

Factors Influencing the Formation of Single Phase Platinum Aluminide Coatings:

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Abstract

To provide more resistance against environmental degradation, turbine alloy coatings have been based on surface enrichment of Al through the formation of high temperature intermetallic nickel or cobalt compounds. These coatings have provided protection by forming an external Aluminum Oxide layer stabilized by the Aluminum content of the intermetallic compound. As operating temperatures increased, the dilution of the intermetallic aluminide by diffusion from the base alloy becomes more rapid and the partially stabilized external alumina deteriorates more quickly. The addition of Platinum to the intermetallic has served to increase the resistance to diffusional dilution.

Application methods for aluminizing the electrodeposited Platinum layer to form the single phase include "out-of-pack" vapor, and chemical vapor deposition (CVD) techniques. Significant to the coating formation is the pre-diffused Pt plating thickness and the activity of the CVD / gas phase aluminide. CVD activity can be enhanced by using an internal molten Aluminum pool as the activator for the highly reactive AlCl species and by varying the activator in "above-the-pack" gas phase techniques. This processing changes the PtAl formation from an inward growth "duplex" phase deposit to a more ductile and stable - but less oxidation/corrosion resistant - outward single phase deposit that has Aluminum and Platinum weight percentages in the 15 to 25% range.

Introduction

Diffusion coatings have been an important factor in providing protection for turbine components since the mid 1950's and noble metal modified diffusion coatings have been utilized since their development in 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 exposed. While many coatings have been developed over the past few decades, diffusion coatings are still undergoing further refinement. Most of these 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.

Protection has been provided by the formation of an external Aluminum Oxide layer stabilized by the Aluminum content of the intermetallic compound. As operating temperatures increased, the dilution of the intermetallic aluminide by diffusion from the base alloy becomes more rapid and causes the partially stabilized external alumina to deteriorate more quickly. The addition of Platinum to the intermetallic has served to increase the resistance to diffusion dilution. Thus, these diffusion coating techniques have been used as the method to produce "stand-alone" aluminized components, as the aluminide diffusion formers for precious metal plated components and as underlayers for the subsequent deposition of overlay coatings such as EBPVD and Low Pressure Plasma Spray.

Coating Selection Factors

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. 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.

When a specific coating type is applied to a component, we need to thoroughly understand the requirements of a tailored coating / substrate system. 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
	High Concentration of scale forming elements within the coating to act as a reserve for scale repair.
Interface Stability	Low rate of diffusion across interface at operating temperature
	Limited compositional change across interface.
	Absence of embrittling phase formation during service.
Good Adhesion	Optimum surface conditions before coating
	Minimization of growth stresses during coating formation
	Matched coating and substrate properties to minimize coating mismatch and stress generation of coating substrate interface.
Mechanical Strength	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.

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 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.

Platinum Modified Diffusion Coatings

As operating temperatures have increased, 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 metals like rhodium and palladium have also been utilized to provide similar benefits. As an example of dual use of two codeposited precious metals, a thin layer of rhodium is 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. As an improved precious metal modified coating - engines coated with this variant will typically run 30,000 to 40,000 hours between overhauls in which the component can be repaired and recoated.

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.

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

- 1) PtAl₂ single phase outer zone
- 2) PtAl₂ + NiAl TWO PHASE OUTER ZONE
- 3) (PtNi)Al Single phase

The structure formed is dependent upon the following process parameters:

- 1) PLATINUM PLATING THICKNESS.
- 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. This coating type tends to exhibit some brittleness as well as 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. Degradation of any inherently protective system is essentially a result of the response of the 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 system. The initial concept of using platinum in a platinum aluminide coating system was based on the formation of 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 served as a diffusion medium during processing which allowed 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 and 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. Thus, more ductile, "single phase" Platinum Aluminides have been developed which do not have the inherent brittleness of the aluminum rich intermetallic binary and ternary phases.

Application methods for aluminizing the electrodeposited Platinum layer include pack cementation, "out-of-pack" vapor, and chemical vapor deposition (CVD) processing techniques. The mechanisms of intermetallic phase formation and diffusion directions depend primarily on temperature and Aluminum activity of the coating source - and to the thickness of the electroplated Platinum deposit. Thus, these factors influence the manner of base alloy constituent segregation. The main technique used to date - pack cementation - forms an "inward" two-phase diffusion coating. Both CVD and "out-of-pack" vapor techniques have demonstrated the ability to produce the outward growth, high temperature, low activity single phase Platinum Aluminide within a specific range of conditions.

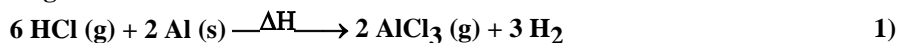
The initial Platinum electroplated deposit is followed by a heat treatment to co-diffuse the Platinum and substrate elements. Variations in diffusion processing after the initial plating and diffusion aluminizing can affect both the ultimate final structure as well as impact on service performance. Other than Platinum, the intermetallic aluminides of Nickel and Cobalt formed by diffusion have relatively low solubilities for other elements. Base alloy constituents segregate as second phase intrusions within the intermetallic and/or enrichments at the boundary between diffusion and base alloy for inward diffusion. These conditions have various effects on the behavior of the intermetallic and the stability of the service formed oxide. The two phase "duplex" Platinum Aluminide coating has the PtAl phase mixed with beta NiAl. Its richer Platinum content gives evidence of superior oxidation/corrosion resistance - but because of its high Platinum content, it has less ductility and is phase unstable. The single phase Platinum Aluminide has a continuous outer, additive layer of PtAl with Al and Pt concentration in the 15 to 25 weight percentage range. While it appears to exhibit less high temperature oxidation/corrosion resistance, it does have enhanced ductility and better thermal phase stability.

EXPERIMENTAL

In the CVD aluminizing process, AlCl_3 gas is produced in external gas generators by reacting HCl with Al chips heated to 300-400° C. The AlCl_3 is next carried to the coating chamber with H_2 that serves as a carrier and a reducing agent. Figure 1 shows the general layout of the CVD system used. The mixture of precursors is then passed over a container of molten Aluminum metal to increase gas activity through the formation of the subchloride. This "disproportionation" process was initially detailed in "Studies on Equilibrium of the Subhalide Reaction by the Bubbling Method".² This reaction can occur by passing the AlCl_3 over an alloy of CrAl chips where the typical Al concentration is in the 30 to 40 weight percentage range. The CrAl reduction reaction is useful if handling of a molten metal inside of a reaction chamber is not desired and a less efficient formation of the AlCl species is acceptable. Effluent gases are exhausted to a liquid ring vacuum pump and then treated in a fume scrubber and neutralization system.

The controlling chemical reactions are:

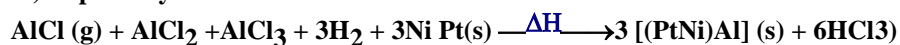
i) External generator



ii) Subchloride formation



iii) Superalloy Diffusion



Three factors critical to the formation of the Platinum Aluminide single phase coatings were considered in the experimental program:

1) Thickness of the plated Platinum - three thickness levels were evaluated - 0.10, 0.15 and 0.20 mils (2.5, 3.75 and 5.0 microns).

- 2) Activity of the gaseous Aluminum precursor feed - with and without a molten Aluminum pool.
- 3) Input of HCl at flow rates at 2.4, 3.2, 3.6, 4, 7 and 12 l/min to the external AlCl₃ generator (12 l/min was used without the molten pool present).

All other experimental factors - time (5 hours), pressure (600 torr) external generator temperature - 350°C., gas flow (except for the HCl variable) and retort temperature (1060°C.) were kept constant.

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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 RT22 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.

RESULTS

Table I details the data obtained with the molten pool activator after the 4 hour post coating vacuum heat treatment at 1080°C. At HCl flow rates of 2.4, 3.2, 3.6, 4 and 7 l/min, no correlation with final thickness or Al profile of the PtAl after heat treatment was noted - on substrates having the same initial Pt plating thickness. There was a correlation between Pt and Al weight percentage after coating and post coating heat

treatment with the initial Pt plating thickness. The thicker the initial Pt, the less the ability to form a single phase coating.

Table II and Figure II illustrate the results without the use of the molten pool. Only one flow rate - 12 l/min - was used. Without the "disproportionation" factor, the average thickness after final diffusion heat treatment was 1.2 mils (30 microns) less than the average coating thickness obtained using the molten pool. Because much less Aluminum was added into the composition, the Platinum concentration was less diluted, thus the PtAl mixture was much richer in Platinum. Note that the Platinum concentration starts out between 15 and 30 weight percentage Platinum and increases across the additive layer to 25 to 48 weight percentage Platinum. The Aluminum concentration tends to start out at between 19 and 22 weight percentage and decreases slightly to between 13 and 16 weight percentage across the additive layer.

Table III and Figure III illustrate the average data obtained with the usage of the molten pool. There is a distinct relationship between initial plating thickness and Al/Pt weight composition. Note that the Platinum weight percentage starts at approximately 26 to 33% at the coating surface while slowly tapering to 20 and 23 weight percentage at the end of the additive zone while the 0.1 mil initial Platinum plated substrate exhibits a flat profile at between 17 and 15 weight percentage. The Aluminum weight percentage is essentially flat across all three thicknesses.

Micrographs I and II show an initial 0.1 mil Platinum plated coating, CVD aluminized, before and after heat-treatment. Prior to post aluminizing heat-treatment, the darkened outer zone indicates an enriched Aluminum zone that can be diffused further into the Platinum-Nickel zone. The distinct "white" phases are Platinum rich segregations. The coating for the original 0.1 mil Platinum deposit grew from 1.9 mils prior to heat treatment to 2.4 mils after heat treatment. As depicted in Micrograph II (HCl flow = 3.6 l/min), the additive zone is approximately 1.25 mils thick. The first reading was taken at 0.2 mils from the surface and had values of 17.3/15.9 wt.%. The second reading was taken at 0.5 mils from the surface and had values of 17.4/15.3 wt%. Reading 3 was taken at 0.7 mils with readings of 17.2/16.1 wt%. The 4th value was read at 0.9 mils with values of 17.1/15.4 wt% and the last SEM reading was at 1.2 mils from the surface - adjacent to the diffusion zone with values of 16.2/14.9 wt%. For Micrograph IV (HCl flow = 3.6 l/min), SEM analyses were taken at 0.2, 0.5, 0.8 1.1, and 1.4 mils over the 1.4 mil additive zone. Micrographs III and IV provides the same comparison except the starting point was 0.2 mils of original Platinum plating. The Platinum "white" phase pools are more noticeable prior to heat treatment. Thickness change before heat treatment to after heat treatment was 0.5 mils - growing from a total preheat treat thickness of 2.0 mils to 2.5 mils after heat treatment.

CONCLUSIONS

A single phase Platinum aluminide coating can be achieved by deposition of an initial 0.10 - 0.15 mil (2.5 - 4.75 microns) of Platinum (nominal 0.12 mils/3 microns) within the set of parameters used for this study. If the molten pool is used as the activator, then a sufficient amount of Aluminum can be added which will permit single phase formation after a 4 hour post aluminizing vacuum heat treatment at 1080°C. Without the assist of the molten pool, the activity of the Aluminum formed by reduction of the $AlCl_3$ with H_2 is not sufficient to diffuse sufficient Al into the substrate to obtain the single phase over the same time. The degree to which this single phase stability is achieved is thus clearly a function of coating/heat treat temperature and chemical environment that has a direct influence upon the diffusivities of key elements within the total system.

REFERENCES

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