

Platinum Plating for Turbine Blades: Technology Development and Process Improvement

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Traditionally turbine blades in both aircraft and power turbines are plated with a platinum deposit to enhance their service life significantly. Such platinum deposits are typically 5 microns in thickness and are subsequently put through a pack diffusion process to form a platinum-alumina composite deposit, with physical properties that are beyond platinum itself. Technology involving either platinum "P" salt or platinum "Q" salt is commonly used in the plating electrolytes. In many of these formulations, plating will involve the use of ammonia and often elevated temperatures, together with lengthy plating times, to give the desired deposit qualities. This paper describes innovative process development that gives benefits in process cycle time and also addresses environmental concerns by eliminating ammonia from the system.

Keywords: *Platinum electroplating, ammonia-free electrolyte, turbine blades.*

Introduction

Turbine blades are a critical part of an aircraft jet engine and also of turbines utilized in the generation of electricity in power stations. Turbine blades are created from a variety of high strength, high temperature alloys which are often referred to as "super-alloys" typically nickel (Ni) and cobalt (Co) alloys containing smaller percentages of elements such as, chromium (Cr), molybdenum (Mo), aluminum (Al), titanium (Ti) and tungsten (W).

These alloys are designed to give strength and performance that are beyond a simple alloy's capability. The composition of these super-alloys is tailored to provide a desirable combination of mechanical strength and resistance to environmental degradation, e.g., oxidation and hot corrosion.

Precision engineering of turbine blades is a highly refined engineering achievement, utilizing investment casting methods, together with complex machining operations to create a finished component with very fine dimensional tolerances in a complex design, a truly precision engineered part. Of course, by definition, such a precision engineered part is costly to produce. Hence any technology which can extend and maximize its service life will be of significant interest to both aircraft engine manufacturers and power turbine users.

Platinum composite coatings are often used to increase the hot corrosion resistance and reduce the level of oxidation, allowing the components made from such super-alloys to be used for extended periods of time before they need to be replaced or repaired.

Platinum plated deposits form a part of a composite platinum-alumina coating with physical properties beyond platinum itself. This composite coating provides a highly refractory, very high temperature-resistant performance, which increases the service life of a turbine blade by a factor of three to four times.

In addition to this, the turbine blades can be "recycled." The blade can be rebuilt and refurbished as the layer can be stripped and the blade recoated with the platinum-alumina layer after wear and damage have been resolved. As a result, individual blades will last as long as fatigue life and airworthiness regulations permit.

Turbine blades: some background information

Turbine blades in the high-pressure turbine of a jet engine are exposed to a very severe environment. Temperatures in the region of 2000°C are combined with the physical stresses associated with rotation at more than 10,000 rpm. An elaborate cooling system combined with a thermal barrier coating is absolutely necessary to avoid even the super-alloy components melting under such extreme conditions.

Aircraft and power turbine blades are usually coated with a thermal barrier coating to enhance the service life. Failure of such coatings would result in melting of the blade. Thermal barrier coatings can considerably enhance the oxidation / hot corrosion resistance of these components.

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In general, in aircraft jet engines, high pressure turbine blades (HPT blades) are expected to last for about 30,000 hr, while for power generation in power station turbines, this figure can vary between 50,000 and 75,000 hr. HPT blades in jet engines will typically undergo one refurbishment (strip coating and recoat) throughout their life. In power generation applications, one or two refurbishments can be achieved depending on the target life. Turbine blades can come in all shapes and sizes as the photographs in Figs. 1 thru 3 indicate. Note the significant size of the turbine blades clearly seen in Fig. 3.

Why is a thermal barrier coating necessary?

A turbine engine works by forcing hot combustion gases from the burning of fuel to flow through a series of blades, causing them to spin like a windmill. In a turbine, the “wind” is a flow of very hot gas and the “windmill blades” are rotating at high revolution speeds, often in the range of 10,000 to 20,000 rpm.¹

To operate efficiently, turbine engines must run at high speeds and high temperatures, which means the stresses on the turbine blades are very high. They have to be strong and more importantly, they have to be very strong at very high temperatures and highly corrosive conditions. Demand for increased engine power and improved fuel efficiency has pushed the operating temperature well beyond 1000°C and figures as high as 2000°C have been documented.

The turbine blades are exposed to many extremes of high pressure, high temperature, physical demands of rotation and also oxidizing gases, resulting in very significant wear rates. Metallic coatings and special materials have been developed and are utilized to help protect the turbine parts from these extreme conditions.²

Turbine blades are usually constructed from a super-alloy. The term “super-alloy” was introduced to describe a group of alloys developed for use in turbo super-chargers and aircraft turbine engines that required high performance at elevated temperatures. The range of applications for which super-alloys are used has expanded to include many other areas and now includes both jet aircraft engines, power turbines, rocket engines and they are also utilized in chemical and petroleum refining plants.

There are many super-alloys but a typical formula would be 50-70% Ni, 8-20% Cr, 5-20% Co and Mo, Al, Ti, W and others at up to 5%. Super-alloys are particularly well suited for these demanding applications because of their ability to retain most of their strength even after long exposure times at high temperatures. Their versatility stems from the fact that they combine this high strength with good low-temperature ductility and excellent surface stability.

Protection provided by platinum-aluminide coatings is due to the selective oxidation of aluminum to form an alumina (Al_2O_3) scale that grows very slowly at high temperature by a diffusion process. Impurities within the coating, notably sulfur, chlorine and phosphorus can segregate to the interface between the coating and the alumina scale, weaken the interface and degrade the protective oxide scale.³

Consequently, there is a need for a plating process that greatly reduces the concentration of impurities (specifically, sulfur, chlorine and phosphorus) present within the plating to levels that are comparable or preferably below the levels present within the super-alloy substrate.

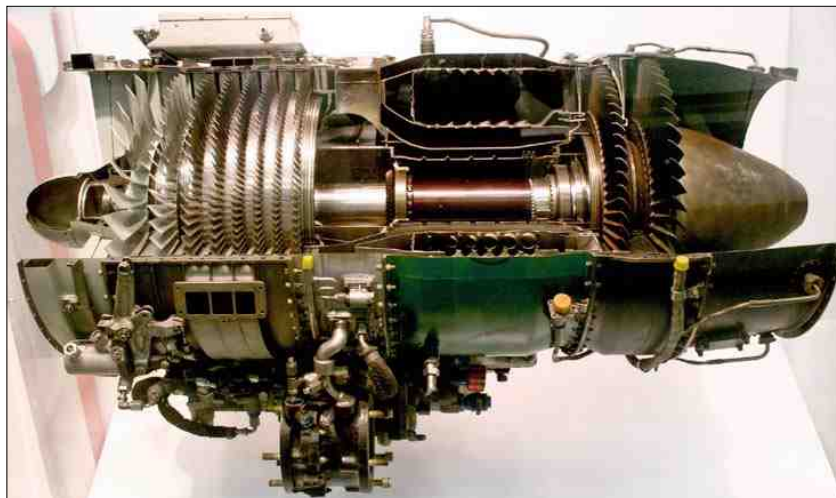


Figure 1—Cross-section through a typical axial-flow gas turbine turbojet, the J85, showing many turbine blades (Photo: Wikimedia Commons, by Sanjay Acharya, 2008; <http://creativecommons.org/licenses/by-sa/3.0/>).

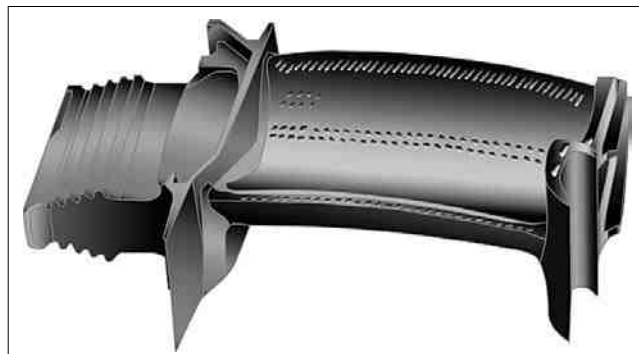


Figure 2—Typical aircraft turbine blade showing detail of cooling channels in the super-alloy precision engineered part; length approx. 10 cm (Photo: Wikimedia Commons, by Tomeasy, 2009; <http://creativecommons.org/licenses/by-sa/3.0/>).



Figure 3—Siemens power turbine assembly with the case open, clearly showing the significant size of the turbine blades (Photo: Wikimedia Commons, 2005; <http://creativecommons.org/licenses/by-sa/3.0/>).

In the production of platinum-modified aluminide diffusion coated gas turbine engine components, such as blades and vanes, the components are processed by utilizing electroplating to deposit platinum metal on their gas path surfaces and then usually a pack diffusion process to form the platinum-aluminized coating.^{4,5,6,7}

Technology developments

Existing processes: electroplating technology

There are many established both “textbook” and “proprietary” formulations for platinum plating that have been established and often patented over the years.⁸ Some of these processes have found significant application in the high quality decorative jewelry industry, where processes need to exhibit properties including whiteness, brightness, clarity, wear resistance, ductility and ease of operation. Other processes are more suited to “industrial” applications where the physical requirements can be very different. Such processes need to exhibit good electrical properties, good ductility, small grain size, good diffusion properties and even thickness distribution. For industrial application, whiteness and brightness are less critical, provided the deposit is adherent and meets all the desired physical properties.

There are three major families of electrolytes that have found application in industrial applications.

(i) Hexa-chloro-platinic acid-based processes (H_2PtCl_6): Hexa-chloro-platinic acid can be used a source of platinum.⁹ These will often utilize a phosphate buffer solution or can be based around an acid chloride type bath. These baths can be utilized in both industrial and decorative applications,¹⁰ but their application in turbine blades is limited.

The processes exhibit high cathode efficiency and usually produce a bright deposit with relatively low stress. Deposits of up to 25 microns have been produced successfully. The presence of chloride has limited their use in turbine applications as concerns related to corrosion are usually associated with chloride-containing electrolytes. Further, these electrolytes often use phosphate buffer systems that could be a concern in codepositing residual traces of phosphorus in the platinum-aluminized layer.

High cathode efficiency often, by default, leads to poor thickness distribution profiles with significant

build-up on high current density areas. This is not so desirable in turbine blade applications. Applications can include protection of electrodes in high temperature applications and medical instruments, together with many and varied decorative uses.

(ii) Platinum “Q” salt-based processes $[(NH_3)_4Pt(HPO_4)]$: “Q” salt-based processes are a valid contender for application on turbine blades and are utilized successfully by some manufacturers.¹¹ The oxidation resistance of platinum-modified aluminide diffusion coatings can be improved by electroplating platinum using a plating solution able to reduce significantly the presence of such harmful impurities as phosphorus, sulfur and chlorine in the platinum deposit and the subsequently created aluminide diffusion coating. Eliminating these elements from the formulation can be a significant factor. “Q” salt baths go part of the way as they do not contain sulfur nor chlorine, but usually would contain some phosphorus within the complex of the “Q” salt itself $[(NH_3)_4Pt(HPO_4)]$. Typical operating parameters are shown in Table 1.

The “Q” Salt baths are usually operated at $[Pt] = 5 \text{ g/L}$, $pH = 10.3$ and temperature = 92°C . The pH is adjusted with sodium hydroxide, which eliminates any need for ammonia. Operating at high temperature leads to high evaporation loss and regular addition of deionized or distilled water is necessary in order to maintain the volume of the bath.

Maintaining high temperature is critical, because the cathode current efficiency is substantially reduced at temperatures below 89°C .¹² Regular checks are essential to ensure that the recommended pH range is maintained. The significant dependency on temperature can easily be seen in Fig. 4, where a drop of over 80% of the efficiency value is seen with only a drop of 10 Celsius

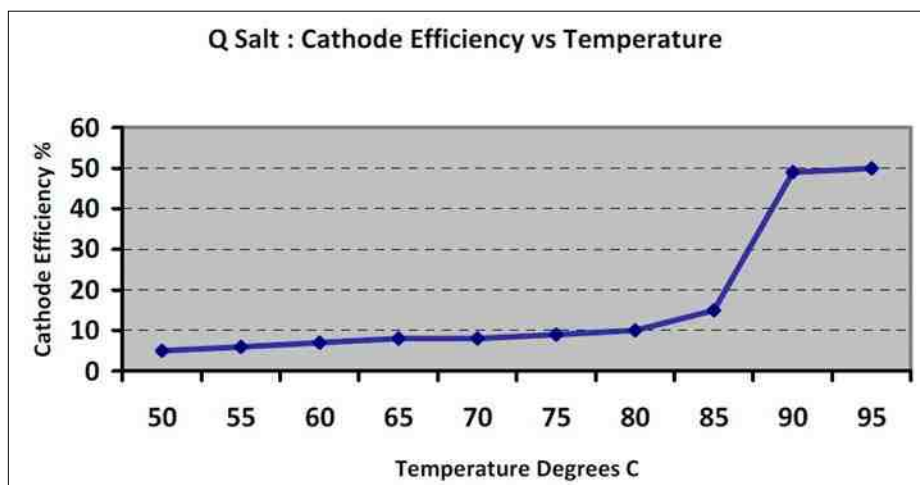


Figure 4—Dependency of cathode efficiency on high temperature in a typical “Q” salt bath.

Table 1

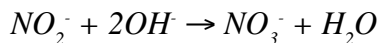
Typical operating parameters for a “Q” salt bath

	Unit	Range	Optimum
Platinum	g/L	3 - 7	5.0
pH	---	10.0 - 10.6	10.3
Temperature	°C	90 - 95	92
Current Density	A/dm ²	0.2 - 0.7	0.5

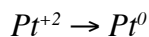
degrees from 90 to 80°C. The cathode current density is usually limited to 0.2 - 0.5 A/dm² at 90 - 95°C.

(iii) **Platinum “P” salt-based processes [(NH₃)₂Pt(NO₂)₂]:** “P” salt baths are very popular⁹ and are usually based on a solution matrix of mixed phosphates. Nitrite is often used as a process stabilizer^{13,14} to help prevent the “P” salt transition from di-amine to tri-amine to tetra-amine, as shown in Fig. 5. Formation of the tetra-amine is undesirable as, being a very stable complex, it has tendency to reduce the overall cathode efficiency of the plating bath.

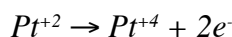
Nitrite however, is in itself an unstable material, particularly at elevated temperatures:



This nitrite-to-nitrate oxidation can easily take place, but has the benefit of helping to facilitate the platinum reduction,



and reducing the undesirable oxidation of Pt⁺²:



Wherever there is oxidation there is always a reduction, and these two electrolysis driven reactions are no exception.¹⁵ This reduction can explain the rapid consumption of nitrite in a typical “P” salt bath, where concentrations of 5.0 g/L are often found, but seldom do they increase far beyond 5.0 g/L despite periodic additions of nitrite.

“P” salt baths are well established in turbine applications and appear to be well suited to the pack diffusion process. They have as a result found significant application in aircraft turbine blade production. The baths usually do not contain any chlorine or sulfur, but will often use a phosphate-based conducting salt.¹⁶ The platinum “P” salt itself [(NH₃)₂Pt(NO₂)₂] does not contain any phosphorus as compared to the “Q” salt [(NH₃)₄Pt(HPO₄)], which contains a phosphate functional group.

“P” salt baths also exhibit excellent distribution profiles which give an added benefit of precise thickness control, which is of paramount importance on such precision engineered parts. The limited throwing power provides another competitive advantage as undesirable plating into the dimensionally stable cooling channels, which an integral part of the turbine blade design, is minimized. There is still the necessity of taking steps during plating to prevent incursion of plating into these fine diameter bores, and waxes, argon gas and stop-off materials are sometimes used to ensure zero penetration.

Ammonia is usually present in the electrolytes and the systems employed operate best at elevated temperatures, typically 90°C. Ammonia is highly volatile at elevated temperatures and this leads to large evaporation losses and, of course, the characteristic pungent smell of ammonia which, in addition to being unpleasant in the working environment, can also be considered harmful.

There is a need for efficient and effective fume extraction, to comply with health and safety requirements, but at elevated temperatures this also increases the evaporation of ammonia and necessitates additional, costly replenishments and a greater need to handle harmful ammonia.

Environmental concerns and elimination of ammonia

Ammonia, while being an excellent material to enable “P” salt baths to function reliably, does offer some drawbacks. Ammonia is harmful and has a characteristic pungent and irritating odor, which dictates that efficient and costly fume extraction is always essential, but additionally the elevated temperature of the bath, 90°C, means that frequent and costly ammonia replenishments are always necessary.

Naturally there are benefits achieved by substituting some of the ammonia in such systems with other alkaline materials such as sodium hydroxide. Figure 6 shows some of the results obtained by the addition of 10 g/L sodium hydroxide to a standard ammoniacal formulation. This can be a way of reducing the ammonia usage in “P” salt baths while considerably enhancing the cathode efficiency. However, build-up of sodium can reduce the bath life in the same way as “Q” salt baths are affected.

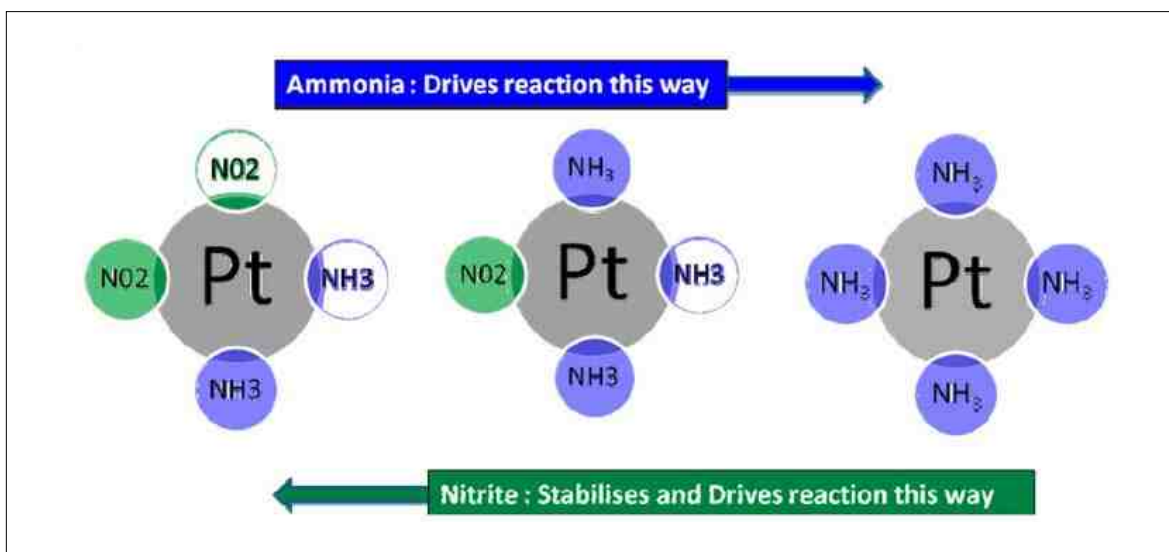


Figure 5—“P” Salt stability in a typical ammoniacal platinum plating bath.

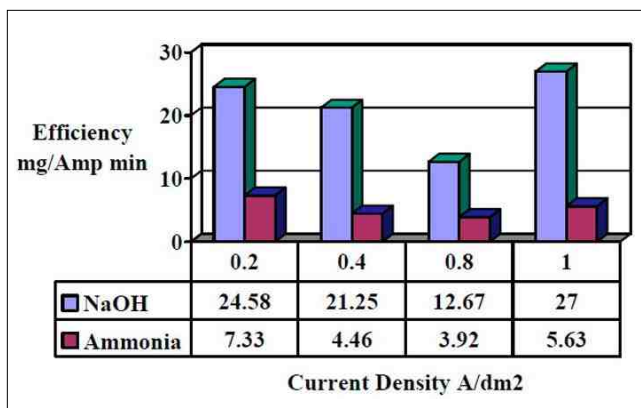


Figure 6—Effect of 10 g/L sodium hydroxide addition on cathode efficiency of a typical ammoniacal “P” salt platinum plating bath.

As seen in Fig. 7, “P” salt baths are not as temperature-dependent on temperature as are “Q” salt baths. Compared with the abrupt loss of cathode efficiency seen in Fig. 4 for the “Q” salt bath, the “P” salt bath is more tolerant to temperature variation.

New improved processes based on “P” salt [(NH₃)₂Pt(NO₂)₂]

“P” salt has been proven to be a good starting material for platinum plating, with established processes well utilized in aircraft turbine blade applications. The processes produce deposits which give good platinum-aluminized barrier coatings and the process control is well established.

Some negative aspects, particularly the use of ammonia, are present in most “P” salt formulations, but improved “P” salt-based baths have been developed to give the features and benefits shown in Table 2.

The new electrolytes have not only reduced ammonia. The only ammonia present is that used to solubilize and stabilize the “P” salt in solution. In addition, the new baths exhibit increased process stability and higher cathode efficiency, leading to reduced plating times and faster production output. A side benefit is increased bath life, as the issue of increasing solution density, leading to low cathode efficiency, is not an issue as the bath ages.

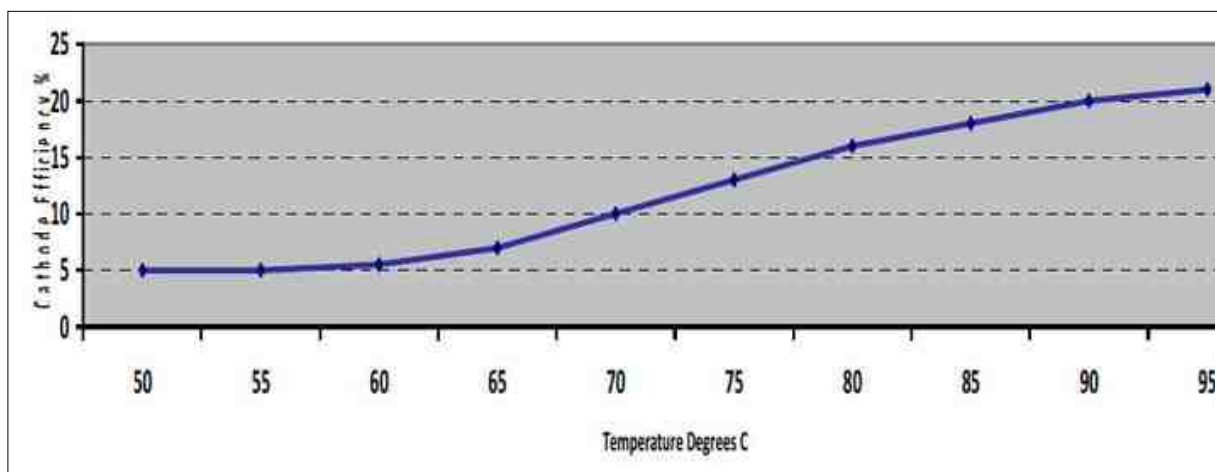


Figure 7—Cathode efficiency vs. temperature in a typical ammoniacal “P” salt platinum plating bath.

Table 2

Features and benefits of improved “P” salt platinum plating bath

Feature	Benefits
Reduced ammonia	Minimal ammonia smell Improved working environment Improved health and safety
Higher plating efficiency	Faster production
Improved electrolyte stability	Easier operation
Reduced current density operation	Easier to operation
Fully analyzable	Improved process control

A typical ammoniacal “P” salt bath would achieve around 20 metal turnovers before the bath is replaced or in practice around six months in a production situation. It is envisaged that the newer formulation would exceed this figure and possibly achieve 30 to 40 metal turnovers or one year, giving an additional cost benefit.

Comparison of deposition speeds

Table 3 shows that the new “P” salt bath exhibits faster deposition speeds than both the conventional ammonia-based “P” salt system (at 3.5 A/dm²) and the typical “Q” salt formulation where current density is more limited (The typical maximum is 0.5 A/dm²). An optimum current density of 1.0 A/dm² is recommended with the improved “P” salt formulation. The cathode efficiency characteristics at the optimum 1.0 A/dm² are shown in Fig. 8.

Improved “P” salt electrolytes

The new non-ammonia “P” salt baths are based on a carbonate electrolyte but also utilize a stabilizer and pH buffer to minimize the need for pH adjustment. Reduced pH adjustment eases process control and also extends the bath life as breakdown of the carbonate yields carbon dioxide which is harmlessly liberated to the air.

Table 3
Comparison of deposition speed from standard “Q,” standard ”P” and improved “P” salt electrolytes

	Unit	Standard “Q” salt	Standard salt “P”	Improved salt “P”
Current density	A/dm ²	0.5	3.5	1.0
Plating speed	microns/hr	3.75	1.25	5.00
Cathode efficiency	%	40 - 60%	5 - 10%	30 - 40%
Cathode efficiency	mg/A-min	30	3	20

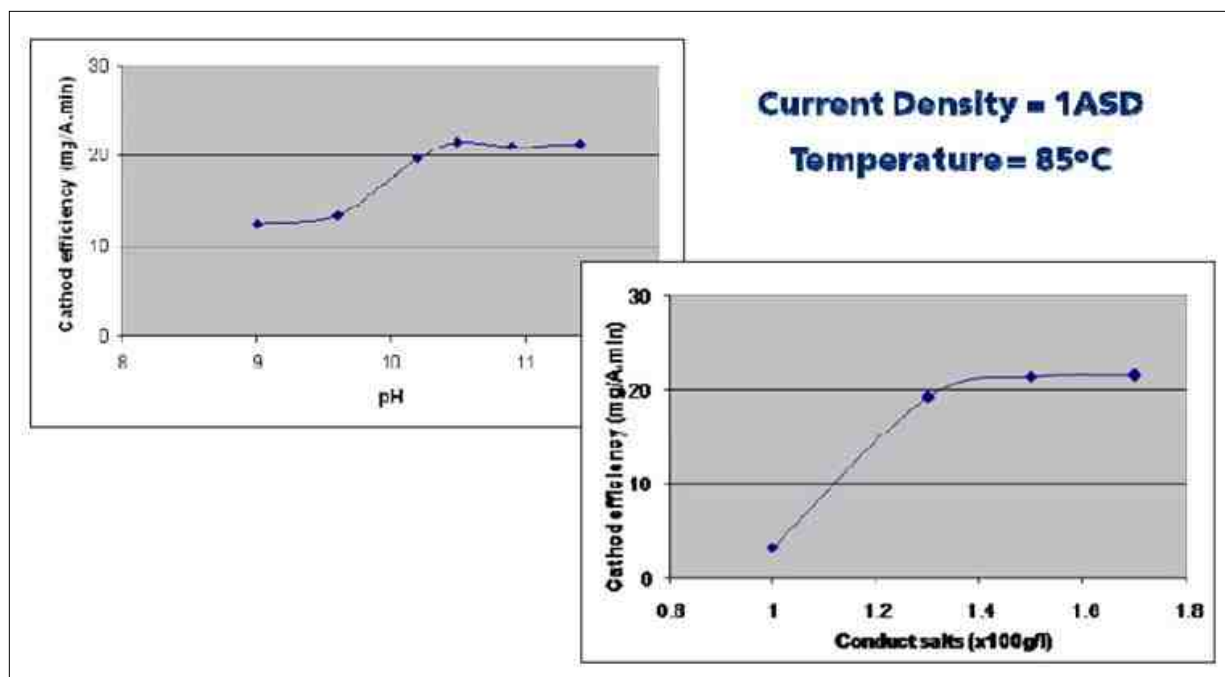


Figure 8—Effect of pH variation and conducting salt concentration on the cathode efficiency of the improved “P” salt electrolytes.

With the buffer system and stabilizer in place the solution density remains largely unchanged as the bath ages. Stable pH, by default, means a more stable cathode efficiency and a more controlled production for ease of operation. Precipitation of platinum that is sometimes seen in older “P” salt baths has not been observed in the new formulations. Figure 9 shows in cross-section the uniformed, fine-grained structure that can be obtained with the ammonia-free electrolyte system.

Summary and conclusions

Aircraft turbine blades are precision engineered from super-alloys, but despite this, they still require further protection to ensure maximum life span in the harsh environment of a jet engine. Platinum plating followed by a pack diffusion process to create a platinum-alumina thermal barrier coating is the process often utilized to achieve this protection for the super-alloy.

Several platinum plating processes are available to meet this need. The majority of users will operate either “Q” salt baths or the well established ammonia-based “P” salt baths. Newer non-ammonia “P” salt baths that increase speed and eliminate the environmental hazards and health and safety risks of ammonia usage are now readily available.

Our industry, the Electroplating / Surface Finishing / Surface Engineering industry, is always striving to improve not only process performance, but more and more the demands and focus lead us formulate greener technologies. Removing ammonia from the plating of turbine blades utilizing “P” salt is a beginning for the new generation of platinum plating processes, which are ammonia-free, exhibit increased bath life, permit increased production speeds, offer a more stable electrolyte and involve no harmful or unpleasant odors

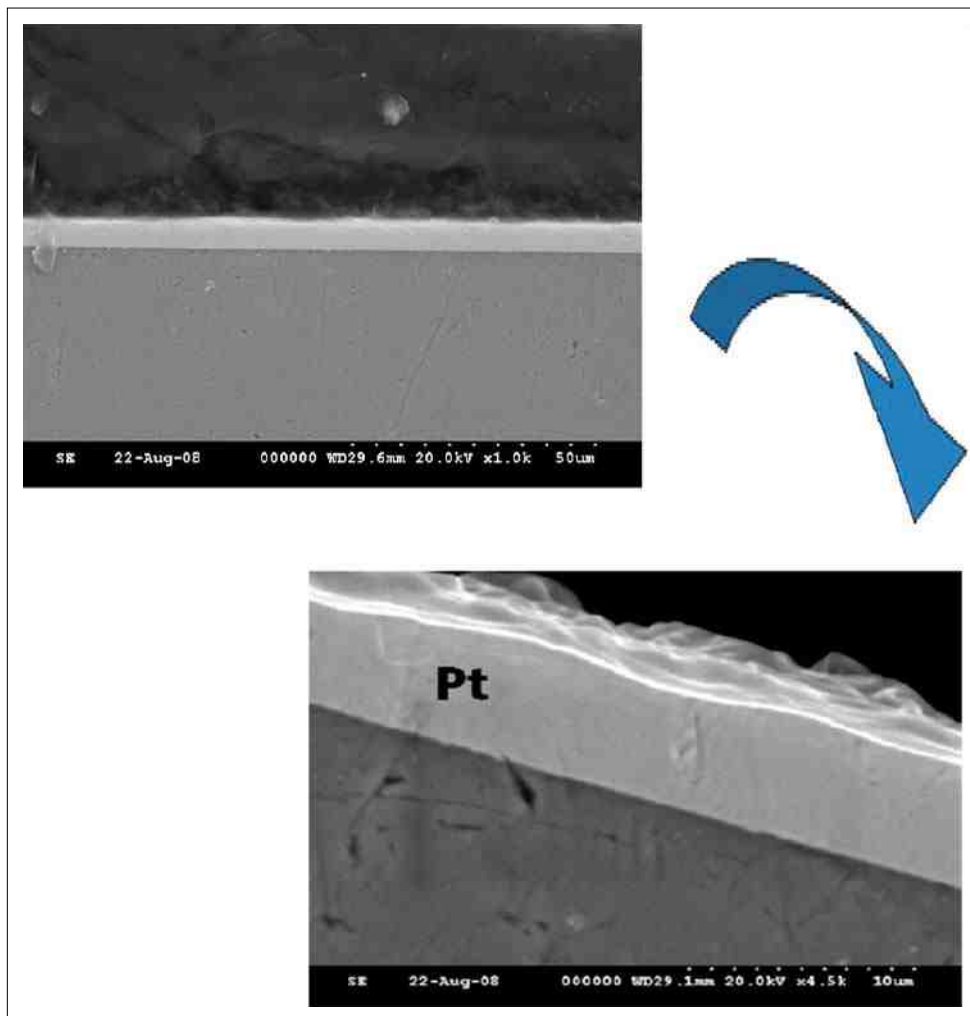


Figure 9—SEM showing the fine-grained uniform platinum structure achieved with the improved “P” salt electrolyte.

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Fact or Fiction

Continued from page 21.

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A Bright Idea



2010 Bright Design Challenge "LOUD PIPES AND CHROME!"

In its 11th year, the Bright Design Challenge has once again challenged students at the College for Creative Studies to push the envelope in creative design to create a concept 2015 Harley-Davidson motorcycle. Key design influences will include a "naked" air-cooled V-Twin engine, "naked" exhaust and will of course feature lots of chrome – some of the many features that Harley-Davidson motorcycles have become famous for around the world.

The Bright Design Challenge, sponsored by the National Association for Surface Finishing (NASF) is a lively, spirited design competition that connects young designers with major OEM design studios such as Harley-Davidson Motor Co. and Ford Motor Co. The winners of the contest receive scholarships on behalf of the NASF as the competition challenges students to balance style and function.

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