored to suit a specific substrate to meet certain property requirements.

The oldest technique used to produce diffusion coatings is pack cementation - where the part is essentially buried in the aluminum reactants and the coating gases are generated from the powder mixture in contact with the parts. This technique advanced to the "above-the-pack" technique where parts are fixtured above the powder in the retort. Again the coating gases are generated from the powder mixture and carried through and over parts by means of a purge gas. There is one principal advantage that the "above the pack" technique and pure CVD has over pack cementation and that is the ability to coat the internal parts of the components - because the active aluminum is carried into the part via a carrier gas. Only the parts in contact with the pack material can coat using pack cementation.

CVD

In the CVD aluminizing process, aluminum halide gas is produced in an external gas generator and then carried into the coating chamber with H₂ and Argon gas. This mixture (*of precursors*) is then passed over a bed of molten aluminum metal or a bed of Chromium - Aluminum alloy pellets (*typically 30 - 40% Al, Balance Chromium*) contained inside the coating chamber to increase gas activity through the formation of the subchloride species. *A balance sheet for the advantages and disadvantages of CVD can be detailed as follows:*

Advantages:

- Environmentally Friendly*
- Ability to coat complex cooling holes*
- Deposition of elements such as Yttrium, hafnium, zirconium, etc.*
- Production of graded and multi-elemented coatings.*

Disadvantages:

- Higher processing costs*
- Higher capital equipment cost*
- Can reproduce only the outward diffusion coating routinely*
- The controlling chemical reactions are:*

CVD ALUMINIZING REACTIONS

i) External generator



ii) Subchloride formation

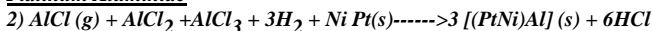


iii) Superalloy Diffusion

Simple Aluminide



Platinum Aluminide



Platinum Modified Diffusion Coatings

As operating temperatures have increased, more protective applications have turned to the deposition of the platinum modified diffusion coatings. The dilution of the intermetallic aluminide by diffusion from the base alloy has become more rapid resulting in quicker component deterioration. To combat this problem, the addition of Platinum over the past 25 years to the intermetallic has been recognized to increase the resistance to diffusional dilution.

The initial coating was formed by the deposition of less than 10 microns (0.0004in.) of platinum onto a nickel based alloy and subsequently aluminizing the platinum plated substrate at approx. 1050 deg. C. using pack cementation techniques.

Other precious metal plating like rhodium and palladium have also been used to provide similar benefits. As an example of dual use of two codeposited precious metals, a thin layer of rhodium can be electroplated prior to applying the electrodeposited platinum. The resultant coating after subsequent heat treatments and aluminizing contained approx. 5 - 10% Rhodium, 40% Platinum and 22+% Aluminum. This is an improved precious metal modified coating. Engines coated with this variant will typically run 30,000 to 40,000 hours between overhaul in which the component can be repaired and recoated. *Various attempts to add other constituents like Yttrium, Silicon, and Hafnium to the aluminum intermetallic have also had some success.*

The deposition of platinum by electroplating has become a well established process that requires very close attention to detail to develop the proper optimized conditions. Platinum aluminides have demonstrated their unique application in both hot corrosion and oxidation environments. This has made them particularly suitable for use in high strength alloys in industrial, marine and aero engines. In addition their resistance to high temperature sulfidation makes them particularly good for use in industrial process environments normally considered corrosive to the best cast or wrought nickel based alloys. Some of the steps involved in platinum aluminide deposition are as follows

CVD / Pack Platinum Aluminide Coating Process

- 1) Incoming Visual Inspection
- 2) Surface prep (Cleaning)
- 3) Masking of non plated areas
- 4) Platinum Electroplate
- 5) Post Plating Heat treatment
- 6) Masking
- 7) Pack or CVD Coating Cycle
- 8) Post Coating Heat Treatment
- 9) Unmasking
- 10) QC Evaluation
- 11) Final Inspection

Depending on the processing techniques, there are three basic Pt-Al structure types that typically can be formed. Those are as follows:

- 1) $PtAl_2$ single phase outer zone
- 2) $PtAl_2 + NiAl$ TWO PHASE OUTER ZONE
- 3) $(PtNi)Al$ Single phase

The structure formed is dependent upon process parameters:

- 1) *PLATINUM PLATING THICKNESS / DENSITY*
- 2) *PLATINUM DIFFUSION TREATMENT*
- 3) *TEMPERATURE AND ALUMINUM ACTIVITY OF COATING PROCESS*
- 4) *POST COATING THERMAL EXPOSURE*

Because of superior resistance against environmental degradation, dual - phase PtAl₂ + NiAl coatings has been the coating industry standard. The aerospace industry has also developed the techniques to form the "single phase" platinum aluminide form by CVD and above the pack techniques. Both coating types have their advantages and disadvantages - primarily in ductility, repairability and oxidation / corrosion resistance. Thus, the application must be looked at closely to evaluate which form suits the particular set of conditions. This coating type tends to exhibit some brittleness as well stress. In addition, prolonged times at high temperatures during aluminizing with subsequent slow cooling from the process temperature can affect the morphology of the gamma nickel aluminide aging precipitate of the substrate alloy. Some loss of creep strength can be associated with this effect. While these negatives must be considered in their specific application, their marked improvement in high temperature corrosion resistance over simple single element diffusion coatings is significant.

Platinum aluminide coating systems that are applied to the surface of nickel based superalloys by diffusion processing can vary in their service performance depending on prior thermal and processing history. It has long been known that degradation of any inherently protective system 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 a function of service, temperature and environment which has a direct influence upon the diffusivities of key elements within the total system. The initial concept of using platinum in a platinum aluminide coating system had its basis on the belief that it would form a diffusion barrier that would overcome problems of aluminum migration to the substrate and thus maintain the activity of surface aluminum where it is essential. It later became understood that platinum itself does not act as a diffusion barrier for aluminum but more as a diffusion medium during processing which allows aluminum to establish a nickel aluminide subsurface structure and simultaneously generate a platinum aluminide intermetallic skin.

With respect to "duplex" and "single phase" Platinum Aluminides, both coating types have advantages that make one type preferable over the other depending on service exposure, life, mechanical needs and reparability. "Single phase" platinum aluminides most often refers to a continuous outer layer of PtAl having Al and Pt concentrations in the 15 to 25 weight percent range. "Duplex" platinum aluminides typically means this same phase mixed with beta NiAl. It needs to be noted that Aluminum rich intermetallics - typical to the "duplex" structure form with considerable expansion while the platinum rich intermetallics form with a contraction. Coating systems based upon the platinum-aluminum binary which specifically generate PtAl₂ at the surface constitute a significant portion of the platinum aluminide layer may undergo as much as a 19% surface volume contraction during service as a result of degeneration from PtAl₂ to PtAl. Such a volume change within an inherently brittle matrix may occur with void formation and cracking. The more typical species present in a single phase coating - PtAl appears to undergo less volume contraction during service. Ductile, "single phase" Platinum Aluminides have been developed which do not have the inherent brittleness of the aluminum rich intermetallic binary and ternary phases.

A look at the performance differences of single and two phase platinum aluminides can be noted as follows:

Properties	
Single Phase Pt Al	Dual Phase PtAl
Less corrosion resistance at high temp.	More corrosion resistant at high temperatures
Less Oxidation Resistance	More Oxidation Resistance
More stable coating (i.e. less interdiffusion of coating with substrate)	Less stable coatings - tends to have more substrate - coating interdiffusion
More Ductile/less brittle - better mechanical properties	More brittle/less ductile. Poorer mechanical properties. Works well where strains or cyclic strain ranges remain small.
Less parent metal consumption.	More parent metal consumption
Less "rumpled" surface since Al is applied using a HTLA process.	More rumpled surface topology because the Al is typically applied using a LTHA process.
Less Cr and refractory metal concentrations in the diffusion zone as a result of both solid and liquid state diffusion.	Higher Cr and refractory metal concentrations in the diffusion zone as a result of both solid and liquid state diffusion.

To conclude, the main Aluminizing techniques for the formation of both single and duplex platinum aluminides are high or low temperature pack cementation systems, "above-the-pack" gas phase and CVD, at high or low temperatures, which can significantly affect the initial phase formations. The advantage of CVD and above the pack gas phase coating is that the coating can be applied to the internal cooling passages of the component. This can't be done utilizing pack cementation unless the inward passages can be injected with a slurry as the activator/aluminum source - which essentially requires straight through holes. After the application of the diffusion coating, post coat heat treatment can next be used to substantially alter the phases present. It should be noted that service conditions will also cause further unexpected departures from initial phase relationships.

With the introduction of the single phase platinum aluminide in the aerospace industry, three factors critical to the formation of the Platinum Aluminide single phase coating were considered in the experimental program:

- 1) Thickness of the plated platinum.
- 2) Activity of the gaseous aluminum precursor feed .
- 3) Input of $AlCl_3$ (through control of HCl feed rate through the external generator).

When the coatings industry developed the processing controls to form the single phase platinum aluminide, three thickness levels were used in the evaluation of the platinum aluminide system. It was apparent that an initial platinum layer as deposited of 2.9 - 3.3 microns) was essential. Chart #1 indicates the relationship between the original platinum deposit and gas flow of HCl with respect to the Percent Aluminum and Platinum found throughout the coating profile. HCl flow into the external generator had minimal impact on the profile of the aluminum and platinum concentration. The coating cycle run without the molten aluminum internal activator pool clearly shows the impact of the enriched aluminum on diffusion capabilities.

With the wide assortment of diffusion, modified diffusion and overlay coatings available today in the aerospace industry, we can tailor our coatings to suit the individual conditions of the turbine component.

The following general case *conclusions* can be made for the use *this aspect* of protective coatings:

- 1) The use of protective coatings is beneficial and often necessary for the successful use of materials in high temperature combustion zone environments.
- 2) Responding to the variety of materials and operating conditions, a large number of coating compositions and processes have been developed and are available.
- 3) Successful use of these coatings require a "systems approach".
- 4) In general, sufficient data are available to allow the coating / process to be incorporated into the design process, manufacturing sequence, and subsequent overhaul and repair procedures.
- 5) When properly engineered, it is no longer appropriate to refer to the detrimental effects of a coating on the mechanical properties of a substrate but rather to consider the considerable component life extension that is obtained.

As a final note to diffusion coatings and the technique called CVD, there is also a reverse coating process which is used to remove oxides from parts prior to braze repair and also used for coating removal. That process is called HF Fluoride ion cleaning and autoclave cleaning. In HF cleaning HF gas is used at high temperatures to convert stable oxides to volatile fluorides - which once formed become a gas and leave the substrate coating free. With autoclave cleaning, hot potassium chloride reacts with an oxide coating to remove it with no adverse substrate reactions.